

VIII. STABILITY OF HYDROPHOBIC COLLOIDS AND EMULSIONS¹⁾

J. TH. G. OVERBEEK

Van 't Hoff Laboratory, University of Utrecht

§ 1. HISTORICAL

The most striking facts to be explained by a theory on the stability of hydrophobic colloids are the valency rule of SCHULZE and HARDY (see chapter II, § 5 c. 1, p. 81) and a certain relation between the stability and the ζ -potential. HARDY² already observed that a sol flocculates when it is nearly "isoelectric" with its surroundings, that is when the ζ -potential is reduced to zero. Later investigations by POWIS³ introduced the concept of a **critical ζ -potential** below which a sol flocculates and above which it is stable. This critical potential was found to be about 25–30 milli-volts. The extension of the experimental material on one hand, and the criticisms rised against the interpretation of electrophoresis measurements (see chapter V, § 6b, p. 210) on the other, made the existence of a critical potential doubtful. Other quantities, connected with the electrolytic character of hydrophobic systems, have been proposed as governing the stability. Of these we mention the function ζ^2/κ introduced by EILERS and KORFF⁴ and the activity coefficient f_a introduced by WO. OSTWALD⁵. In the theory of VERWEY and OVERBEEK which will be set out in the next sections, the role of the ζ -potential is less conspicuous although the electrical double layer remains of fundamental importance.

BREDIG⁶ was the first to explain the stabilizing action of the double layer. He ascribed the tendency to flocculation to the surface tension of the particles and suggested that the charge of the particles diminishes this surface tension and thus decreases the tendency to flocculation.

The same explanation has been put forward in greater detail by PERRIN⁷ and more recently by RICE⁸. Although these authors were on the right track in connecting the stability of a sol with the negative free surface energy of the double layer, they applied this principle in an incorrect way. They calculated a certain degree of dispersion for which the normal positive free energy of the interface and the negative free energy of the double layer just equilibrate each other. This would mean that a colloidal suspension

¹ The contents of this chapter have been extensively discussed between the author and G. H. JONKER, S. A. TROELSTRA, and E. J. W. VERWEY of the *Philips' Research Laboratories*, Eindhoven.

² W. D. HARDY, *Z. physik. Chem.*, 33 (1900) 385.

³ F. POWIS, *Z. physik. Chem.*, 89 (1915) 186.

⁴ H. EILERS and J. KORFF, *Chem. Weekblad*, 33 (1936) 358; *Trans. Faraday Soc.*, 36 (1940) 229.

⁵ WO. OSTWALD, *Kolloid-Z.*, 73 (1935) 320, and many subsequent papers.

⁶ G. BREDIG, *Anorganische Fermente*, Leipzig 1901, p. 15.

⁷ J. PERRIN, *J. chim. phys.*, 3 (1905) 50.

⁸ O. K. RICE, *J. Phys. Chem.*, 30 (1926) 189, 1660.

could be stable in the thermodynamic sense, and for instance would not be subject to "coarsening" (See chapter VII, § 9, p. 300).

As far as we know no hydrophobic system is ever stable in this strict sense. Therefore this theory is not applicable to practical cases, as was already rightly recognized by MARCH¹.

This author, starting from the same assumptions as PERRIN, came to the correct conclusion that the free energy of the double layer and the entropy of the free particles (which also counteracts flocculation) together are still much too small to explain stability in a thermodynamical sense. To explain stability against coagulation he assumed therefore some unknown force, connected with solvation which should cause a repulsion between colloidal particles and thus prevent coagulation.

GYEMANT² and LEWIS³ also considered the possibility of a stability of colloids as a consequence of the interplay of surface tension and charge but in their theories the free energy of the double layer is taken as positive and therefore these authors can only explain stability by additional rather special assumptions about the charge.

It can be shown, however, that although the free energy of the double layer is not sufficiently large to entail stability in the thermodynamical sense, it is more than strong enough to give rise to a dynamical stability, due to a potential barrier between two particles, much larger than the energy of BROWNIAN motion.

Several theories have been put forward to explain the influence of electrolytes on the stability. Of these the chemical theory, proposed among others by DUCLAUX⁴ and by PAULI⁵ considers flocculation as the formation of an insoluble salt or in a modified form as the formation of a non-ionized compound in the double layer. This theory, however, is difficult to reconcile with the comparatively great lack of specificity in flocculation values.

A more physical explanation, given by FREUNDLICH⁶ and based upon the difference in adsorbability of the flocculating ions has been distinctly refuted by experimental evidence⁷. Both these theories considered a *discharge* of the double layer as the cause of flocculation.

On the basis of the theory of the diffuse double layer it is possible to show that already a compression of the double layer by electrolytes is sufficient to explain loss of stability. It may be remarked that in order to explain certain specific effects in flocculation it is necessary to extend the double layer theory by some modification such as STERN's theory (*cf.* chapter VI, § 8, p. 263) which in essence is a partial return to elements of the chemical theories and the adsorption theory of FREUNDLICH.

§ 2. STABILITY AND FLOCCULATION EXPLAINED BY POTENTIAL CURVES. RULE OF SCHULZE AND HARDY

Potential curves, as treated in chapter VI, § 12, p. 271, describing the energy of interaction between two colloidal particles, can explain various aspects of hydrophobic

¹ A. MARCH, *Kolloid-Z.*, 45 (1928) 97.

² A. GYEMANT, *Grundzüge der Kolloidphysik*, Braunschweig, Sammlung Vieweg (1925); *Z. Physik*, 36 (1926) 457.

³ W. C. M. LEWIS, *Trans. Faraday Soc.*, 28 (1932) 597.

⁴ J. DUCLAUX, *Les colloïdes*, 3rd ed., Paris 1925, p. 240.

⁵ W. PAULI, *Naturwissenschaften*, 12 (1924) 421, 548.

⁶ H. FREUNDLICH, *Z. physik. Chem.*, 73 (1910) 385.

⁷ H. FREUNDLICH, K. JOACHIMSOHN, and G. ETTISCH, *Z. physik. Chem.*, A141 (1929) 249; E. J. W. VERWEY and H. R. KRUYT, *Z. physik. Chem.*, A 167 (1934) 312.

stability, as has been indicated first by DE BOER¹ and HAMAKER² and later in more detail by VERWEY and OVERBEEK³. When a potential barrier of sufficient height is present, the corresponding sol will be stable whereas in the absence of a barrier the attraction will prevail, leading to rapid coagulation. The transition between stable and flocculated systems can be represented by a potential curve of the type sketched in Fig. 1, where the energy of interaction is just negative or zero for all distances. The form of the potential curve depends on the values of the surface potential ψ_0 , dielectric constant ϵ , valency z and concentration of ions c , temperature T , VAN DER WAALS constant A and dimensions of the particles (for instance their radius a). When the discussion is restricted to aqueous solutions at room temperature which fixes ϵ and T , and when the particles are assumed to be comparatively large and flat faced, so that they may be approximated as flat plates, this limit of stability can be described as a function of ψ_0 and c , using z and A as parameters.

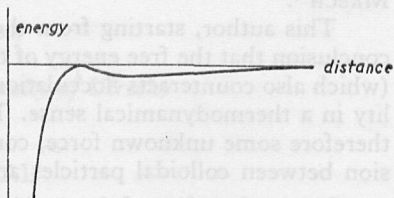


Fig. 1. Type of potential curve forming the transition between flocculated and stable systems.

Fig. 2, derived from Figs. 19–23 of chapter VI, p. 273, shows curves for a few chosen values of A and z , separating the regions of stability (top left, high ψ_0 and small c) and flocculation (bottom right, low ψ_0 and large c).

It is immediately clear from this figure that the rule of SCHULZE and HARDY is satisfactorily explained. *E.g.*, for $\psi_0 = 100$ mV and $A = 2 \cdot 10^{-12}$, the flocculation

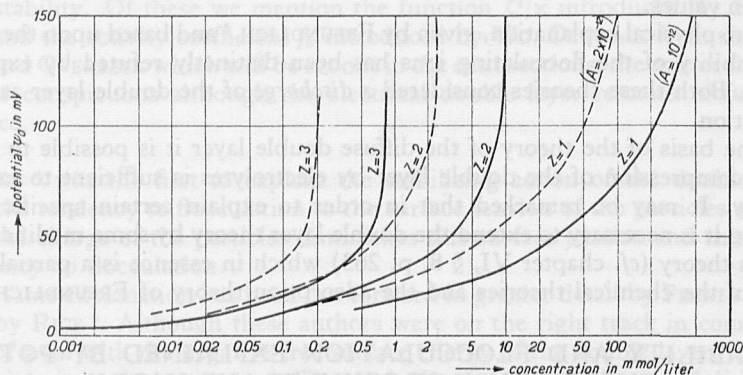


Fig. 2. Conditions of limiting stability (flocculation values) for two values of the LONDON-VAN DER WAALS constant A and the valencies $z=1$, $z=2$ and $z=3$. Left and top = stable, right and bottom = unstable.

values for mono-, di- and tri-valent electrolytes are 50, 2 and 0.2 millimol/l respectively. The values of ψ_0 and A are within the range of expectations.

Now usually the flocculation values determined experimentally are not really rapid

¹ J. H. DE BOER, *Trans. Faraday Soc.*, 32 (1936) 21.

² H. C. HAMAKER, *Rec. trav. chim.*, 55 (1936) 1015; *Chem. Weekblad*, 35 (1938) 47.

³ E. J. W. VERWEY and J. TH. G. OVERBEEK, *Theory of the stability of lyophobic colloids*, Amsterdam 1948; *Trans. Faraday Soc.*, 42 B (1946) 117; E. J. W. VERWEY, *Philips Research Repts.* 1 (1945) 33; *J. Phys. & Colloid Chem.*, 51 (1947) 631.

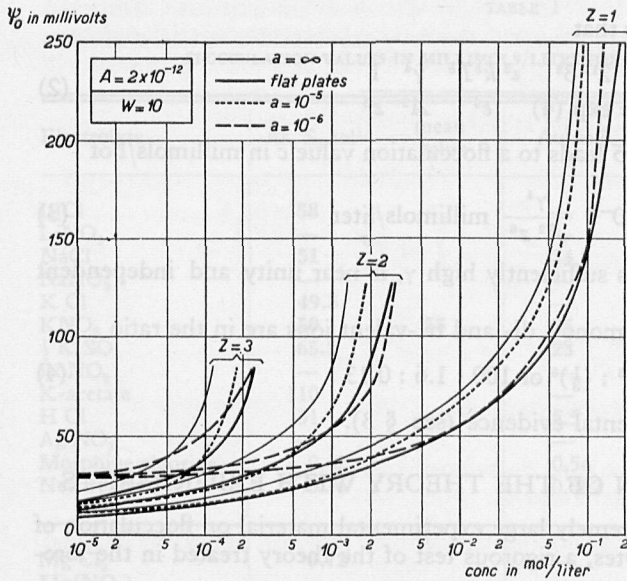


Fig. 3. Flocculation values for a flocculation retarded by a factor 10 ($W = 10$).

flocculations, but slow flocculations with a time of flocculation depending upon the stability criterion chosen (usually between 5 min and several hours). This does not affect the given explanation as the curves for small potential barriers differ only slightly from those of Fig. 2.

As the absolute value of the energy of interaction depends strongly of course upon the dimensions of the particles, a potential barrier can only be introduced into the calculations when at the same time the dimensions of the particles are fixed. Figs. 3 and 4 have been constructed for spherical particles of radius 100 Å or 1000 Å. They show that a retardation of the flocculation by a factor 10 or even 10^5 does not alter the curves materially. Only for small particles ($a = 10^{-6}$ and smaller) where an energy-barrier of given height is more difficult to attain, is a tendency to smaller stability present.

An analytical expression for the rule of SCHULZE and HARDY can be derived by combining the approximate expression (24) p. 256 from chapter VI for the repulsion between flat plates with eq. (37) p. 267 from chapter VI for the attraction. A potential curve of the type of Fig. 1 satisfies the conditions $V=0$ and $\frac{dV}{dd} = 0$ for the same value of d .

$$V = \frac{64 n k T}{\kappa} \gamma^2 e^{-2 \kappa d} - \frac{A}{48 \pi d^2} \quad (1)$$

The symbols used are the same as in chapter VI.

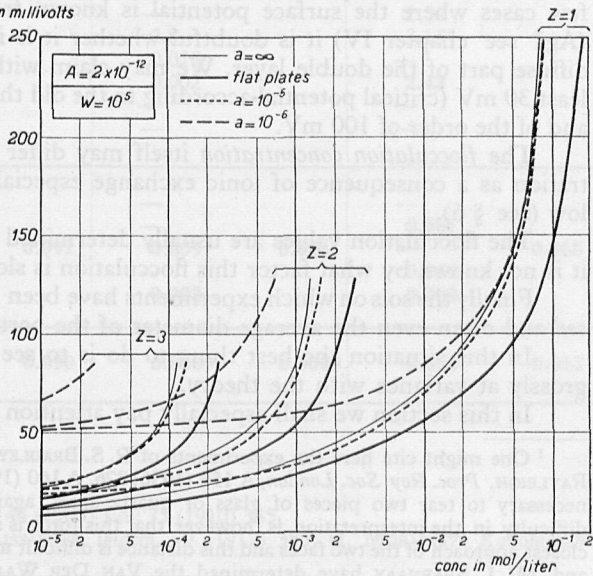


Fig. 4. As Fig. 3 but retardation factor 10^5 ($W = 10^5$).

From $V = d \frac{dV}{dd} = 0$ it follows that

$$n = \frac{2^{11} 3^2}{\pi \exp(4)} \frac{\epsilon^3 k^3 T^5}{e^6} \frac{\gamma^4}{A^2} \frac{1}{z^6} \quad (2)$$

which for $T = 298^\circ$ and $\epsilon = 78.55$ leads to a flocculation value c in millimols/l of

$$c = 8.10^{-22} \frac{\gamma^4}{A^2 z^6} \text{ millimols/liter} \quad (3)$$

When the surface potential is sufficiently high γ , is near unity and independent of the valency.

So the flocculation values of mono-, di- and tri-valent ions are in the ratio

$$1 : \left(\frac{1}{2}\right)^6 : \left(\frac{1}{3}\right)^6 \text{ or } 100 : 1.6 : 0.13 \quad (4)$$

in good agreement with experimental evidence (see § 3).

§ 3. FIRST COMPARISON OF THE THEORY WITH EXPERIMENTS

Although there exists an extremely large experimental material on flocculation of hydrophobic colloids by electrolytes, a rigorous test of the theory treated in the foregoing pages is not possible.

