

The Chairman now gave the floor to Mr. Overbeek.

Concerning the protective and sensitizing action of hydrophilic colloids on hydrophobic sols

by

J. Th. G. Overbeek (Utrecht).

1. Protective action.

It is a well known phenomenon, that the flocculation of a hydrophobic sol is hampered by the addition of a hydrophilic colloid, and a lot of experimental work has been carried out on the subject, the results of which in several cases have been applied to practical purposes. An example may be found in several pharmaceutical preparations, in which dispersion of a substance is maintained by the addition of a protective colloid (e.g. Collargol); whilst organic chemistry occasionally applies protective action, when carrying out reductions by means of colloidal Pd, where gum arabic effects the protection of the Pd.

Systematic investigations in this field were initiated by Zsigmondy¹⁾ who introduced the principle of "gold-number", which, though an arbitrary unit, enabled him to study the phenomenon in a quantitative way.

The gold-number represents the number of milligrams of substance, necessary for the protection of a fixed quantity of a certain gold sol (10 cm³ containing 0.6 mg of Au) against the flocculating action of a considerable excess of NaCl solution. Gold-numbers may vary between 0.01 for gelatine and 25 for starch, all hydrophilic substances exerting a more or less pronounced protective action.

It has been established, that the behaviour of protecting agents towards various hydrophobic sols is similar to that towards the gold sol; consequently a small gold-number of a certain hydrophilic colloid in general also implies a strong protective action with any suspensoid.

Zsigmondy²⁾ assumed that protective action might be due to a mutual union of lyophilic and lyophobic particles. Since lyophilic particles are usually much smaller than lyophobic ones, this assumption resolves itself in most cases in an envelopment of the latter by the former; consequently the surface of the lyophobic particles is composed of a layer of less easily flocculating material, like gelatin, gum arabic, or such like.

Zsigmondy's assumption is substantially supported by results of experimental work on the electrophoretic velocity of protected sols. Several investigators examined the electrophoretic velocity of sols and suspensions on addition of lyophilic colloid; by increasing the concentration of lyophilic colloid the observed electrophoretic velocity approaches a constant value, the electrophoretic velocity of the lyophilic substance. An example of this effect may be found in the work of Bendien³⁾, who studied the influence of gelatin on gold sol at various concentrations. His results are shown in fig. 1.

¹⁾ R. Zsigmondy, Z. anal. Chem. 60, 697 (1901); R. Zsigmondy-Thiessen, Das kolloide Gold, Leipzig, 1925, p. 173.

²⁾ R. Zsigmondy, Verh. Ges. Naturf. Ärzte (Hamburg) 1901, 168.

³⁾ W. M. Bendien, thesis Delft, 1926; W. Reinders and W. M. Bendien, Rec. trav. chim. 47, 977 (1928).

The same author also investigated the influence of other lyophilic colloids (e. g. dextrine, gum arabic) and found their behaviour to be closely similar to that of gelatin⁴⁾.

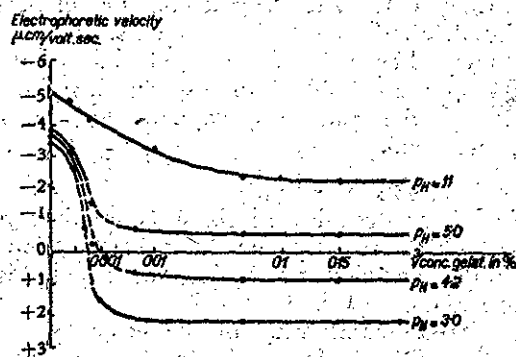


Fig. 1.

Attention must be drawn to the fact, that in all these cases the electrophoretic velocity of the lyophilic colloid is smaller than that of the suspensoid particles, which clearly indicates, that the increase in stability cannot be due to an increase in ζ -potential of the particles.

It has not been definitely established, which portion of the curve represents the range where protective action occurs. From the investigations of Bendien the impression prevails, that the range of protection coincides with the flat portion of the curve; an accurate investigation of the problem, carried out with a reliable technique, however, is still lacking.