In the first place, the VAN DER WAALS constant A has never been determined in an independent way¹. Our knowledge of this quantity is restricted to theoretical evaluations from which at best an order of magnitude of $A \approx 10^{-12}$ may be deduced.

Moreover the exact circumstances of flocculation experiments are usually not known well enough. The *surface potential* is either not determined or is evaluated from electrophoresis which is usually not reliable for the reasons given in chapter V. In the few cases where the surface potential is known from electrochemical investigations (AgI see chapter IV) it is doubtful whether it is identical with the potential in the diffuse part of the double layer. We may claim with certainty that the potential is at least 30 mV (critical potential according to the old theories), but probably much higher and of the order of 100 mV.

The *flocculation concentration* itself may differ seriously from the gross concentration as a consequence of ionic exchange especially when the flocculation value is low (see § 6).

The flocculation values are usually determined for a certain *slow flocculation*, but it is not known by what factor this flocculation is slower than the ideal rapid one.

Finally the sols on which experiments have been made are mostly *far from isodispersed* and often even the average diameter of the particles is unknown.

In this situation the best thing to do is to see whether the experiments are not grossly at variance with the theory.

In this section we shall especially pay attention to the rule of SCHULZE and HARDY

¹ One might cite here the experiments of R. S. BRADLEY, *Phil. Mag.*, 13 (1932) 853, and of Lord RAYLEIGH, *Proc. Roy. Soc. London*, A 156 (1936) 326, A 160 (1937) 507, who have determined the force necessary to tear two pieces of glass or quartz apart, against the VAN DER WAALS attraction. The difficulty in the interpretation is however that this force is strongly dependent upon the distance of closest approach of the two faces and this distance is difficult to estimate. Recently J. Th. G. OVERBEEK and M. J. SPARNAAY have determined the VAN DER WAALS attraction between glass or quartz plates at distances of the order of 1 μ . *Proc. Koninkl. Nederland. Akad. Wetenschap.* B 54 (1951) 387.

TABLE I

FLOCCULATION VALUES IN MILLIMOLS/LITRE FOR NEGATIVELY CHARGED SOLS

Electrolyte	As ₂ S ₃ sol ¹	mean value	Au-sol ²	mean value	AgI-sol ³	mean value
LiCl	58	—	—	—	—	—
LiNO ₃	—	—	—	—	165	—
NaCl	51	—	24	—	—	—
NaNO ₃	—	—	—	—	140	—
K Cl	49.5	—	—	—	—	—
KNO ₃	50	55	25	24	136	142
$\frac{1}{2}$ K ₂ SO ₄	65.5	—	23	—	—	—
RbNO ₃	—	—	—	—	126	—
K-acetate	110	—	—	—	—	—
H Cl	31	—	5.5	—	—	—
Ag NO ₃	—	—	—	—	0.01	—
Morphine chloride	0.42	—	0.54	—	—	—
New fuchsin	0.11	—	0.002	—	—	—
Mg Cl ₂	0.72	—	—	—	—	—
Mg(NO ₃) ₂	—	—	—	—	2.60	—
Mg SO ₄	0.81	—	—	—	—	—
Ca Cl ₂	0.65	—	0.41	—	—	—
Ca(NO ₃) ₂	—	—	—	—	2.40	—
Sr Cl ₂	0.635	0.69	—	0.38	—	2.43
Sr(NO ₃) ₂	—	—	—	—	2.38	—
Ba Cl ₂	0.69	—	0.35	—	—	—
Ba(NO ₃) ₂	—	—	—	—	2.26	—
Zn Cl ₂	0.685	—	—	—	—	—
Zn(NO ₃) ₂	—	—	—	—	2.50	—
UO ₂ (NO ₃) ₂	0.64	—	2.8	—	3.15	—
Cu SO ₄	—	—	0.015	—	—	—
Pb(NO ₃) ₂	—	—	0.002	—	2.43	—
Quinine sulphate	0.24	—	—	—	—	—
Benzidine nitrate	0.09	—	—	—	—	—
Al Cl ₃	0.093	—	—	—	—	—
Al(NO ₃) ₃	0.095	—	—	—	0.067	—
$\frac{1}{2}$ Al ₂ (SO ₄) ₃	0.096	0.091	0.009	0.006	—	0.068
La(NO ₃) ₃	—	—	—	—	0.069	—
Ce(NO ₃) ₃	0.080	—	0.003	—	0.069	—
Th(NO ₃) ₄	0.090	0.090	0.0009	0.0009	0.013	0.013

¹ H. FREUNDLICH, *Z. physik. Chem.*, 44 (1903) 129; 73 (1910) 385.² H. FREUNDLICH and G. VON ELISSAFOFF, *ibidem*, 79 (1912) 385; H. MORAVITZ, *Kolloidchem. Beihefte*, 1 (1910) 301.³ H. R. KRUYT and M. A. M. KLOMPÉ, *Kolloid.-Beihefte*, 54 (1942) 484.

and we shall realize that the ratio $1 : (1/2)^6 : (1/3)^6$ etc. is an extreme case. Different deviations from the ideal case will tend to make the ratio smaller. *Adsorption of electrolyte* will be more pronounced the higher the valency. A relatively low ζ -potential will lower the ratio; in the most extreme case, when the approximation of DEBYE and HÜCKEL holds well, even to $1 : (1/2)^2 : (1/3)^2$ etc.

Indeed if eq. (3) is developed for the case of small potentials one finds

$$c = 8.10^{-22} \frac{\gamma^4}{A^2 z^6} = \frac{8.10^{-22}}{A^2 z^6} \left(\frac{e \frac{ze \psi_0}{2kT} - 1}{e \frac{ze \psi_0}{2kT} + 1} \right)^4 \approx \frac{8.10^{-22}}{A^2 z^6} \left(\frac{ze \psi_0}{2kT} \right)^4 =$$

$$= \frac{8.10^{-22} e^4}{256 A^2 k^4 T^4} \cdot \frac{\psi_0^4}{z^2} = 8 \times 10^{-30} \frac{\psi_0^4}{A^2 z^2}$$

where ψ_0 is expressed in millivolts and c in millimols per litre.

The influence of *particle radius* and *flocculation velocity* on the SCHULZE-HARDY rule is not very pronounced (cf. Figs. 3 and 4).

Table 1 gives examples of flocculation values for three different negatively charged sols.

Considering the values for one valency, they fall distinctly into two classes. The simple inorganic cations show about the same flocculation values, organic ions, hydrogen ions and some ions of heavy metals fall outside the range. For each valency the "normal values" have been printed in bold type and their mean value is mentioned in a separate column.

Table 2 gives these mean flocculation values, their ratio and for comparison the ratio of the inverse sixth powers of the valency.

TABLE 2
MEAN FLOCCULATION VALUES OF NEGATIVE SOLS

	As ₂ S ₃ mean floccu- lation value	ratio	Au mean floccu- lation value	ratio	Ag I mean floccu- lation value	ratio	theoretical value (z^{-6})
Monova- lent	55	1	24	1	142	1	1
divalent	0.69	0.013	0.38	0.016	2.43	0.017	0.016
trivalent	0.091	0.0017	0.006	0.0003	0.068	0.0005	0.0013
tetravalent	0.090	0.0017	0.0009	0.00004	0.013	0.0001	0.00024

For mono- and di-valent ions the accordance is very good; for the polyvalent ions less good but the order of magnitude is still right.

For positive sols the material is less abundant but is again in good accord with the theory as is demonstrated by Tables 3 and 4.

TABLE 3
FLOCCULATION VALUES in millimols/litre FOR POSITIVELY CHARGED SOLS

Electrolyte	Fe ₂ O ₃ -sol ¹	mean value	Al ₂ O ₃ -sol ²	mean value
NaCl	9.25		43.5	
KCl	9.0		46	
NH ₄ Cl	—		43.5	
$\frac{1}{2}$ Ba Cl ₂	9.65		—	
KBr	12.5	11.8	—	52
KI	16		—	
KCNS	—		67	
KNO ₃	12		60	
$\frac{1}{2}$ Ba(NO ₃) ₂	14		—	
HCl	> 400		—	
$\frac{1}{2}$ Ba (OH) ₂	0.42		—	
Na picrate	—		4.7	
K ₂ SO ₄	0.205		0.30	
Tl ₂ SO ₄	0.22		—	
Mg SO ₄	0.22	0.21	—	0.63
K ₂ Cr O ₄	—		0.95	
K ₂ Cr ₂ O ₇	0.195		0.63	
K ₂ oxalate	—		0.69	
H ₂ SO ₄	~0.5		—	
K ₃ Fe(CN) ₆	—		0.080	0.080
K ₄ Fe(CN) ₆	—		0.053	0.053

TABLE 4
MEAN FLOCCULATION VALUES OF POSITIVE SOLS

	Fe ₂ O ₃	ratio	Al ₂ O ₃	ratio	theoretical
monovalent	11.8	1.00	52	1.00	1.00
divalent	0.21	0.018	0.63	0.012	0.016
trivalent	—		0.080	0.0015	0.0013
tetravalent	—		0.053	0.0010	0.00024

Another consequence of the theory which is relatively easily tested is the dependence of the flocculation value on the surface potential. For low potentials the stability

¹ H. FREUNDLICH, *Z. physik. Chem.*, 44 (1903) 151.

² N. ISHIZAKA, *Z. physik. Chem.*, 83 (1913) 97.

is lost, irrespective of the concentration of electrolyte as is demonstrated very clearly in all those cases where the charge of the colloidal particles may be reversed (for instance many oxides by OH^- ions, silver halides by silver or halide ions etc.). When, however, the surface potential is high, the flocculation value should not depend very much on the exact value of the potential. This is already shown by the fact that colloids of very different origin have nearly the same flocculation value. But it is better demonstrated by the slight dependence of the flocculation value upon the content of potential-determining ions as for instance from Miss KLOMPÉ's¹ data for AgI.

TABLE 5

FLOCCULATION VALUES AS A FUNCTION OF SURFACE POTENTIAL

Diluted AgI-sol charged to different potentials by I-ions. Total double layer potential 240, 300, 360 mV for conc. $\text{I}^- = 10^{-3}, 10^{-3}, 10^{-4}$.

Flocculation values in m mol/l

double layer potential	KNO_3	$\text{Ba}(\text{NO}_3)_2$	$\text{La}(\text{NO}_3)_3$
240 mV	84	2.58	0.084
300 mV	90	2.28	0.072
360 mV	100	2.28	0.066

Although the dependence upon the surface potential is slight, it is present. But only in the case of KNO_3 is it in the expected direction (more easy flocculation for lower potential), whereas in the case of di- and tri-valent ions the most highly charged sol is most easily flocculated. The explanation may be that the polyvalent ions act to a certain extent as cementing centres between colloidal particles² and that this effect is more pronounced the higher the charge or the surface potential of the particles.

§ 4. SPECIFIC EFFECTS OF FLOCCULATING IONS

In order to draw the reader's whole attention to the very typical effects of the valency of the counter ions, all specific effects of the ions on the stability have been neglected in the preceding section. It is however immediately clear from Tables 1 and 3 that, apart from the valency, the specific nature of the added salts has a certain influence on the flocculation value.

a. Specific effects of counter-ions

The simple theory of the diffuse double layer presents no starting point for the treatment of specific influences of the ions, these being treated as point-charges. Only after the introduction of a refinement like STERN's theory (Ch. IV, § 4d, p. 132 and Ch. VI, § 8, p. 263) can specific effects be explained. In this theory a specific adsorption potential is introduced and the dimensions of the ions are accounted for by the thickness of the molecular condenser (or by its finite capacity).

¹ H. R. KRUYT and M. A. M. KLOMPÉ, *l.c.*

² An analogous effect has been found in the turbidity of flocculating sols. See chapter VII § 8, p. 299.

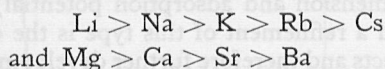
It has been mentioned in chapter VI, § 8, p. 263 that STERN's correction results in a lower potential drop in the diffuse double layer (ψ_δ instead of ψ_0). The potential in the diffuse layer, instead of being only dependent on the amount of potential-determining ions, now also depends upon the total electrolyte concentration and is lower, the higher the electrolyte content. This explains why in several cases a sort of critical ζ -potential has been found and it shows how in the refinements of the double layer theory of stability, conceptions of the older theories (like discharge by adsorption of counter ions) again play a role.

The potential ψ_δ depends — other things being equal — on the thickness of the molecular condenser and indeed is larger, the thinner the molecular condenser is. The thickness of the molecular condenser will be determined by the magnitude of the counter-ions. So we may expect that the larger counter-ions will give rise to a lower ψ_δ and consequently to lower stability and lower flocculation values.

The evidence from adsorption experiments (chapter IV, § 5a, p. 146, Hg, § 6a, p. 160, AgI) pointing to a complete lack of specificity of cations, is not contrary to changes in ψ_δ at the flocculation value. In the electrocapillary case the concentration of electrolyte is usually so high that the diffuse double layer is practically absent, and in the AgI case on the contrary, the electrolyte concentration was far lower than the flocculation value.

The second typical addition in STERN's theory is the specific adsorbability. When the counter-ions are strongly adsorbed (otherwise than by their charge alone) they will give rise to a sharp depression of ψ_δ and thus to a low stability and a low flocculation value.

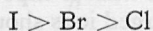
For the A series of ions the first prediction is on the whole confirmed by experiments. Usually the order of flocculation values is



as is demonstrated by Table 1, p. 307 and more material to confirm this is cited by PAULI and VALKÓ².

The greater polarizability of the larger ions will be expected to increase their adsorbability and thus to act in the same direction.

For many positive sols (see Fe₂O₃-sol, Table 3, p. 309) however the order is just reversed so that here the larger ions have the greatest flocculation value



An exception is formed by some very special positive sols² (Au-sols whose charge had been reserved by the addition of Al or Th salts) where again the smaller ions (Cl⁻, Br⁻) have a higher flocculation value than the larger one (I⁻). This exception may be explained in the same way as the behaviour of cations.

The normal rule for positive sols has, however, not yet found a satisfactory explanation.

Another interesting case³ which shows clearly how complicated these specific effects may be is given by the sulphur sol. The sulphur sol prepared according to VON

¹ W. PAULI and E. VALKÓ, *Elektrochemie der Kolloide*, Vienna 1929, p. 179.

² A. VOET and F. BALKEMA, *Rec. trav. chim.*, 52 (1933) 371.