If one compares the protective action of a certain quantity of hydrophilic colloid against the flocculating power of ions of various valency, then it is found, that protection is highest in the case of the strongly flocculating ions of high valency; i.e. protective action tends to minimize the Schulze-Hardy rule.

Table 1*).

Flocculation value of Carey Lea's silver sol in mixtures with gum arabic.

Gum arabic in mg/l.	Flocculation value in m mols/l.		
	NH ₄ NO ₃	Sr(NO ₃) ₂	La(NO ₃) ₃
0	21	0.52	0.026
20	—	0.54	0.037
40	—	0.59	0.047
100	—	0.64	0.079
200	21	0.86	0.21
300	—	1.2	0.58
400	37	1.5	1.16
1000	> 99	8.6	—

*) H. Freundlich and E. Loening, Kolloid-Beihfte 16, 1 (1922).

A maximum value for the thickness of the protecting layer may be computed on the assumption of a total adsorption of the lyophilic substance by the suspensoid particles. In the case of gelatin and gold sol a value is found of 8 Å at the concentration of the gold number; for albumin and quartz particles, 4 Å at the beginning of the flat part in the electrophoresis

⁴⁾ Also c.f. H. Freundlich and H. A. Abramson, Z. physik. Chem. 133, 51 (1928); H. Limburg, Rec. trav. chim. 45, 875 (1926).

curve (Abramson and Freundlich, l.c.). These numbers may point to the conclusion that proteins are spread on the solid substratum in a rather flat position.

We thus come to the conclusion that in protected sols the original double layer has lost most of its importance. The sol has adopted the peculiarities of the lyophilic colloid in all respects, while only the nucleus of the particles happens to consist of foreign material.

2. Sensitizing action.

It has been found that there is another phenomenon, which may occur in systems containing hydrophilic as well as hydrophobic colloids: i.e. sensitization.

On careful examination of the effect of addition of small quantities of lyophilic colloid to a suspensoid, it may be noticed that not only a protective influence is lacking, but a de-stabilizing action may even be involved. The flocculation value becomes smaller than that of the original sol and may even decrease to zero.

This sensitization has been observed in widely divergent systems and seems to be just as general a phenomenon as the protective action. Apparently sensitization often escaped the attention of the investigators who, being in search of the presence of a protective action, may have been inclined to be only interested in the behaviour of their systems on addition of an electrolyte concentration exceeding the flocculation value. In that case, sensitization, no influence and weak protection are liable to be summarized under the heading: "no protective action".

In order to obtain a complete picture of the interaction of lyophilic and lyophobic sols it is imperative to determine the flocculation value at all concen-

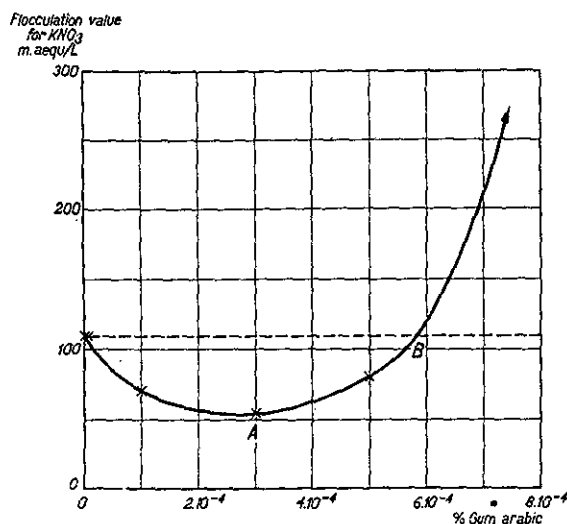


Fig. 2.

trations of lyophilic substance. Fig. 2 shows the changes of the flocculation value of AgI sol on addition of gum arabic⁵⁾.

Until B sensitization occurs, which is maximum at A. At concentrations exceeding B protective action is present. The flocculation value in the minimum (A) of the curve may vary between the

⁵⁾ Unpublished results obtained by C. Horsting.

flocculation value of the original sol (i.e. no sensitization at all) and 0 (i.e. spontaneous flocculation).

The concentration of lyophilic colloid at which the minimum A occurs is usually a very low one. An AgI sol of 5 millimols/l is sensitized by 2 mg of gum arabic per l. The maximum sensitization of a 0.01 % gold sol is brought about by 0.0005 % of gelatin, the influence of 0.00005 % of gelatin still being detectable.

The electrophoretic velocity of sensitized sols appears to coincide with the downward portion of the curves of fig. 1. The dotted portion of these curves indicates the zone of sensitization. It may seem reasonable to attribute the decline of stability to a decrease of the ζ -potential assuming the influence of the increase in hydrophilic stability at such small concentrations of lyophilic colloid still to be negligible. Unfortunately the literature on the subject provides hardly any evidence for checking this assumption. Records of measurements of electrophoretic velocity and stability in the zone of sensitization are given by Bendien and Limburg. From the work of Limburg (l.c.) the following data may be collected, concerning sensitization of oil emulsions by gelatin. In table 2 have been summarized those gelatin concentrations, which produce the same electrophoretic velocity of 3.5 at various p_H . At p_H 5.5 the corresponding gelatin concentration lies well within the boundaries of the sensitization zone. Consequently a disproportionately low stability is exhibited in that case, while the stabilities observed at p_H 2.8 and 4.7 show that an electrophoretic velocity of 3.5 by itself does not necessarily involve low stability.

Table 2.
Sensitization of oil emulsions by gelatin.

p_H	% gelatine	electrophoretic velocity	Stability
2.8	0	-3.48	0.40
4.7	0	-4.41	0.71
5.5	0	-4.67	0.74
2.8	0	-3.5	0.4
4.7	0.000001	-3.5	0.5
5.5	0.00006	-3.5	0.2

This means that no support is gained for the assumption, that decrease of the stability should be due entirely to a decrease in ζ -potential. On the other hand neither do these numbers provide a definite disproof of the assumption.

What all this boils down to is an urgent need of more experimental work with well defined material (e.g. AgI sol and gum arabic) and a reliable technique. At present it seems advisable to consider whether another explanation may better fit the facts.

In those cases where sensitization is most obvious, i.e. where the flocculation value drops to zero, the charge of the lyophilic and lyophobic particles always appears to be of opposite sign. The negative gold sol is flocculated by a minute concentration of gelatin if the p_H is smaller than 4.7. Brossa and Freundlich⁶⁾, made extensive investigations on

⁶⁾ A. Brossa and H. Freundlich, Z. physik. Chem. 89, 306 (1915).

mixtures of positive $\text{Fe}(\text{OH})_3$ sol and negative serum albumin.

They observed that a certain quantity of serum-albumin is flocculated by a small quantity of $\text{Fe}(\text{OH})_3$ but that the precipitate dissolves in excess $\text{Fe}(\text{OH})_3$. With such a sol-mixture, containing an excess $\text{Fe}(\text{OH})_3$, flocculation experiments were carried out.

The flocculation value is usually smaller than that of the original $\text{Fe}(\text{OH})_3$ sol, which indicates that the sol has been sensitized but, on increasing the concentration of electrolyte, a second zone is reached where stability prevails; c.f. fig. 3, in which the abscissa represents concentrations of electrolyte and the ordinate the degree of flocculation in arbitrary units.

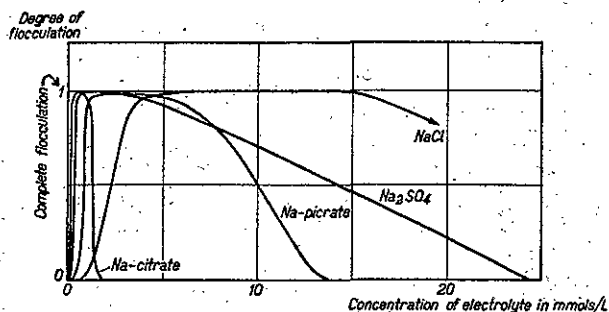


Fig. 3.

The sequence in which electrolytes of various valency flocculate and restabilize the $\text{Fe}(\text{OH})_3$ sol shows a striking resemblance to the way in which electrolytes affect the stability of complex coacervates. If namely a coacervate is made containing an excess of particles of one charge then the first addition of electrolyte will cause an increase of turbidity while a further increase of the amount of electrolyte will bring about the disunion of the coacervate due to lack of oppositely charged particles.