³ H. FREUNDLICH, *Kapillarchemie II*, Leipzig 1932, p. 387.

WEIMARN by pouring an alcoholic solution of sulphur into water behaves analogous to the negative sols treated above.

The sulphur sol prepared, however, by acidification of $\text{Na}_2\text{S}_2\text{O}_3$ (S-sol of RAFFÓ) shows an extremely strong spreading of flocculation values that can scarcely be ascribed to an influence of the ionic radius alone.

TABLE 6
FLOCCULATION VALUES of S-sol of VON WEIMARN and of RAFFÓ

	VON WEIMARN	RAFFÓ
LiCl	34	750
NaCl	33	190
KCl	32	85
RbCl	31	80
CsCl	30	95

The influence of strong adsorbability is demonstrated by the very low flocculation values of complicated organic ions. For a few examples see Table 1.

Although in some cases application of the STERN correction allows of a simple interpretation of observed facts it should be kept in mind that the introduction of two new parameters (ionic dimension and adsorption potential) makes the theory rather elastic. On the other hand a refinement of this type is the only way of attacking and understanding specific effects and therefore further development in this direction seems indicated.

b. Ions bearing the same charge as the colloid. Antagonism of ions

It has been found frequently that highly charged ions of the same charge as the colloid lead to a higher flocculation value. This has been called by VALKÓ¹ the "relieving effect". Now this is just the reverse of what is expected on the basis of the double layer theory. There, indeed, the highly charged ions should contribute their part of the ionic strength and thus compress the double layer and decrease the flocculation value.

An explanation of the "relieving effect" may be found by comparing it to some cases of ionic antagonism observed in flocculation experiments with mixtures of electrolytes. The efficiency of a polyvalent counter-ion may be severely depressed by the presence of a certain amount of electrolyte of lower valency even to such an extent that, in the presence of this second electrolyte, a larger quantity of the polyvalent ion is necessary to flocculate the sol than if the second electrolyte were absent.

KRUYT and VESTER² explained this antagonism by remarking that according to the theory of DEBYE and HÜCKEL the activity of the polyvalent ion may be very much lower

¹ W. PAULI and E. VALKÓ, *Elektrochemie der Kolloide*, Vienna 1929, p. 192.

² C. F. VESTER, *Thesis*, Utrecht 1935; H. R. KRUYT, *Proc. Koninkl. Nederland Akad. Weienscha*, 38 (1935) 464.

than one and they succeeded indeed in showing that the antagonism disappears or nearly so, when instead of flocculation concentrations flocculation activities are compared. (See Figs. 5 and 6). The "relieving effects" may be explained in the same way.

This means an introduction of the DEBYE and HÜCKEL effects in the bulk of the liquid (outside the double layer) which hitherto have been neglected¹. Essentially this

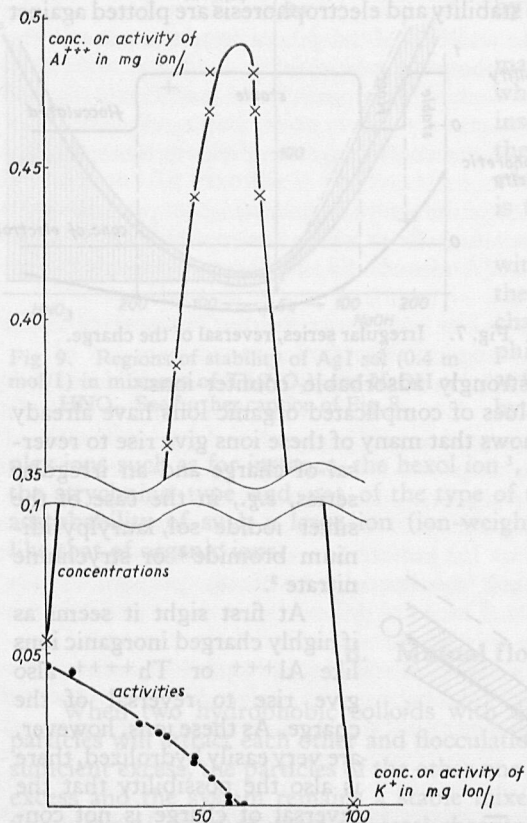


Fig. 5. Flocculation values of AgI by mixtures of $\text{Al}(\text{NO}_3)_3$ and K_2SO_4 .

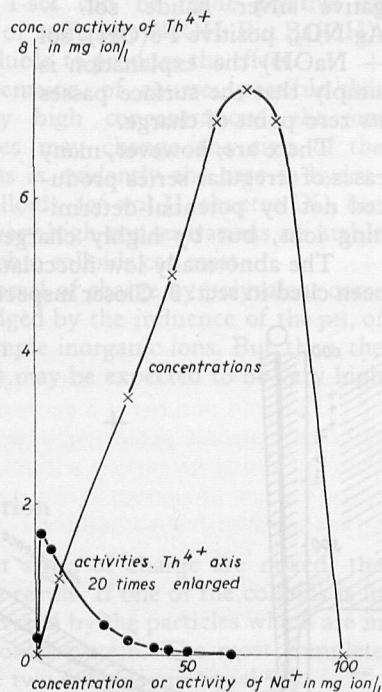


Fig. 6. Flocculation values of AgI by mixtures of $\text{Th}(\text{NO}_3)_4$ and Na_2SO_4 .

amounts to taking into account that also outside the double layer the polyvalent ion is preferentially surrounded by ions of the other sign and therefore is not at a mean potential zero but at a much lower one.

It is quite conceivable that the antagonism or "relieving effects", remaining after this activity correction should be ascribed to a normal (not very large) adsorption potential.

¹ cf. for a first quantitative treatment A. L. LOEB, *Thesis*, Harvard 1949.

c. Reversal of the charge of a colloid

In the frame work of GOUY's theory, addition of electrolyte can never lead to a reversal of the sign of the charge or potential. In reality, however, there are several electrolytes that lead to a reversal of the charge, as is proved both by electrophoresis and by the appearance of a second region of stability (Irregular series). Schematically the phenomenon is illustrated in Fig. 7 where stability and electrophoresis are plotted against the amount of electrolyte.

When an irregular series is produced by addition of potential-determining ions (negative silver halide sol + AgNO_3 , positive Fe(OH)_3 sol + NaOH) the explanation is simply that the surface passes its zero point of charge.

There are, however, many cases of irregular series produced not by potential-determining ions, but by highly charged or strongly adsorbable counter-ions.

The abnormally low flocculation values of complicated organic ions have already been cited in sect. 3. Closer inspection shows that many of these ions give rise to reversal of charge and an irregular series, e.g., in the case of the silver iodide sol, laurylpyridinium bromide¹ or strychnine nitrate².

At first sight it seems as if highly charged inorganic ions like Al^{+++} or Th^{++++} also give rise to reversal of the charge. As these ions, however, are very easily hydrolyzed, there is also the possibility that the reversal of charge is not connected with the ions but with the products of hydrolysis which presumably are positively charged colloidal oxides or hydroxides. The work of TROELSTRA² has made it extremely probable that only the products of hydrolysis are able to reverse the sign of the charge whereas the simple ions are

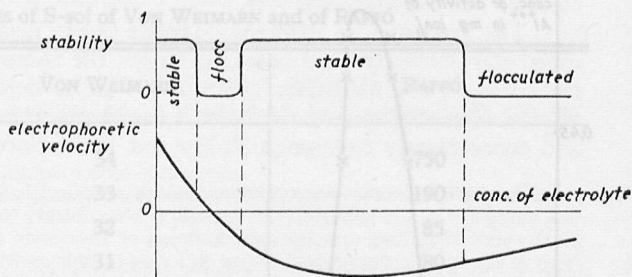


Fig. 7. Irregular series, reversal of the charge.

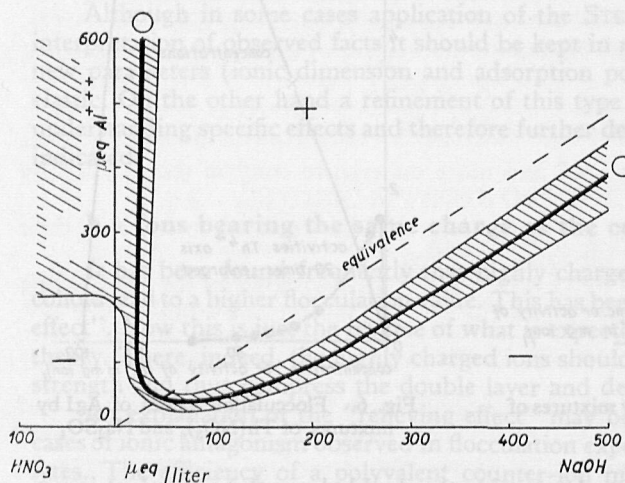


Fig. 8. Regions of stability of AgI sol (0.4 m mol/l) in mixtures of $\text{Al(NO}_3)_3$ and HNO_3 or NaOH

— = stable negatively charged
+ = stable positively charged
hatched = unstable

On the curve 0—0 the particles are uncharged

¹ A. LOTTERMOSER and R. STEUDEL, *Kolloid-Z.*, 82 (1938) 319; 83 (1938) 37.

² S. A. TROELSTRA, *Thesis*, Utrecht 1941, p. 125, 132; H. R. KRUYT and S. A. TROELSTRA, *Kolloid-Beihefte*, 54 (1943) 284, 277.

not. The arguments are that in acid solutions reversal of charge is absent or, when the pH is not very low, at least difficult. In alkaline medium reversal of charge may be effected by very small quantities of the polyvalent "ion" but at still higher pH the reversal of charge is again absent because now the hydroxides formed are themselves negatively charged by OH^- ions. TROELSTRA gives for instance the Figs 8 and 9 for the reversal of charge of diluted AgI sols by $\text{Al}(\text{NO}_3)_3$ and $\text{Th}(\text{NO}_3)_4$.

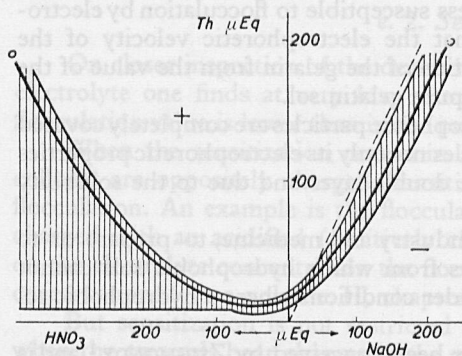


Fig. 9. Regions of stability of AgI sol (0.4 m mol/l) in mixtures of $\text{Th}(\text{NO}_3)_4$ and NaOH or HNO_3 . See further caption of Fig. 8.

The same type of reversal of charge may be produced even by bivalent ions when only their hydroxides are sufficiently insoluble. So with Cd, Zn, Mg, Be nitrate the Ag I-sol can be made positive on addition of sufficient NaOH. But $\text{Ba}(\text{OH})_2$ is too soluble to produce the effect.

It remains, of course, possible that with very high concentrations the ions themselves may change the sign of the charge, as is evidently the case in hydrophilic colloids (cf. vol II, chapter IX), but at these very high concentrations no stable hydrophobic colloids can exist.

Reversal of charge by polyvalent complex ions such as for instance, the hexol ion¹, is, judged by the influence of the pH, of the strychnine type and not of the type of the simple inorganic ions. But then the adsorbability of such a large ion (ion-weight 698) may be expected to be very high like that of organic ions.

d. Mutual flocculation

When two hydrophobic colloids with different signs of charge are mixed, the particles will attract each other and flocculation may result. If one of the colloids is in sufficient excess, the particles of the other one are covered by the particles which are in excess and the system remains a stable mixed colloidal system. The most complete flocculation is reached when the total charges of the two colloids are equal².

WIEGNER³ has remarked that the electrostatic attraction between the oppositely charged colloidal particles leads to a large increase of VON SMOLUCHOWSKI'S radius of attraction (cf. chapter VII, § 1, p. 278) and indeed during a flocculation experiment between positive copper hydroxide and clay the radius of attraction was $65 a$ (a = radius of primary particles) at the beginning and, as larger and more neutralized aggregates were formed, diminished gradually to: 40-30-16-10-4 times the radius of the particles.

¹ hexol = $[\text{Co} \{(\text{OH})_2 \text{Co} (\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2\text{NH}_2)_2\}_3]^{6+}$

² A. LOTTERMOSER and K. MAY, *Kolloid-Z.*, 58 (1932) 61; S. A. TROELSTRA, *l.c.*

³ G. WIEGNER, *Kolloid-Z.*, 58 (1932) 167.

e. Influence of lyophilic colloids on flocculation

e. 1. Protecting action

The most conspicuous influence of the addition of lyophilic colloids to lyophobic ones is the "protective action". A sufficient (usually not very large) quantity of, for instance, gelatin makes a lyophobic sol much less susceptible to flocculation by electrolytes. Electrophoresis measurements show that the electrophoretic velocity of the hydrophobic particles has changed by the addition of the gelatin from the value of the pure hydrophobic sol to a value proper to the pure gelatin sol.

It is rather obvious to assume that the hydrophobic particles are completely covered by a layer of gelatin which imparts to the particles not only its electrophoretic properties but also an extra repulsion independent of the double layer and due to the solubility of the gelatin.

Protective action is frequently applied in industry and medicine, to prepare or to protect fine dispersions of insoluble substances from which hydrophobic sols cannot easily be prepared or which have to be used under conditions where a hydrophobic sol would not be stable.

A quantitative test of protective action has been conceived by ZSIGMONDY¹ and is still the most frequently used tool of investigation in this domain.

ZSIGMONDY determined the quantity of a hydrophilic colloid which could just prevent the flocculation of 10 ml of a gold-sol (colour change from red to blue) by 1 ml of a 10% solution of Na Cl. This quantity expressed as milligrams of the hydrophilic colloid is termed its "gold number" and forms a reciprocal measure of the protective action. Gold numbers may vary from 0.005 for very well protecting colloids to 25 and more for poorly protecting substances.

The gold number is a general measure for protective action as it is found empirically that strong protective action against the flocculation of the gold-sol usually involves strong protection with other sols. There are differences in detail which is not surprising as protective action rests not only on the solubility of the protecting substance in water but also on the ease of its adsorption by the hydrophobic particle.

Table 7 gives a few values of the gold numbers and of analogously defined silver numbers, rubin numbers (sol of congorubin) sulphur numbers, Prussian blue-numbers and iron oxide-numbers.

TABLE 7
PROTECTIVE ACTION OF HYDROPHILIC COLLOIDS AGAINST DIFFERENT SOLS²

	gold number	silver number	rubin number	sulphur number	Prussian blue number	iron oxide number
gelatin	0.01	0.035	2.5	0.00012	0.05	5
sodium caseinate	0.01	—	0.4	—	—	—
hemoglobin	0.03-0.07	—	0.8	—	—	—
egg-albumin	2.5	1.5	2.0	0.025	25	15
gum arabic	0.5	1.25	—	0.024	5	25
dextrin	20	100	—	0.125	250	20
potato starch	20	—	~20	—	—	—
saponin	115	35	—	0.015	2.5	115

¹ R. ZSIGMONDY, *Z. anal. Chem.*, 40 (1901) 697; see also: R. ZSIGMONDY and P. A. THIESSEN, *Das Kolloide Gold*, Leipzig 1925, p. 173.

² H. FREUNDLICH, *Kapillarchemie*, II, Leipzig 1932, p. 449; J. TRAUBE and E. RACKWITZ, *Kolloid-Z.*, 37 (1925) 131.

In the case of strongly protecting colloids the thickness of the protecting layer around the hydrophobic particles may be calculated from the assumption that almost the whole of the hydrophilic colloid is adsorbed. For the protecting layer of gelatin in a gold sol one finds in this way a thickness of about 10 Å, of the order of just one complete monolayer.

e. 2. Sensitizing action

On closer inspection of the dependence of the protecting action on the amount of electrolyte one finds at very low amounts of protecting colloid a region where the flocculation value is lower than in the pure sol, that is a region of *sensitization*.

When the sensitization occurs in a system where hydrophobic and hydrophilic colloids are oppositely charged, sensitization is easily explained as a form of mutual flocculation. An example is the flocculation of an (acid) gold sol which is negatively charged with an acidified (positively charged) gelatin solution. In their dependence on the electrolyte concentration the flocculations show strong resemblance to complex coacervations¹ (see volume II, chapter X).

But sensitization is not restricted to cases of mutual flocculation; it also exists when the two sols bear charges of the same sign.

In the reaction of LANGE (1912) between gold sol and cerebrospinal liquid the phenomena involved are dominated mainly by the sensitization of the gold sol by albumin and globulin of the same sign².

BENDIEN³ who investigated the interaction between gold sols and gelatin found sensitizations at a pH higher than 4.7 where the gelatin is negatively charged.

Not only with amphoteric colloids as in the examples cited above, but also with exclusively negative hydrophilic colloids like gum arabic or starch, sensitization can be produced⁴ with a negative sol like AgI.

Even an important technical process⁵ for the rapid flocculation of tenacious coal and clay suspensions with starch and lime is based upon a sensitization of this kind.

This sensitization has been explained by assuming the formation of agglomerates of lyophobic particles held together by the lyophilic ones. When larger amounts of the hydrophilic colloid are available each particle is completely covered with it. But when the quantity of hydrophilic colloid is very small, insufficient to cover the particles, a more complete contact between hydrophobic and hydrophilic particles is possible by the formation of agglomerates in which one hydrophilic particle touches two or more hydrophobic ones. As a rough picture of sensitization this is probably right, but it must be refined to explain several peculiarities in this phenomenon.

Neither in electrophoresis, nor in BROWNIAN motion are sol particles changed by the addition of the sensitizing colloid. It seems as if adsorption of the two colloids takes only place after the addition of the flocculating electrolyte. The repulsion of the two colloids has to be diminished before they can reach each other.

¹ cf. J. TH. G. OVERBEEK, *Chem. Weekblad*, 35 (1938) 117 (in English).

² cf. E. JOEL, *Das Kolloide Gold in Biologie und Medizin*, Leipzig 1925, p. 32, 59.

³ W. M. BENDIEN, *Thesis*, Delft 1926; W. REINDERS and W. M. BENDIEN, *Rec. trav. chim.*, 47 (1928) 977.

⁴ See H. R. KRUYT and C. W. HORSTING, *Rec. trav. chim.*, 57 (1938) 737; J. DEVEUX, *J. chim. phys.*, 36 (1939) 5; J. TH. G. OVERBEEK, *l.c.*;

⁵ R. A. HENRY, French patent 658306 (1928); *Geologie en mijnbouw*, 10 (1931) 74; *Engineering*, 138 (1934) 213, 293; 142 (1936) 607; F. K. TH. VAN ITERSOM, *Proc. Koninkl. Nederland Akad. Wetenschap*, 41 (1938) 81; H. A. J. PIETERS and J. W. J. HOVERS, Dutch patent 61401.

Sensitization against flocculation by monovalent ions is much more pronounced than against polyvalent ions as is shown schematically in Fig. 10. TROELSTRA¹ explains this by assuming that the polyvalent ions form connective bridges between hydro-

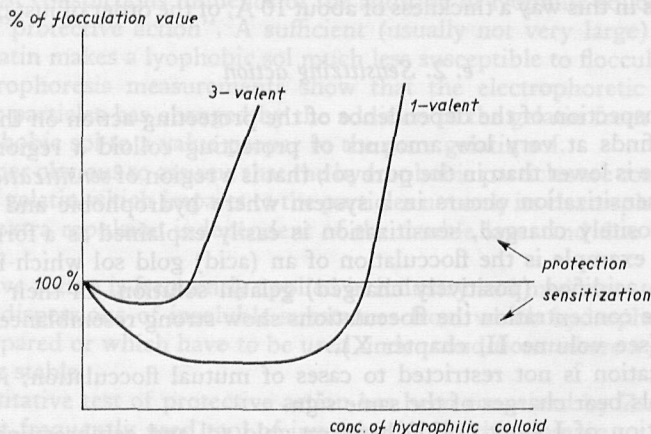


Fig. 10. Protecting and sensitizing action by a hydrophilic colloid against flocculation by monovalent and trivalent ions (schematically).

phobic and hydrophilic particles whereby the two sorts of particles are very rigorously held together and a uniform spreading of the hydrophilic colloid over the hydrophobic one is promoted.

§ 5. FLOCCULATION VELOCITY AS A FUNCTION OF THE CONCENTRATION OF ELECTROLYTES

A flocculation value gives only one rather arbitrary set of corresponding values of the rate of flocculation and the concentration of electrolyte. A further test of the theory of the stability can be obtained by examining the concentration dependence of the rate of flocculation. It has been described in Ch. VII, § 3, p. 283 how the rate of slow flocculation can be related to the form of the potential curve representing the interaction of two particles. This relation has already been used in the construction of Figs. 3 and 4, p. 305 of this chapter.

The retardation factor W , giving the ratio between the rates of rapid flocculation (no interaction) and slow flocculation for an energy of interaction V , is given by eq. (36) of Ch. VII, p. 285.

$$W = 2 \int_2^{\infty} \exp(V/kT) \frac{ds}{s^2} \quad (5)$$

The method of calculation of the energy of interaction V as a function of the distance between two colloidal particles has been described in Ch. VI § 12 b, p. 271.

¹ S. A. TROELSTRA, *Thesis*, Utrecht 1941, p. 81; S. A. TROELSTRA and H. R. KRUYT, *Kolloid-Beihfte*, 54 (1943) 251.

These calculations have been carried out for a series of concentrations of electrolytes and for certain specified values of the radius of the (spherical) particles, a , the VAN DER WAALS constant A , and assuming that during the interaction the surface potential ψ^0 has the constant value of 75.8 mV.

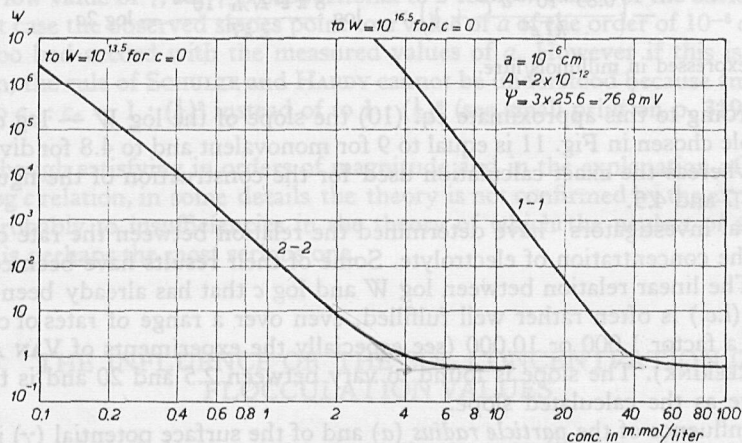


Fig. 11. Theoretical dependence of the rate of flocculation on the concentration of electrolyte.

Fig. 11 shows the results of these calculations plotted in a $\log W - \log c$ diagram. It is remarkable that in the major region of slow flocculation the relation between $\log W$ and $\log c$ is nearly linear.

REERINK¹ has indicated how this linear relationship follows from an approximative evaluation of the integral in eq. (5).

As the $\exp(V/kT)$ has a very sharp maximum when plotted as a function of s (cf. fig. 3, Ch. VII, p. 285) the value of W can to a good approximation be represented by (Ch. 7, eq (37) p. 285).

$$W \approx \frac{1}{2\kappa a} \exp. (V_{\max.}/kT) \quad (6)$$

or

$$\log W = \frac{V_{\max.}}{kT} \log e - \log 2\kappa a \quad (7)$$

Applying for the repulsive part of the interaction the eq.²)

$$V_{\text{rep.}} = 4.62 \cdot 10^{-8} \frac{\alpha r^2}{z^2} e^{-(s-2)\kappa a} \quad (8)$$

and for the attraction (see eq (41) Ch. VI, p. 270)

$$V_{\text{attr.}} = -\frac{A}{12(s-2)} \quad (9)$$

¹ H. REERINK, *Thesis*, Utrecht 1951 (to be published).

² E. J. W. VERWEY and J. TH. G. OVERBEEK, *Theory of the stability of lyophobic colloids*, Amsterdam 1948, p. 140.

the value of V_{\max} is easily derived. The resulting equation for the retardation value W is then

$$\log W = - \left(\frac{0.85 \cdot 10^{-6} a \gamma^2}{kTz^2} + \frac{1}{2} \right) \log cz^2 - \frac{1.70 \cdot 10^{-6} a \gamma^2}{kTz^2} \times \log \frac{4.9 \cdot 10^4 z^2 A}{\gamma^2} - \left(\frac{0.85 \cdot 10^{-6} a \gamma^2}{kTz^2} + \frac{1}{2} \right) \times \log \frac{8 \pi e^2 N_{Av} 10^{-6}}{\epsilon kT} - \log 2a \quad (10)$$

where c is expressed in millimols/litre.

According to this approximate eq. (10) the slope of the $\log W - \log c$ curve for the example chosen in Fig. 11 is equal to 9 for monovalent and to 4.8 for divalent electrolytes, whereas the exact calculation used for the construction of the figure leads to the values 7 and 4.5.

Several investigators¹ have determined the relation between the rate of coagulation and the concentration of electrolyte. Some of their results have been collected in Fig. 12. The linear relation between $\log W$ and $\log c$ that has already been described by PAINE (*l.c.*) is often rather well fulfilled, even over a range of rates of coagulation exceeding a factor 1,000 or 10,000 (see especially the experiments of VAN ARKEL and those of REERINK). The slope is found to vary between 2.5 and 20 and is thus in the same range as the calculated slope.

The influence of the *particle radius* (a) and of the surface potential (γ) is less easy to test. WESTGREN does not find any influence of a variation of the particle radius between 50 and 120 μ on the rate of slow coagulation of gold sols, whereas TUORILA for the same object finds a quicker coagulation for larger particles which for compara-

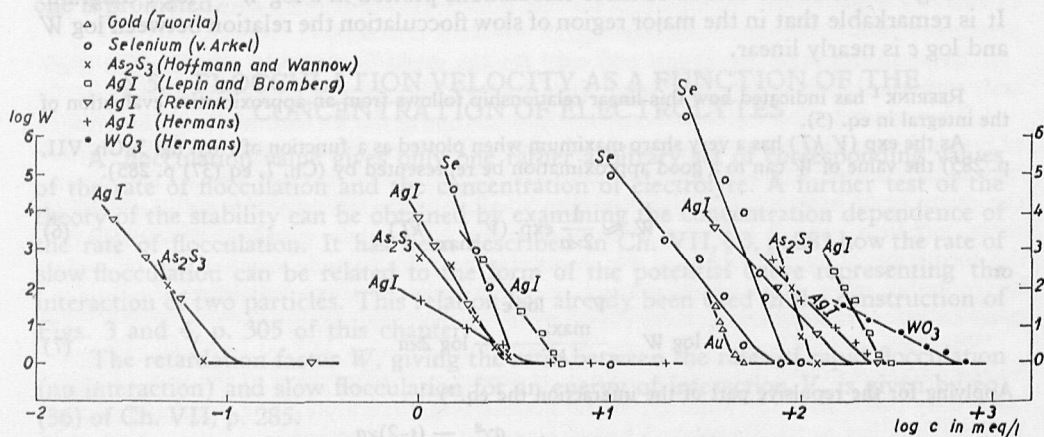


Fig. 12. Relation between rate of flocculation and concentration of electrolyte as determined experimentally. The three groups of curves relate to monovalent, divalent and trivalent electrolytes.

¹ H. H. PAINE, *Kolloidchem. Beihefte*, 4 (1912) 24, **Cu**; A. WESTGREN, *Arkiv Kemi Mineral. Geol.*, 7 (1918) no. 6, **Au**; A. E. VAN ARKEL, *Thesis*, Utrecht 1920, **Se**; A. E. VAN ARKEL and H. R. KRUYT, *Rec. trav. chim.*, 39 (1920) 656; 40 (1921) 169; P. TUORILA, *Kolloidchem. Beihefte*, 22 (1926) 191, **Au**; K. HOFFMANN and H. A. WAMIOW, *Kolloid-Z.*, 83 (1938) 258, **As₂S₃**; J. J. HERMANS, *Rec. trav. chim.*, 58 (1939) 139, 725, 741, **AgI**, **WO₃**; L. LEPIN and A. BROMBERG, *Acta Physicochim. U.R.S.S.*, 10 (1939) 83, **AgI**; H. REERINK, *Thesis*, Utrecht 1951, **AgI**.

tively rapid coagulations is in accordance with eq. (10). With AgI, REERINK found steeper curves for larger particles, although the influence of the size of the particles was smaller than it should have been according to eq. (10).

The curves for *different valencies* are on the whole of the same slope, which points to a rather low value of γ , for γ is proportional to z for low values of the surface potential. In that case the observed slopes point to a value of a of the order of 10^{-5} cm, which is not in too bad accord with the measured values of a . However if this is the right explanation, the rule of SCHULZE and HARDY cannot be understood because small values of γ lead to $c_1 : c_2 = 1 : (\frac{1}{2})^2$ instead of to $1 : (\frac{1}{2})^6$ (see small print on p. 319).