Figure 4 represents the influence of a neutral salt on the degree of turbidity of mixtures of lecithin and gelatin at a p_H of 2.89. The initial coacervate (salt concentration 0) is positive, i.e. contains excess of gelatin ⁷⁾.

This assumption brings all the results of Brossa and Freundlich into agreement. The precipitate contains $\text{Fe}(\text{OH})_3$ as well as albumin; pure albumin is negatively charged; the mixture with $\text{Fe}(\text{OH})_3$ is positive, owing to the excess of $\text{Fe}(\text{OH})_3$; the stable sol at high concentration of electrolyte is negative.

It may seem surprising that $\text{Fe}(\text{OH})_3$ behaves like a hydrophilic sol but this may be explained by the assumption, that in the zone of stability at high salt-concentration the $\text{Fe}(\text{OH})_3$ particles are protected by albumin.

There are a great number of cases, where sensitization can be explained as mutual flocculation. Oil emulsions are flocculated by small quantities of gelatine, if the p_H is smaller than 4.7 (Limburg l.c.) $\text{Fe}(\text{OH})_3$ sol is sensitized by amyllum, glycogen, saponine. In several of the cases where sensitization of negative sols (SiO_2 , mastix, Ag, Au, As_2S_3 , V_2O_5 , etc.) was brought about by proteins, there is considerable probability, that the p_H was on the acid

⁷⁾ H. G. Bungenberg de Jong and R. F. Westerkamp, *Biochem. Z.* 234, 386 (1931).

side of the isoelectric point; consequently in those cases also mutual flocculation may have been involved ⁸⁾.

For the characterization of this phenomenon Zsigmondy introduced the principle of: "Umschlagzahl" ⁹⁾ (U-number).

The U-number represents the number of milligrams of sensitizing substance necessary in order to effect a change of colour from red to violet with a certain amount of an acid gold sol. For proteins these U-number are about 0,002—0,004 (the gold number of gelatin is 0,005—0,01).

Although mutual flocculation frequently underlays the phenomena described in the literature, this mechanism cannot be held responsible for all the cases

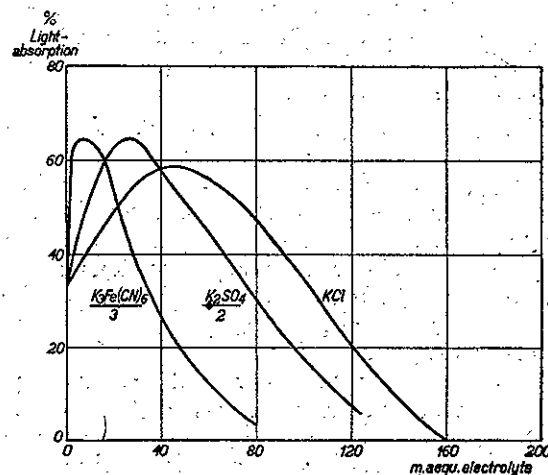


Fig. 4.

of sensitization which are known at present; because there are a number of cases, in which an unsuspected negative suspensoid is sensitized by a lyophilic colloid of equally well known negative charge.

In the reaction of Lange (1912) between gold sol and cerebro-spinal liquid the phenomena involved are dominated mainly by the sensitization of gold sol by albumin and globulin of the same sign ¹⁰⁾.

In the work of Bendien and Limburg examples may be found of sensitization of gold sol and oil emulsions respectively by gelatin at a p_H higher than 4.7 in this case by negative gelatin.

Much more convincing, however, than these cases of sensitization by an amphoteric colloid, in which one may still be inclined to leave open the possibility of opposite charges being involved (e.g. locally situated) is the sensitization of negative colloids by gum arabic or amylose.

A very interesting example of a technical procedure applying this mechanism may be found in the process of Henry ¹¹⁾ in which the liquid, used for washing coal, which contains a very tenacious coal suspension is rapidly flocculated on addition of starch and lime (i.e. Ca^{++} ions). De Smet ¹²⁾ made

⁸⁾ For a summary c.f. S. Ghosh and N. R. Dhar, *Kolloid-Z.* 41, 229 (1927).