So although satisfying in orders of magnitude and in the explanation of the linear $\log W - \log c$ relation, in some details the theory is not confirmed by the experiments, pointing probably to insufficiencies in the theory of which the neglect of the STERN correction is perhaps the most serious one.

§ 6. THE INFLUENCE OF THE SOL CONCENTRATION ON FLOCCULATION VALUES

There is a relatively large number of investigations on the dependence of flocculation values on the concentration of the colloid. The results of the older investigations can be divided schematically into three types represented by the Figs. 13, 14 and 15. In these figures the flocculating values for a low concentration of colloid have been arbitrarily taken as 100%.

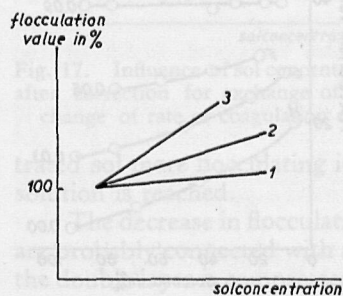


Fig. 13. Influence of sol concentration Type I.

In all cases the flocculation value for trivalent flocculating ions mounts more steeply or descends less steeply than that for divalent ions and monovalent ions with increasing sol concentrations.

With sols of iron hydroxide¹, stannic hydroxide², aluminium hydroxide², chromium hydroxide², manganese dioxide², prussian blue³, type I in which all flocculation values increase with increasing concentration has been found.

Type II, increase of flocculation value for polyvalent ions and decrease for monovalent ions, is the usual one and frequently cited as the rule of BURTON and BISHOP⁴. It was found for $As_2 S_3$ by KRUYT and VAN DER SPEK⁵ and later by many other investigators.

¹ H. R. KRUYT and J. VAN DER SPEK, *Kolloid-Z.*, 25 (1919) 1.

² K. C. SEN and N. R. DHAR, *Kolloid-Z.*, 34 (1924) 262; S. GOSH and N. R. DHAR, *J. Phys. Chem.*, 31 (1927) 187.

³ H. B. WEISER and H. O. NICHOLAS, *J. Phys. Chem.*, 25 (1921) 742.

⁴ E. F. BURTON and E. BISHOP, *J. Phys. Chem.*, 24 (1920) 701.

⁵ J. N. MUKHERJEE, *J. Am. Chem. Soc.*, 37 (1915) 2024; J. N. MUKHERJEE and K. C. SEN, *J. Chem. Soc.*, 115 (1919) 461; H. R. KRUYT and J. VAN DER SPEK, *l.c.*; E. F. BURTON and E. BISHOP, *l.c.*; H. B. WEISER and H. O. NICHOLAS, *l.c.*; E. F. BURTON and E. D. MC INNES, *J. Phys. Chem.*, 25 (1921) 517; A. BOUTARIC and G. PERREAU, *J. chim. Phys.*, 24 (1927) 496.

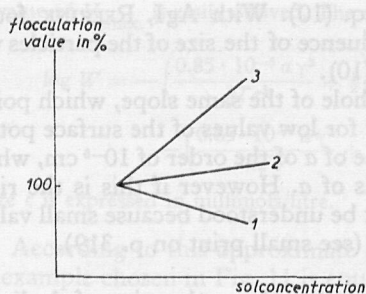


Fig. 14. Influence of sol concentration Type II (BURTON and BISHOP).

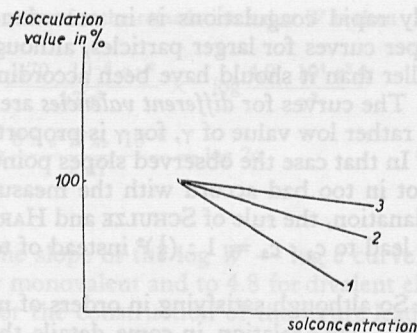


Fig. 15. Influence of sol concentration Type III.

The same behaviour is found for CuO ¹, mastix¹, Ag ², S ³.

Type III finally in which all flocculation values decrease with increasing concentration has been found for emulsions of oil in water⁴ and for a CuS sol⁵.

In a later period it was realized that dilution of a hydrophobic colloid is not at all an *innocent* process. With dilution peptizing and contaminating electrolytes are also diluted and this may give rise either to a decrease or an increase of stability.

SORUM⁶ investigated the effect of dilution on a chromium hydroxide and iron hydroxide sol to which different quantities of peptizing electrolyte (CrCl_3 , FeCl_3) had been added. The flocculation value for monovalent ions of a very pure sol increases with dilution but that of a sol with much peptizing electrolyte shows the opposite behaviour. See Fig. 16.

CHATTERJEE⁷ found an analogous behaviour in the case of an uranium ferrocyanide sol with potassium ferrocyanide. The investigation by FISHER and SORUM on chromium hydroxide peptized with CrCl_3 is still more complete. For monovalent ions they found the same behaviour as for $\text{Fe}(\text{OH})_3$. For flocculation with polyvalent ions they found

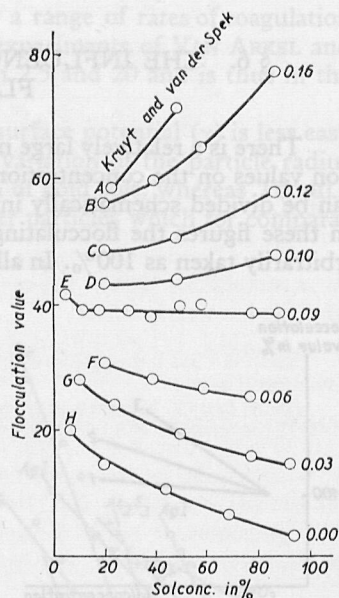


Fig. 16. Flocculation values of iron oxide sols to which FeCl_3 has been added. The numbers along the curves give the number of millimols FeCl_3 /1 sol.

¹ E. F. BURTON and E. BISHOP, *l.c.*

² H. FREUNDLICH and E. LOENING, *Kolloidchem. Beihefte*, 16 (1922) 1.

³ H. FREUNDLICH and P. SCHOLZ, *Kolloidchem. Beihefte*, 16 (1922) 241; A. FODOR and R. RIWLIN, *Kolloid-Z.*, 44 (1927) 69.

⁴ S. S. BHATNAGAR, *J. Phys. Chem.*, 25 (1921) 735; S. GHOSH and N. R. DHAR, *J. Phys. Chem.*, 30 (1926) 294.

⁵ J. N. MUKHERJEE and K. C. SEN, *J. Chem. Soc.*, 115 (1919) 461.

⁶ C. H. SORUM, *Kolloid-Z.*, 58 (1932) 314; E. FISHER and C. H. SORUM, *J. Phys. Chem.*, 39 (1935) 283; R. C. JUDD and C. H. SORUM, *J. Am. Chem. Soc.*, 52 (1930) 2598.

⁷ N. P. CHATTERJEE, *Kolloid-Z.*, 52 (1930) 214.

behaviours according to type II (rule of BURTON and BISHOP) independent of the concentration of peptizing electrolyte.

WANNOW and collaborators¹ could confirm the rule of BISHOP and BURTON with a somewhat more modern technique for many cases like As_2S_3 , CuO , $\text{Al}(\text{OH})_3$, $\text{Fe}(\text{OH})_3$, $\text{Cr}(\text{OH})_3$ etc., but for very great dilution they always found increasing stability according to type III.

In trying to explain these results it should be realized that in all these investigations the influence of the sol concentration has been contaminated by other effects. After dilution the flocculation criterion should be changed and the state of flocculation should be judged after a longer period (smaller rate of coagulation). Moreover the concentration of peptizing electrolyte should be kept constant or at least controlled and a correction should be applied for the exchange of flocculating ions against double layer ions which may, especially in the case of concentrated sols and polyvalent ions, seriously disfigure the results.

When these corrections are applied, Miss KLOMPÉ² finds for the influence of sol concentration on the flocculation value of AgI just the reverse of the BURTON-BISHOP rule, *i.e.*, a decrease of flocculation values with dilution for monovalent and an increase for di- and tri-valent ions as shown schematically in Fig. 17.

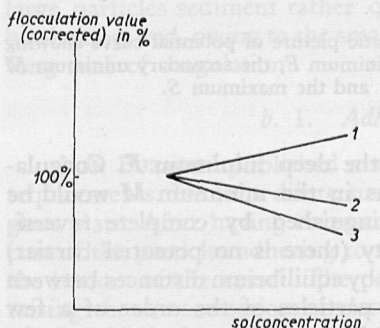


Fig. 17. Influence of sol concentration after correction for exchange of ions, change of rate of coagulation etc.

As the application of all these corrections makes the final results less accurate, one should say that as yet in the authors' opinion there is no certainty whether there is any *direct* influence of the sol concentration on the flocculation value. But on the other hand rules like that of BISHOP and BURTON must certainly be explained by *indirect* influences of the sol concentration.

The increase in flocculation values for polyvalent ions in type I and type II has to be explained by ionic exchange. In the more concentrated sol more flocculating ions are necessary before a certain critical activity in the solution is reached.

The decrease in flocculation value especially for monovalent ions in type II and III, are probably connected with a change in surface potential. After addition of electrolyte the double layer is compressed, the charge increases, the free concentration of peptizing electrolyte decreases and the stability decreases. This process is most pronounced for the most concentrated sols.

¹ H. WANNOW and K. HOFFMANN, *Kolloid-Z.*, 80 (1937) 294; H. WANNOW, *Kolloid-Beihefte*, 50 (1939) 367; H. KAUFFMANN, *Kolloid-Z.*, 92 (1940) 343; 93 (1940) 86.

² M. A. M. KLOMPÉ, *Thesis*, Utrecht 1941.

§ 7. THE MINIMUM IN THE POTENTIAL CURVES FOR LARGE DISTANCES BETWEEN THE PARTICLES

a. Theoretical

A characteristic feature of the potential curves to which we have hitherto paid no attention is the minimum for relatively large distances between the particles (M in Fig. 18).

This minimum, which is always present owing to the slow falling off of the VAN DER WAALS attraction, should be a cause for coagulation if it is deep enough. This coagulation, however, would have a different character from the coagulation treated in the foregoing sections which was dependent

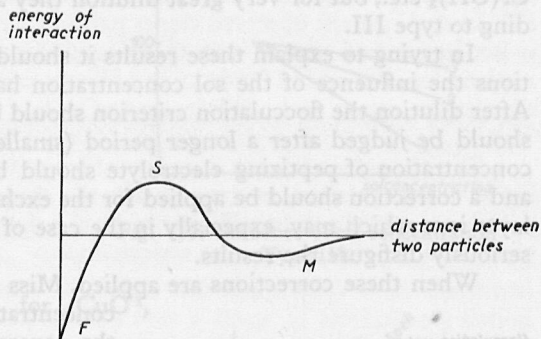


Fig. 18. Schematic picture of potential curve showing the primary minimum F , the secondary minimum M and the maximum S .

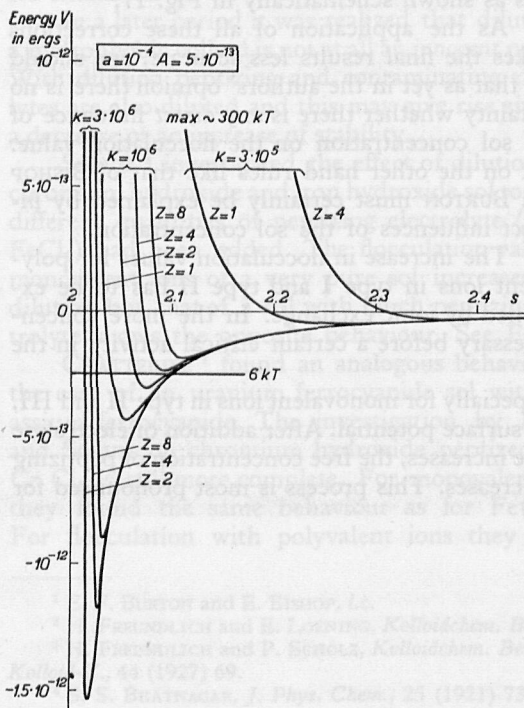


Fig. 19. Secondary minima in the energy curves for coarse particles ($a=10^{-4}$, $A=5 \cdot 10^{-13}$). For $\kappa=10^6$, that is $c \sim 0.001 n$ the minimum may already be deeper than $-6kT$.

on the deep minimum F . Coagulations in the minimum M would be distinguished by complete reversibility (there is no potential barrier) and by equilibrium distances between the particles of the order of a few times the thickness ($1/\kappa$) of the double layer.

To give rise to observable effects the minimum M must be at least several times kT deep. Then from a quantitative inspection of the potential curves of chapter VI, § 10 it follows that for colloidal particles of the usual dimensions (10^{-6} cm and smaller) the minimum M is never deep enough when the maximum S is large enough to prevent normal flocculation. So for ordinary hydrophobic sols the minimum at large distances does not interfere with the rules for stability treated in the foregoing sections.

If, however, the particles are larger (coarse suspensions) or only larger in one or two directions (rods or plates) an influence of the

minimum M is expected to exist, unless the retardation correction to the LONDON force (chapter VI, § 10b) should destroy it. As the magnitude of this retardation is still less predictable than the value of the LONDON force, we shall inspect the experimental data for evidence of the existence of the minimum M .

b. Experimental indications for long range equilibria

Experimental indications for the existence of this minimum M will be difficult to find in the case of more or less spherical particles. In this case indeed practically the only indication would be a relatively low flocculation value for coarse suspensions. The minimum M could be deep enough at electrolyte concentrations where S is still far too high to allow normal flocculation. Fig. 19 shows for instance how, in case of particles of 2μ diameter, flocculation could be brought about by 1 or a few millimols/l of a monovalent electrolyte.

But in the case of such coarse suspensions the difference between stability and flocculation is unfortunately much less pronounced than for smaller particles, as the large particles sediment rather quickly on their own account, are easily redispersed by shaking, and, owing to the small number of particles per unit of volume, show a very long time of coagulation.

b. 1. Adherence numbers of VON BUZAGH

VON BUZAGH¹ published a series of experiments which come rather close to our requirements. He let a dilute suspension of quartz or glass particles sediment upon a glass plate. After having reversed the glass plate, keeping it submerged, he observed part of the particles adhering to the plate and part of them falling off and dropping to the bottom of the vessel. The percentage of particles adhering increased strongly on raising the concentration of electrolyte above one or a few milli equivalent per litre of a univalent electrolyte (see Table 8), and obeyed to the SCHULZE-HARDY order.

TABLE 8
CONCENTRATION OF ELECTROLYTE NECESSARY TO INCREASE THE ADHERENCE NUMBER OF QUARTZ PARTICLES FROM 50% (value in pure water) TO 95%

Electrolyte	millimols/l
LiCl	1.4
NaCl	1.0
KCl	0.4
CaCl ₂	0.04
SrCl ₂	0.03
BaCl ₂	0.02
AlCl ₃	0.04
Th(NO ₃) ₄	< 0.002

The adherence was most evident for particles with a diameter of the order of 3μ , the smaller ones falling off because the minimum was too shallow and the larger ones because they were too heavy.

Not only the low "flocculation value" is in accord with the supposition that here

¹ A. VON BUZAGH, *Kolloid-Z.*, 47 (1929) 370; 51 (1930) 105, 230.

is a case of flocculation in the secondary minimum, but also the fact mentioned especially by VON BUZAGH, that the adhering particles retain their lateral BROWNIAN motion which seems only possible if they are separated from the plate by a layer of liquid of sufficient thickness.

b. 2. Tactoid formation

Several colloidal systems containing anisodimensional particles may under certain circumstances show a reversible separation into two phases. The oldest example is the iron hydroxide sol described by COTTON and MOUTON¹. The same phenomenon has been studied more extensively on iron hydroxide, vanadium pentoxide, tungsten trioxide, benzopurpurin and other dyes by ZOCHER², SZEGVARI³, HELLER⁴ and recently on tobacco mosaic virus by BERNAL and FANKUCHEN⁵ and on cucumber virus by BAWDEN and PIERIE⁶.

When the colloids just mentioned are sufficiently concentrated and their electrolyte content is not so high as to cause irregular flocculation, the sol separates into two phases: a dilute isotropic and a more concentrated birefringent one. Under the microscope between crossed nicols one observes that the anisotropic phase forms spindle-shaped islands in the dilute phase. When the original sol is very concentrated the reverse phenomenon is observed, *i.e.*, isotropic spindles are formed in an anisotropic sol. The anisotropic spindles have been called tactoids by FREUNDLICH⁷. Fig. 20 gives a fine

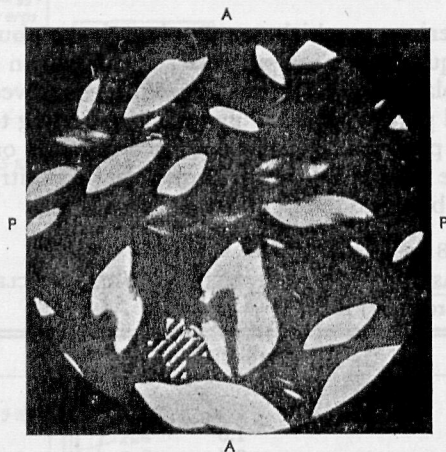


Fig. 20. Tactoids of vanadium pentoxide
PP=orientation of polarizer.
AA=orientation of analyzer.



Fig. 21. Negative tactoids of isotropic solutions in the anisotropic phase of tobacco mosaic virus.

¹ A. COTTON and H. MOUTON, *Ann. chim. et phys.*, (8) 11 (1907) 185.

² H. ZOCHER, *Z. anorg. u. allgem. Chem.*, 147 (1925) 91; H. ZOCHER and K. JACOBSON, *Kolloid-Z.*, 41 (1927) 220; *Kolloidchem. Beihefte*, 28 (1929) 167.

³ A. SZEGVARI, *Z. physik. Chem.*, 112 (1924) 295.

⁴ H. ZOCHER and W. HELLER, *Z. anorg. u. allgem. Chem.*, 186 (1930) 75; W. HELLER, *Compt. rend.*, 201 (1935) 831.

⁵ J. D. BERNAL and I. FANKUCHEN, *Nature*, 139 (1937) 923; *J. Gen. Physiol.*, 25 (1941) 111.

⁶ F. C. BAWDEN and N. W. PIERIE, *Proc. Roy. Soc. London*, B 123 (1937) 274; *Nature*, 139 (1937) 546; *Birt. J. Exptl. Path.*, 18 (1937) 275.

⁷ H. FREUNDLICH, *Kapillarchemie*, II, Leipzig 1932, p. 55.

example of positive tactoids of V_2O_5 and Fig. 21 one of negative tactoids in tobacco mosaic virus¹.

By one sided dark field illumination (SZEGVARI, Fig. 22) and also by determination of the sign of the birefringence it has been ascertained that in the spindles the rodlike particles are situated nearly parallel to the long axis of the spindle as shown schematically in Fig. 23¹.



Fig. 22. The same field as Fig. 20 now illuminated in the direction BB¹.

X-ray reflections which could be interpreted as due to a regular hexagonal packing of parallel rods at distances between the rods varying from 180–600 Å (the diameter of the rods themselves is about 150 Å). The distance between the rods responds to the pH of the solution and to its salt content in a manner which proves that the repulsive force is of electrical nature. Indeed for high salt contents and in the iso-electric point of the T.M.V. the rods are nearly close-packed and the distance between them increases with diminishing content of electrolyte and with pH deviating from the I.E.P. See Fig. 24 from BERNAL's and FANKUCHEN's work.

This phase separation could be explained by the secondary minimum in the now familiar potential curves. It should be mentioned, however, that some authors, judging that the attracting LONDON forces are too weak to make themselves felt over distances of the order of 500 Å, in this case seek other explanations².

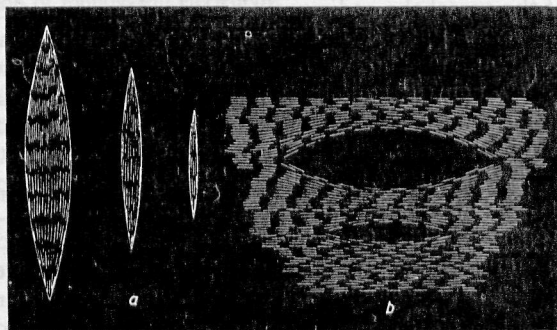


Fig. 23. Positive and negative tactoids in colloids with rodlike particles.

¹ J. D. BERNAL and I. FANKUCHEN, *l.c.*

² S. LEVINE, *Trans. Faraday Soc.*, 42 B (1946) 102, 128; G. OSTER, *Rec. trav. chim.*, 68 (1949) 1123; L. ONSAGER, *Phys. Rev.*, 62 (1942) 558 (abstract); *J. Gen. Physiol.*, announced; *Ann. N. Y. Acad. Sci.*, 51 (1949) 627.

The most attractive explanation is that by ONSAGER who considers the phase-separation as a pure entropy effect. The very long particles like those of T.M.V. effectively hinder each other in their BROWNIAN motion because there is a great a priori possibility of two particles touching each other. This effect increases strongly with concentration. Now for a given mixture of solution and long particles a random mixture may be less advantageous than a separation in a concentrated and a dilute phase because the particles in the concentrated phase lose only comparatively little freedom in rotational movement (for they *had* so little of it) whereas the particles in the dilute phase have a great gain in entropy, being now free to develop their rotational motions.

In the present form, however, the theory explains only phase separations with a small difference in concentration in the two phases (for instance 30%) whereas in reality the difference may be much larger. It is quite possible that further refinements of the theory will lead to a better quantitative agreement.

For the calculations themselves, which are a rather complicated form of statistical mechanics, the reader is referred to the original papers.

b. 3. SCHILLER layers

In old iron hydroxide sols and in tungsten trioxide sols a remarkable layer formation under the influence of gravity has been observed¹. On the bottom of the vessel the sedimenting blade-shaped particles arrange themselves in horizontal layers in which the particles are separated by distances of the order of 2000–4000 Å. These layers are called SCHILLER layers; they show very beautiful interference colours that may be used to determine the separating distance.

Again this distance becomes smaller on the addition of electrolytes and BERGMANN, LÖW-BEER, and ZOCHER² have given a quantitative theory³ of the phenomenon assuming that the particles are kept apart by double layer repulsion which is counteracted by the force of gravity. At these very large distances the LONDON interaction is expected to be very weak, but gravity now takes its place in the potential curves. See Fig. 25.

The essential difference between SCHILLER layers and tactoids is that the last-mentioned structures are real phase separations independent of gravity whereas the SCHILLER layers seem to be simple partitions of the colloidal particles in the field of gravity.

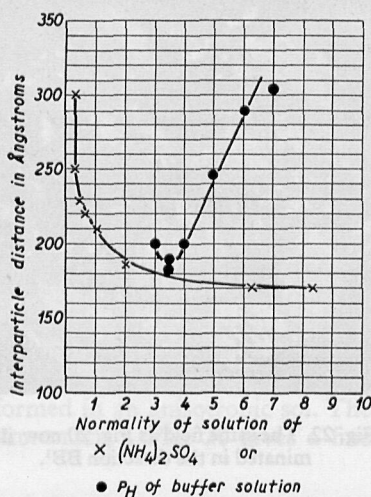


Fig. 24. Relation of interparticle spacing and concentration of salt solution and pH, for solutions of tobacco mosaic virus.

¹ H. ZOCHER, *Z. anorg. u. allgem. Chem.*, 147 (1925) 91; See also W. HELLER, *Compt. rend.*, 201 (1935) 831.

² P. BERGMANN, P. LÖW-BEER, and H. ZOCHER, *Z. physik. Chem.*, A 181 (1938) 301.

³ Their theory of the repulsion of two parallel double layers is completely equivalent to the theory treated in Chapter VI, § 3, p. 247, but was only worked out by them for the case of large distances and weak interaction.

tures of lecithin and sphingomyelin which contain stronger basic groups and thus have the nature of bipolar ions. These last two lipides only show the long range structures to a limited extent.

Usually all these phosphatides contain a certain amount of phosphatidic acid, which enhances the negative character (See Vol II, Ch. VII, p. 192).

The thickness of the water layer between the cephalin leaflets may be as large as 85 Å. It is diminished by the addition of electrolytes which, as far as investigated, act according to the SCHULZE-HARDY order as is shown in Fig. 26.

Especially the last mentioned fact showing that the leaflets approach each other when the repulsion is less far reaching, indicates that an attractive force is present and it seems acceptable to assume that the equilibrium distances measured by PALMER and SCHMITT are to be explained as flocculations in the secondary minimum.

The great similarity in behaviour between phosphatides and soaps gives rise to the expectation that leaflet structures are also present in soap solutions.

The long range interferences which have been observed in soap solutions¹ have been explained in this way. However, there is still much controversy² as to the question whether soap micelles are leaf-shaped, cylindrical or spherical and it seems advisable therefore to suspend judgment until X-ray interferences have been analysed more completely in this case.

b. 5. Gelformation

HELLER³ and BERNAL and FANKUCHEN⁴ have pointed out the possibility of explaining gel-formation in sols with rod-shaped or blade-shaped particles by assuming a local orientation and fixation of particles by long range forces, the whole system being solidified by a network of chains of particles thus held more or less rigidly near to each other. Fig. (27).

b. 6. Conclusion

We would summarize this section by emphasizing that there are undoubtedly long range equilibrium structures. These structures may be explained by the secondary

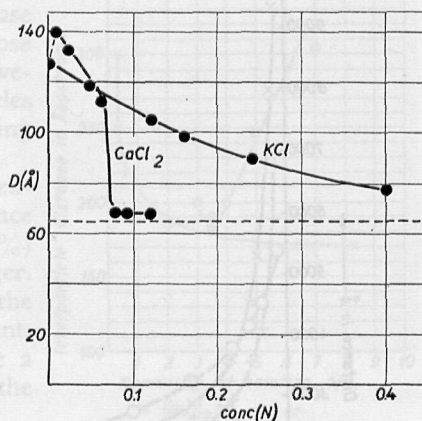


Fig. 26. Effect of KCl and CaCl₂ on the long-spacing identity period of 33% emulsions of total lipide.

¹ See volume II, chapter XIV, on Association colloids § 3, p. 692. K. HESS, W. PHILIPPOFF, and H. KIESSIG, *Kolloid-Z.*, 88 (1939) 40; J. STAUFF, *Kolloid-Z.*, 89 (1939) 224; J. W. MCBAIN and O. A. HOFFMAN, *J. Phys. & Coll. Chem.*, 53 (1949) 39; A. P. BRADY, *J. Phys. & Coll. Chem.*, 53 (1949) 947; W. PHILIPPOFF and J. W. MCBAIN, *Nature*, 164 (1949) 885.

² W. D. HARKINS, *J. Chem. Phys.*, 16 (1948) 156; M. L. CORRIN, *J. Chem. Phys.*, 16 (1948) 844; W. D. HARKINS and ROSE MITTELMANN, *J. Colloid Sci.*, 4 (1949) 370; G. S. HARTLEY, *Nature*, 163 (1949) 767.

³ W. HELLER, *J. Phys. Chem.*, 45 (1941) 1203; W. HELLER and G. QUIMFE, *J. Phys. Chem.*, 46 (1942) 765.

⁴ J. D. BERNAL and I. FANKUCHEN, *J. Gen. Physiol.* 25 (1941) 111.

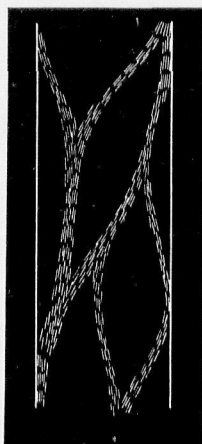


Fig. 27. Formation of a network by strains of parallel particles.

minimum in the potential curves. In no case, however, has a crucial experiment been made to distinguish between the theory presented here and that of ONSAGER who only uses the repulsive force in combination with entropy effects.

§ 8. THE INFLUENCE OF NON-ELECTROLYTES ON STABILITY; SOLS IN NON-AQUEOUS MEDIA

The addition of non-electrolytes may influence the stability in many different ways.

A change of the viscosity changes the rate of flocculation. The change in index of refraction may influence the judgment on stability as measured by turbidity or light absorption. But even if we neglect these more trivial influences there remain changes of the dissociation of the electrolytes (usually a decrease), a change in the zero point of charge, in the dielectric constant, in the LONDON-VAN DER WAALS constant, in the STERN absorption potentials etc.¹ This makes it difficult to predict even qualitatively how the non-electrolytes will change the stability.