⁹⁾ Zsigmondy and Thiessen, *Das kolloide Gold*, Leipzig, 1925, 191 etc.

¹⁰⁾ c.f. Joel, *Das kolloide Gold in Biologie und Medizin*, Leipzig, 1925, p. 32, 59.

¹¹⁾ R. A. Henry, *Chem. Zentr.* 1936, I, 1476, French patent 787831.

¹²⁾ M. de Smet, *Natuurw Tijdschr.* 18, 118 (1936).

further investigations of this process. He was able to show that finely ground anthracite has a negative charge. In addition he found that amyllum Merck (free from proteins) was as well suited for sensitization as potato starch.

Negative AgI sol may also be sensitized by amyllum and gum arabic, as has been shown in fig. 2.

Thus in classifying the interaction between lyophilic and lyophobic colloids a distinction must be made between three cases — which distinction was also maintained by Zsigmondy for gold sol — namely:

1. above a certain concentration protective action occurs irrespective of the sign of the charge;

2a. Below that concentration mutual flocculation occurs with opposite sign of charge; b. if sign of charge is similar sensitization frequently occurs at such small concentrations.

H. Freundlich¹³⁾ suggested that sensitization might be due to a reaction between lyophilic colloid and the peptizing electrolyte of the suspensoid. For the sensitization of $\text{Fe}(\text{OH})_3$ sol by proteins this explanation is consistent with the well known fact, that proteins are able to bind Fe^{+++} ions and that according to Lindau¹⁴⁾ its capacity of binding iron runs parallel with its capacity of sensitizing $\text{Fe}(\text{OH})_3$ sols.

It does not follow however that this mechanism should be accepted in explanation of sensitization in general. It does not hold for instance in the cases AgI-starch, AgI-gum arabic, and coal-starch, where a reaction with the peptizing electrolyte is not only rather improbable, but even contradictory to the experimental facts. In the experiments of De Smet concerning coal and starch the p_H is not altered on addition of the starch. According to electrometric determination neither starch nor gum arabic affect the concentration of I^- ions of dilute KI solution or AgI sol. Thus only the explanation first

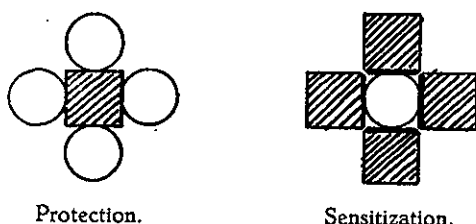


Fig. 5.

suggested by Zsigmondy remains. The two colloids exhibit an appreciable tendency to unite irrespective of their charge. This is obvious from the protective action where envelopment of the lyophobic particles occurs. Now the same tendency will be in operation between lyophilic and lyophobic particles at small concentrations of the former; in this case, however, the suspensoid particles will tend to envelop the lyophilic ones, which leads to a decrease of the stability of the suspensoid particles. A very schematic picture is shown in fig. 5, where a square represents a gold particle and a circle a gelatin particle.

Even though this explanation seems rather attractive and generally applicable, and provides us with

an elegant explanation of the influence of the size of the particles¹⁵⁾ of lyophobic and lyophilic colloid, there are two facts which require a more detailed explanation.

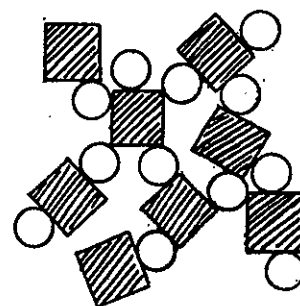
In the first place under the ultramicroscope no difference is observed between the original AgI sol and the same sol after such a quantity of amyllum or gum arabic has been added that maximum sensitization is brought about. Neither Brownian movement nor the number of particles have been affected in any respect. Consequently it is not allowable to conclude that aggregations have been formed consisting of more than one AgI particle.