For large concentrations of non-electrolyte or for sols in pure non-aqueous media it may be expected that the change in dielectric constant will have the most striking influence as this constant may vary greatly between different substances and it enters into the equation for the flocculation value (eq. (2) p. 306) in the third power.

Results of WEISER and MACK² on HgS and of MACKOR³ on AgI are indeed in not too bad accord with this third power prediction. See Table 9.

TABLE 9

COMPARISON OF FLOCCULATION VALUES (f) IN M MOL/L IN MEDIA OF DIFFERENT DIELECTRIC CONSTANTS (ϵ)

Sol	flocculating electrolyte	flocculation value medium 1	flocculation value medium 2	$f_1 f_2$	$(\epsilon_1/\epsilon_2)^3$
AgI	Na Cl O ₄	142 water	1.4 acetone	100	51
Hg S	Li Cl	4.7 methanol	13 water ³ (NaCl)	$\frac{1}{3}$	$\frac{1}{18}$
	Ca Cl ₂	0.095 methanol	0.88 water ³ (SrCl ₂)	$\frac{1}{9}$	$\frac{1}{18}$
	Li Cl	4.7 methanol	3.3 propanol	1.4	2.8
	Ca Cl ₂	0.095 methanol	0.044 propanol	2.2	2.8
	Ca Cl ₂	0.095 methanol	0.0120 pentanol	7.9	7.5

For smaller additions of non-electrolytes the situation is more complicated, the behaviour of the sol being then governed especially by the influences on the zero point of charge and on the adsorption potentials, which are already changed by small amounts of the non-electrolyte, where the influence on the dielectric constant is still negligible.

Data in the literature seem to converge to a sensitizing of most hydrophobic sols

¹ H. B. WEISER and G. L. MACK, *J. Phys. Chem.*, 34 (1930) 86, 101.

² E. L. MACKOR, *Thesis*, Utrecht 1951; *Rec. trav. chim.*, 70 (1951) 841.

³ The values for water do not occur in the paper of WEISER and MACK. They have been taken from H. FREUNDLICH and H. SCHUCHT, *Z. physik. Chem.*, 85 (1913) 641.

by most of the non-ionic additions against univalent ions¹ (notable exception: the flocculation value of negative AgI has increased about 40% by addition of 10% by volume of acetone²).

Against polyvalent ions a protection, that is an increase of the flocculation value is perhaps the usual thing although there are many exceptions. KRUYT and VAN DUYN (*l.c.*) for instance found on the sol of As₂S₃ a decrease of flocculation values of mono- and tri-valent and an increase for di- and tetra-valent ions by addition of amyl alcohol, phenols etc.

The difficulty in formulating a general rule is clearly seen from the following table³ which gives the change in flocculation values for negative AgI sols after the addition of several non-electrolytes (— = decrease, + = increase, two signs = change > 30%, three signs = change > 100%).

TABLE 10
INFLUENCE OF NON-ELECTROLYTES UPON FLOCCULATION VALUES OF AgI

Flocculating ion	ethyl alcohol 19 vol %	isoamyl alcohol 1.1 vol %	acetone 3.7%	phenol 2.8%	resorcinol 4.9%	urea 7.2%
K ⁺	—	—	+	— —	—	—***
Ba ⁺⁺	— —	++	+	++	+	+
La ⁺⁺⁺	—	+	+*	+	+**	+
Al ⁺⁺⁺	—	— —	++	++	+++*	— —
Th ⁺⁺⁺⁺	+++	++	+++*	++	++++**	+++

* acetone content 2%

** resorcinol content 6.3%

*** urea content 3.2%

Data on the stability of sols in pure non-aqueous media are rather scarce. They have been prepared in great variety⁴. It has been found that small additions of water or of dissociating salts (potential-determining ions) make the preparation easier, but a systematic investigation of the stability and flocculating conditions is lacking.

Although some examples of sols in completely apolar media (liquid methane, pentane etc.) have been described⁵ and suspensions of this type are rather common (raw mineral oil, used lubricating oil⁶, paints and varnishes), by far the greater part of the data relate to sols in alcohols, acetone, nitrobenzene and other media with a certain

¹ H. R. KRUYT and C. F. VAN DUYN, *Kolloidchem. Beihefte*, 5 (1914) 269; C. F. VAN DUYN, *Kolloid-Z.*, 17 (1915) 123; H. B. WEISER, *J. Phys. Chem.*, 28 (1924) 1253; H. LACHS and S. CHWALINSKI, *Z. physik. Chem.*, A 159 (1932) 172; J. N. MUKHERJEE, S. G. CHAUDHURY, and S. MUKHERJEE *J. Indian. Chem. Soc.*, 3(1926) 349; K. C. SEN, *J. Phys. Chem.*, 29 (1925) 517; S. G. CHAUDHURY, *J. Phys. Chem.*, 32 (1928) 1481. S. G. CHAUDHURY and A. GANGULI, *J. Phys. Chem.*, 32 (1928) 1872; S. G. CHAUDHURY and N. P. CHATTERJEE, *J. Phys. Chem.*, 33 (1929) 244.

² E. L. MACKOR, *l.c.* p. 331.

³ W. J. VAN ESSEN, private communication.

⁴ H. B. WEISER and G. L. MACK, *J. Phys. Chem.*, 34 (1930) 86, 101; THE SVEDBERG, *Herstellung Kolloider Lösungen anorganischer Stoffe*, Dresden 1909; H. FREUNDLICH, *Kapillarchemie, II*, Leipzig 1932, p. 282.

⁵ See for instance THE SVEDBERG, *Herstellung Kolloider Lösungen*, Dresden 1909, p. 476 and following pages.

⁶ See *e.g.*, J. L. VAN DER MINNE, *Rec. trav. chim.*, 65 (1946) 549.

dissociating power, so that the existence of sols in the latter media may probably be explained in the same way as the stability of the hydrosols. One of the factors which is important in these media has already been mentioned in chapter IV, § 6c, p. 165. It is a shifting of the zeropoint of charge owing to big changes in the χ -potential.

Some very remarkable sols have been described by VOET.¹ He prepared stable sols of different metals (Pt, Pd) and salts (sulphides, halides) in very concentrated electrolytes like sulphuric acid, phosphoric acid, saturated calcium chloride in water etc. Dilution with water made these sols coagulate in a short time. There is no theory as to the cause of their stability. One might think of an increasing dissociation caused by the addition of water.

§ 9. REPEPTIZATION PHENOMENA

Repeptization is the phenomenon that a hydrophobic sol, after having been flocculated, can be redispersed by agitation after removing the flocculating agent. In many cases repeptization is difficult to bring about or even completely absent. Among other things this may be due to rapid ageing or recrystallization of the precipitate.

In other cases, however, repeptization is relatively easy and it is even the customary method of preparation of several sols (sulphide sols, V_2O_5 -sol, clay suspensions). In order to repeptize a precipitate it is never sufficient to dilute the flocculating electrolyte to just below the flocculation value. On the contrary the precipitate must be washed out thoroughly so that the concentration of electrolyte is brought to a very small value before repeptization can occur. In addition it is often helpful or necessary to add small quantities of the potential-determining (therefore also called peptizing) electrolyte.

Qualitatively this behaviour can be very well derived from the properties of the potential curves. Apart from the double layer repulsion and the LONDON-VAN DER WAALS attraction it is necessary to introduce now the short range repulsion (BORN-repulsion) mentioned in chapter VI because without this short range repulsion the flocculated particles would be in an infinitely deep minimum of energy, and repeptization would be impossible.

With the BORN repulsion added we may draw a series of potential curves as in Fig. 28, where the numbers of the curves give the order of increasing content of electrolyte. Let the stable sol be represented by curve 1. Flocculation does not occur until the amount of electrolyte has been increased to 4. Decreasing the electrolyte content causes the particles to pass through the curves in the reversed order. As the particles are flocculated they are in the deep minimum of energy F and repeptization cannot occur until a curve such as no. 1 is reached where the distance between the minimum F and the maximum S is not much larger than kT .

A quantitative² application of this line of thought is still lacking, which is to be regretted, as the phenomenon of repeptization could furnish information on the innermost part of the potential curves.

One particular fact should be mentioned here about repeptization, which is of great practical importance. Even in those systems where repeptization is relatively easy when the sol has been flocculated by monovalent ions, repeptization after flocculation

¹ A. VOET, *Thesis*, Amsterdam 1935.

² Qualitatively this discussion has already been given by H. C. HAMAKER, *Rec. trav. chim.*, 56 (1937) 3; See also Chapter VI, § 12 d, p. 276.

with polyvalent ions is practically absent. See Table 11. This behaviour is at least partly due to the difficulty of expelling the polyvalent ions from the double layer (great adsorbability and exchangeability), for if the first washing is performed with a concentrated

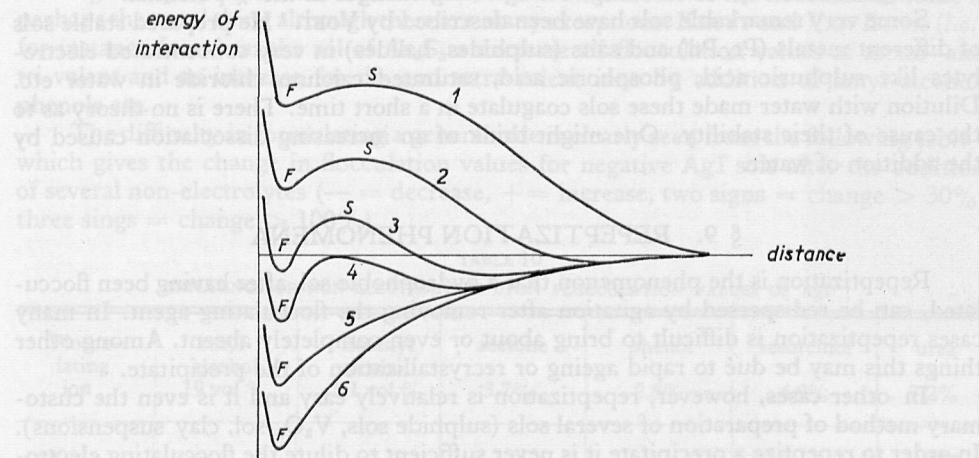


Fig. 28. A series of potential curves illustrating schematically the transition from stable to flocculated systems. Curve 4 corresponds to the flocculation value. For re-peatization curve like 1 or 2 is necessary.

KCl solution which exchanges the polyvalent for monovalent ions, re-peatization is just as easy as after flocculation with KCl¹.

TABLE 11

PEPTIZATION OF Mo_2O_5^- SOL AFTER FLOCCULATION BY DIFFERENT ELECTROLYTES

The precipitate was washed several times with a constant volume of water until peptization occurred²

COAGULANT	PEPTIZATION		
NaCl	Complete after one	washing at	18°—20°
NH ₄ Cl	" " "	" " "	" "
KCl	" " two	washings	" "
Morphine chloride	" " three	" "	" "
Tl ₂ SO ₄	Traces " seven	" "	" "
Sr (NO ₃) ₂	Complete " six	" "	" "
BaCl ₂	Traces " seven	" "	" "
Al ₂ (SO ₄) ₃	" " seven	" "	" "

Recently MACKOR³ found that re-peatization may be strongly influenced by non-electrolytes. Silver iodide, which usually is rather difficult to re-peatize, can be easily and completely re-peatized when flocculation and re-peatization are carried out in a medium containing at least 10% of acetone. As this relatively small amount of acetone is expected to act by being adsorbed at the surface, we see here that re-peatization reacts sensitively on changes in the innermost part of the potential curve as was expected from the reasoning given with Fig. 28.

¹ D. STIGTER, private communication.

² H. FREUNDLICH and W. LEONHARD, *Kolloidchem. Beihefte*, 7 (1915) 179.

³ E. L. MACKOR, private communication.

§ 10. ANOMALOUS TYPES OF FLOCCULATION

a. Gel formation in systems with anisodimensional particles

In several hydrophobic sols, especially those with flat or elongated particles it is possible to induce gelation by the addition of an amount of electrolyte not quite sufficient to lead to a normal flocculation. Evidently the partly discharged particles are attached to each other at a very few spots, still repelling each other on the main part of their surface and thus forming a network which immobilizes the included intermicellar liquid.

That this form of gelation is closely connected with coagulation is clearly proved by the fact that the concentrations of different electrolytes, necessary to bring about gelation, obey the rule of SCHULZE and HARDY (Table 12) and Table 13 shows the quasi-continuous transition from stability over gelation to flocculation.

TABLE 12
CONCENTRATION OF ELECTROLYTE IN MILLIMOLS/L REQUIRED TO BRING ABOUT GELATION

Al ₂ O ₃ -sol ¹ positively charged		CeO ₂ -sol ² positively charged		SiO ₂ -sol ³ negatively charged	
Electrolyte	conc.	Electrolyte	conc.	Electrolyte	conc.
NaCl	77	NaBr	5	Na Cl	100
KCl	80	NaClO ₄	5	$\frac{1}{2}$ Na ₂ SO ₄	100
K ₂ SO ₄	0.28	NaCl	3.5	Ba Cl ₂	15
K ₂ (COO) ₂	0.36	Na ₂ SO ₄	0.15		
K ₃ Fe(CN) ₆	0.10	Na ₂ HPO ₄	0.16		
K ₄ Fe(CN) ₆	0.08				

TABLE 13
CHANGE IN PROPERTIES OF A BENTONITE SUSPENSION BY THE ADDITION OF POTASSIUM CHLORIDE⁴

Conc. of KCl millimols/l	Aspect
11.9	Translational BROWNIAN motion stops
21.1	No visible BROWNIAN motion
27.4	Notable aggregation
37.4	Flocculation

It seems improbable that the gelation mentioned in this section is based upon flocculation in the secondary minimum that has been treated in § 7b. 5, because the concentrations of electrolyte are too high and too near the normal flocculation values.

¹ J. A. GANN, *Kolloidchem. Beihefte*, 8 (1916) 64.

² H. R. KRUYT and Miss J. E. M. VAN DER MADE, *Rec. trav. chim.*, 42 (1923) 277.

³ H. R. KRUYT and J. POSTMA, *ibidem.*, 44 (1925) 765.

⁴ E. A. HAUSER, *Kolloid-Z.*, 48 (1929) 57.

We may better compare these gels to slow coagulations stopped by remaining repulsions and by immobilization of the particles in the network formed.