In the second place it must be born in mind, that sensitization (as well as protection) is not independent of the nature of the flocculating ion. Sensitization and protection occur in smaller concentration of lyophilic colloid if flocculation is brought about by ions of high valency; e.g. point B (fig. 2) in the case of addition of $\text{Ce}(\text{NO}_3)_3$ to AgI sol is reached at a concentration of gum arabic ten times smaller than if KNO_3 is used as a flocculating agent.

In addition, sensitization is far less intensive in the case of $\text{Ba}(\text{NO}_3)_2$ and $\text{Ce}(\text{NO}_3)_3$ than of KNO_3 . (The depth of the minimum A is less in these cases).

A similar behaviour was observed in the case of alkali-blue and tannine by Freundlich and Mitsukuri¹⁶⁾ and in the case of SnO_2 and As_2S_3 with tannine and gelatin as sensitizers by Ghosh and Dhar¹⁷⁾.

We are thus inclined to assume, that until electrolyte is added aggregates consisting of one suspensoid particle with one or more lyophilic particles are formed; the double layer, however, maintains its capacity of exerting such repulsive action that these complexes cannot aggregate further; the image in the ultramicroscope will therefore remain unchanged.



Flocculation of a sensitized sol.

Fig. 6.

Apparently the formation of these complexes is promoted by the presence of polyvalent ions; which is not too surprising, since by addition of such ions positive charges may come into operation on the surface of the particle which will attract gum arabic; consequently sensitization may occur at smaller concentration of electrolyte.

If the concentration of electrolyte is increased till flocculation of the sensitized sol occurs, aggregates

¹⁵⁾ R. Zsigmondy and E. Joel, Z. physik. Chem. 113, 299 (1924).

¹⁶⁾ Freundlich and Mitsukuri, Kolloid-Z. 39, 123 (1926).

¹⁷⁾ S. Ghosh and N. R. Dhar, Kolloid-Z. 41, 229 (1927).

¹³⁾ H. Freundlich, Kapillarchemie II, 471, Leipzig, 1932.

¹⁴⁾ Lindau, Biochem. Z. 219, 385 (1930).

will be formed in which AgI particles alternate with gum arabic particles, as is schematically represented by fig. 6.

This may serve as an example of a case in which flocculation is induced not only by a decrease of the mutual repulsion, but also by an increase of the attraction (caused by the tendency of the lyophilic colloid to occupy the interface AgI-water)¹⁸⁾.

No explanation has been given of the fact, that sensitization is less intense when flocculation is brought about by polyvalent ions.

Attention must be drawn to the importance of sensitization in practice. The example of coal-starch in which sensitization induced a rapid flocculation of a tenacious lyophobic suspension has been mentioned before.

The opposite procedure has been applied as well; Michaelis and Rona¹⁹⁾ developed a method for freeing solutions from proteins by precipitating the protein by the addition of a mastix suspension.

In methods for the purification of sewage sensitization may frequently play a part.

It has frequently been observed, that flocculation of sensitized sols leads to the formation of flakes, which settle very quickly, and this property makes these systems particularly attractive for practical application.

Until now the systems under consideration always contained one lyophobic and one lyophilic component. If both of the sols are of the lyophobic type, real protection and sensitization are not to be expected, since the particles exert no particular attraction on one another.

We may find traces of sensitization in the case of sols of opposite charge ($\text{Fe}(\text{OH})_3$ and As_2S_3), sensitization caused by chemical reaction (As_2S_3 and the S-sol of Odén) or minor protection by chemical reaction (AgI sol and gold-sol)²⁰⁾.

3. *Summary.* In the preceding lines we have aimed at giving a review of the phenomena involved in the interaction of lyophilic and lyophobic colloids and we have tried to give an explanation of these facts. This is a rather detached domain of the dynamics of hydrophobic colloids in which the influence of the double layer is considerably reduced.

Substantially the phenomena are dominated by a strong attraction between lyophilic and lyophobic particles, irrespective of the sign of their charge. They combine with each other in all concentrations while it depends on the proportion of the concentrations whether this will result in protection or in sensitization.

If the two colloids are of opposite charge, or if they are liable to react with each other, the results will be superimposed on the phenomena in general.

Discussion.