The systems mentioned here often show thixotropy, that is, isothermal reversible transformation of sol into gel. Thixotropy will be treated in chapter IX on rheology.

b. Oriented flocculation

It is conceivable that with crystalline particles the interaction varies for different crystal faces or for different mutual orientations of the particles. In that case slow coagulation might lead to a formation of very regularly and compactly built flocks whereas rapid coagulation leads to a loose and irregular coagulum. JONKER¹ probably found such systems in very diluted silver halide sols which originally contain very small particles. When these sols are prepared with different excesses of halide or silver ions and at

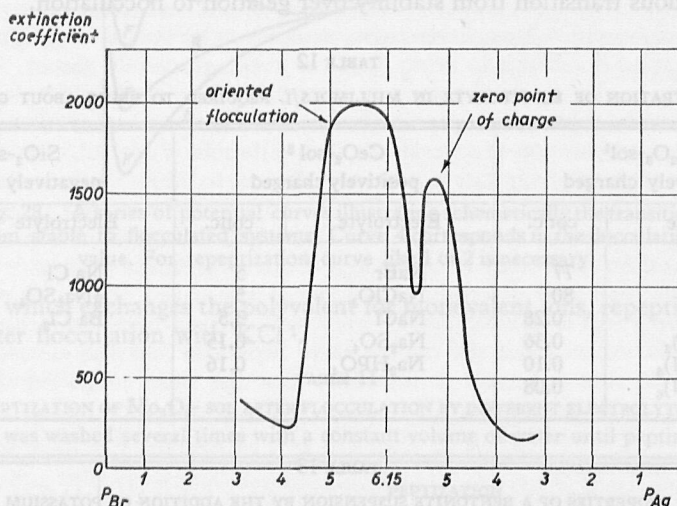


Fig. 29. Extinction curve of a sol containing $2 \cdot 10^{-5}$ mol AgBr per litre, 20 hours after the formation, against the logarithm of the concentration of potential-determining ions. There are clearly two flocculation regions, one at $p_{Ag} \sim 5.2$ in the zero point of charge, and the other at a slight excess of bromine ions which is ascribed to an oriented flocculation.

such a dilution that the primary particles can be supposed to be monocrystals, not only the normal flocculation regions are observed at the zero point of charge and at large excesses of silver or halide salt but a fourth flocculation region is found for a small excess of the halide ion. This fourth flocculation region is distinguished by the formation of very dense particles showing a much larger TYNDALL scattering than that of the more usual flocculations. That this is a real flocculation and not a coarsening (*cf.* chapter VII, § 9) is proved by the fact that the phenomenon is especially pronounced at a p_{Ag} where the solubility is low and therefore recrystallization cannot be expected to be especially strong. Moreover it is repressed by electrolytes in the SCHULZE-HARDY

¹ G. H. JONKER, *Thesis*, Utrecht 1943.

order which lower the stability to such an extent, that in the more rapid flocculation no opportunity is left for preferential orientation.

A typical graph demonstrating this region of oriented flocculation is given by Fig. 29 representing the extinction of a silver bromide sol as a function of the p_{Ag} 20 hours after the mixing of the solution of silver nitrate and potassium bromide.

§ 11 STABILITY OF COARSE SUSPENSIONS

a. Flocculation

In principle the stability of suspensions is governed by the same factors as that of sols. In practice, however, we find very clear differences between the two sorts of systems, due to the larger particle dimensions ($> 1 \mu$) of suspensions. Moreover in the applications suspensions take a much more important place than sols do.

The larger particles of suspensions sediment rather rapidly. The flocculation velocity of a suspension is slow, owing to the relatively small number of particles. Therefore the sedimentation velocities of a flocculated and a stable suspension do not differ pronouncedly, although in special cases this difference is applied (blood sedimentation).

There are, however, great differences in the sediments of stable and flocculated suspensions. The stable sediments are very closely packed because in forming the sediment the particles retain their individual freedom and roll over each other until the closest packing is reached. The flocculated sediments are more loosely built because once the sedimenting particles touch each other they adhere in the haphazard way in which they first touched and are no longer able to proceed into a more favourable position.

Although the stable sediment is the denser one, it flows for low rates of shear like a (very viscous) NEWTONIAN liquid, whereas the flocculated sediment on the contrary often shows a pronounced yield value and non-NEWTONIAN behaviour.

We return to these mechanical properties and their applications in chapter IX.

It has already been mentioned in § 7a that one might expect fine suspensions ($1-5 \mu$) to show flocculations in the secondary minimum, if this has not been reduced by the retardation correction (see chapter VI, § 9c, p. 266). This kind of flocculation has not yet been verified experimentally.

b. Repeptization

The ease of repeptization of suspensions is remarkable. By vigorous shaking the original degree of dispersion may usually be restored, which is an impossibility in the case of sols.

Qualitatively this easy repeptization can be explained in the following way. By agitation a shearing motion of the liquid is excited. This causes a force trying to tear two neighbouring particles apart, which force is proportional to the radius of the particles (STOKES' law) and to the distance between their centres (difference in velocity of the liquid). So the separating force is proportional to the square of the radius of the particles. On the other hand the attractive force is, at best, proportional to the first power of the radius of the particles (LONDON force for spherical particles) and if the particles are not very regularly formed the attractive force will soon be independent of the overall dimensions.

This means that there must be a particle-diameter for which the attraction is small-

ler than the hydrodynamic force. If, however, we work out this picture in a more quantitative way, the critical diameter found is too large and of the order of 100μ instead of 1 or 0.1μ . This means that, when the particles are very close, the LONDON-VAN DER WAALS force is less steep than we estimated in the foregoing section or the influence of short range repulsion by solvation and BORN effect is by no means negligible.

Again in accordance with our picture is the ease of repectization of even very small clay particles¹ (equivalent diameter $\sim 20 \text{ m } \mu$) because these are in reality blade-shaped and therefore may experience a comparatively large hydrodynamic force and a small attraction.

It may be remarked here that although a flocculated suspension is easily repectized it is very difficult to redisperse the compact sediment of a stable suspension. This is not a case of difficult repectization, however, (in the sediment the particles are still separated by double layer forces) but the sediment is so compact that the particles can only be attacked by hydrodynamic motions layer by layer which evidently is a very slow process.

§ 12. STABILITY OF EMULSIONS

a. Double layer in emulsions

It has been shown in chapter VI § 7, p. 261 that the repulsion between two oil² droplets in water or between two water droplets in oil is much smaller than the repulsion between two solid particles covered with a double layer. Therefore emulsions of two pure liquids are never stable. It is possible to prepare and investigate such emulsions in an extremely dilute form, so that the flocculation time will be very large, but a reasonably stable emulsion can only be prepared by the addition of at least one component more to the system. This third component should be chosen in such a way as to change the double diffuse double layer at the oil/water interface into a normal double layer in the water phase only.

This may be effected by the addition of soaps or soaplike substances. These paraffin-chain salts are strongly adsorbed at the interface with their polar ends turned to the water. By dissociation of the polar groups the oil phase receives a charge situated at the interface and the counter ions form a diffuse double layer in the water.

A second method to stabilize emulsions of oil droplets in water is the addition of finely divided, rather hydrophilic substances, with a contact angle smaller than 90° with water. These small particles will then be adsorbed at the oil/water interface but turn their larger parts to the water. See Fig. 30a.

Two oil drops covered with these particles will now repel each other due to the double layers on the solid particles. Suitable solids for stabilizing oil emulsions are, among others: bentonite, $\text{Al}(\text{OH})_3$, SiO_2 .

A third method for stabilization is the addition of hydrophilic colloids like gelatin

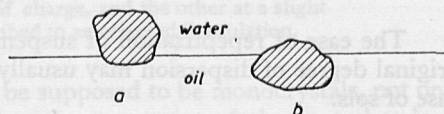


Fig. 30. Illustrating emulsification by solid particles.

a = contact angle $< 90^\circ$. Gives oil in water.

b = contact angle $> 90^\circ$. Gives water in oil.

¹ C. E. MARSHALL, *The colloid chemistry of the silicate minerals*, New York 1949, p. 67 ff.

² By "oil" we mean here any non-polar or slightly polar liquid immiscible with water.

or gum arabic. This method is completely equivalent to the protecting action on hydrophobic sols (*cf.* § 4e, p. 316) and, although certainly important in practice (fresh Hevea latex for instance is stabilized in this way), will not be further treated here.

b. Two types of emulsions

In the foregoing subsection our attention has been concentrated on emulsions of oil droplets in water. The reverse system, an emulsion of water droplets in oil is also possible. Which of the two types of emulsion is formed on shaking the two phases depends primarily on the emulsifier added. The second type of stabilization especially, *viz.* the addition of finely divided solids, may be used to stabilize water in oil emulsions, when the contact angle with water is larger than 90° so that the major part of the solid particles extend into the oil phase. (See Fig. 30b). As stabilizers for water-in-oil emulsions different forms of carbon (soot, finely powdered graphite), heavy-metal soaps and long-chain alcohols or esters may be used.

The two types of emulsions may be readily distinguished experimentally by one of the three following methods.

α . The electrical conductivity of a water-in-oil emulsion is much smaller than that of an oil-in-water system.

β . An oil-in-water system is easily coloured by a water-soluble dye and not by a dye soluble in oil whereas for a water-in-oil system the reverse is the case.

γ . An emulsion may be diluted with its continuous phase when this is added in pure form.

c. The stability of an emulsion is not governed by double layer effects alone

There exist several indications that the stability of emulsions in water is not governed exclusively by double layer effects. In the first place the flocculation values are usually rather high and when the oil drops are coagulated they do not unite to form a coherent layer of oil. Secondly, emulsions may be stabilized by non-ionic detergents which, however, cannot be considered as a finely divided third phase but which are molecularly or micellarly dispersed in the solution. Finally it seems as if the mechanical properties of the interface are important, a condensed fluid film at the interface promoting an oil-in-water system and a rigid film a water-in-oil emulsion¹.

In the prevention of coagulation and especially of coalescence, therefore, the solidity of the boundary phase between oil and water, must also be considered. This solidity may either arise from a solid type of monomolecular layer or from a fairly close packing of particles of a third phase as is treated above.

Quite distinct from the colloid-chemical stability are the effects of gravity on emulsions. As the droplets in an emulsion are usually not very small ($> 1 \mu$) the rate of sedimentation is comparatively large and the droplets may sink to the bottom or float at the surface of the continuous phase without uniting to a coherent layer. This phenomenon is called creaming, and in itself is not a sign of loss of stability although the processes of coagulation and coalescence may be accelerated by the high concentration in the cream layer.

¹ J. H. SCHULMAN and E. K. RIDEAL, *Proc. Roy. Soc. London*, B 122 (1937) 29, 46; J. H. SCHULMAN and E. G. COCKBAIN, *Trans. Faraday Soc.*, 36 (1940) 651, 661.

d. Preparation of emulsions

Emulsions are prepared by shaking or stirring the two components with the addition of the emulsifier. It will be clear that a low interfacial tension greatly facilitates the breaking up of the phases into separate droplets and thus, although in itself not a sufficient reason for stability, will promote the emulsification. The success of certain branched-chain emulsifiers may well be explained by the very low interfacial tension¹ (~ 0.1 dynes/cm) which they may give because just the branched form of the chain hampers the formation of micelles in the solution and therefore allows the activity of these branched-chain compounds to become greater than that of the straight-chain compounds can ever be.

Under certain circumstances emulsification is so easy that no external force is necessary. One speaks then of "spontaneous emulsification". This does not mean, however, that now the emulsion is more stable in the thermodynamical sense than the separated compounds. It only means that at the macro interface oil/water processes occur which give rise to local turbulent motions strong enough to break the cohesion of one of the phases and emulsify it in the other phase.

Such processes may be:

a. A chemical reaction, as occurs in the formation of an emulsion from an oil, in which a long chain fatty acid has been dissolved, in a lye solution. The formation of the soap at the interface which lowers the surface tension locally, is here the cause of emulsification.

b. The passage through the interface of a substance originally dissolved in one of the two phase but which has a great solubility in the other phase.

c. A modification of *b.* occurs when the oil is strongly solubilized in the soap-containing water phase².

It is often desired to prevent creaming by reducing the size of the particles of an emulsion. For this purpose several instruments, called homogenizers, have been developed. They all use the principle of generating strong shearing motion in the emulsion. The emulsion drops are then elongated and when the elongation passes a certain limit, they become unstable and break up into several small drops. The shearing motion is carried out for instance by forcing the emulsion through a narrow slit, or by letting it pass through the slit between a rapidly rotating rotor and a stator. (Fig. 31).

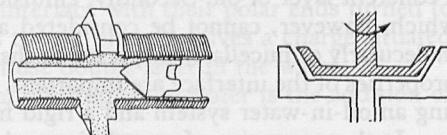


Fig. 31. Two types of homogenizers.

e. Breaking of emulsions and inversion of the emulsion type

The breaking of emulsions is technically often of the greatest importance either to destroy undesired emulsions like those present in natural mineral oils (mostly w/o type), or to make a coherent phase of a substance which occurs in or has been prepared

¹ G. S. HARTLEY, *Trans. Faraday Soc.*, 37 (1941) 130.

² A. KAMINSKI and J. W. Mc BAIN, *Proc. Roy. Soc. London*, A 198 (1949) 447.

in emulsion form (natural and synthetic latices). It is not always sufficient to suppress double layer repulsion by the addition of salts, especially not in the case of emulsions protected by lyophilic colloids. In addition it is often necessary to apply mechanical means in order to destroy the resistant skins at the interface by kneading for instance or to change the character of the emulsifier (denaturing of protein layers, addition of polyvalent of heavy ions to a soap stabilized emulsion, dissolving of the particles of the third phase by acid etc.).

In some instances especially in the manufacture of butter and margarine it is necessary to reverse the type of emulsion. Starting with an emulsion of oil in water (milk, cream) one arrives at the reverted emulsion of water in oil by acidification, which changes the character of the emulsifier, and mechanical action (churning).

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 are to be found, whereas the rheological peculiarities of stable systems are more often a nuisance than an advantage. Therefore it is the more respectable that theories, as far as they go, are only distinguished 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.

(2) 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 of the class 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.

THE VISCOSITY OF STABLE SOLS

The basis for considerations on the viscosity of suspensions has been given by Einstein, who calculated the viscosity of a dilute suspension of rigid spherical particles. Making the assumption 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 equations...

¹ A. Einstein, Ann. Physik (4) 19 (1906) 289, 34 (1911) 289; Kolloid-Z. 37 (1923) 107. See also R. Simha, Kolloid-Z. 76 (1932) 16, who demonstrated the existence of eq. (1) also for flow in a capillary, whereas Einstein had only derived the equation for a cell of flow with constant rate of shear as approximated in a Couette viscosimeter.