Dr. Pieters remarks: In Henry's process so much lime is added that the effect of the addition of starch becomes practically negligible. Nevertheless

¹⁸⁾ c.f. H. C. Hamaker, Rec. trav. chim. 56, 745 (1937).

¹⁹⁾ Michaelis and Rona, Biochem. Z. 2, 219 (1907); 3, 109 (1907); 4, 11 (1907); 5, 365 (1907); 7, 329 (1908); 8, 350 (1908); 13, 121 (1908); 14, 476 (1908).

²⁰⁾ H. R. Kruyt and C. A. Nierstrasz, Kolloid-Z. 78, 26 (1937).

the effect of very small amounts of starch on the flocculation of fine suspensions is often very striking. In this respect I should like to draw the attention of Mr. Overbeek to the observation we made that by the addition of starch to the effluent of a coal washery, the coarser particles are readily precipitated, while the finer and colloiddally dispersed matter is apparently unaffected. It would be of great interest to devise a means of explaining this behaviour of the starch sol.

Prof. Kruyt says: Ir. de Groot of Oranje-Nassau-mine claims, that not a single component of the Henry-mixture can be missed to get a satisfactory clearing of sewage water. De Smet (Gent) started his research with a suspension of anthracite to which he added starch; then we took gum arabic and later on sodium arabinat in stead of starch and at last AgI in stead of coal, thus continuously simplifying the model. In every case we found the sensibilisation with very small amounts of the hydrophilic colloid. Horsting completed the investigation as mentioned in Overbeek's paper.

Mr. Overbeek means: It might be of interest to compare the behaviour of fine and coarse coal particles with that of fine and coarse Au-sols, as described by Zsigmondy and Joel*). The coarser Au-sols appear to be sensitized by smaller concentrations of gelatin than the finer ones.

Dr. Limburg is of the opinion, that the sensitization of f.i. an oil emulsion when adding increasing amounts of gelatin can still be explained by the two factors, which work in opposite directions, viz. the decreasing charge of the particles and the increasing stabilisation by the gelatin-film. It is not clear why the data collected in table 2 of Mr. Overbeek's paper should plead against this theory. They only show, that with *different* concentrations of gelatin, the charge of the particles is not the only factor which governs the stability. This however is the very starting point of the above mentioned theory.

Also sensitization of a negatively charged sol by a negatively charged lyophilic colloid is not in contradiction with this theory. In all those cases in which determinations of the cataphoretic velocity have been carried out, the lyophilic colloid decreased the charge of the sol particles (cf. Limburg, Rec. trav. chim. 45, 875 (1926); Reinders and Bendien, Rec. trav. chim. 47, 976 (1928)). At small concentrations of lyophilic colloid the charge decreasing effect is stronger than the stabilising effect. Hence the stability is decreased and sensitization results.

Mr. Overbeek answers: In Dr. Limburg's train of thought, two emulsions carrying an *equal* charge, at *different* concentrations of gelatin would have a different stability, the emulsion containing the greater amount of gelatin being the more stable. Table 2 shows the opposite to be the case. At p_{H} 5.5 the stability is low at a relatively high concentration of gelatin.

This indicates, that there must be another factor, besides the lowering of ζ , which diminishes the stability of sensitized sols.

Mr. Sarluy asks: In experiments with electro-dialysed hydrophobe sols and protein sols Pauli

*) R. Zsigmondy and E. Joel, Z. Physik. Chem. 113, 229 (1924).

found, that in the absence of electrolytes protective action never occurs. What, according to the speaker, is the role of minute quantities of electrolytes in the mechanism proposed by Zsigmondy, and what is the speaker's opinion about Pauli's experiments?

Mr. Overbeek says: In all probability the absence of protective action in Pauli's experiments must be explained by the acid reaction of electro-dialysed sols. This gives rise to a positive charge of the protein, so that mutual flocculation may result.

Dr. Müller says:

1. Was calcium hydroxide added in De Smet's tests, and, if so, was the carbon suspension still negative after this addition?

2. You said that in sensitization, aggregates of one suspensoid particle with one or more lyophilic particles are formed, the repulsive force between the suspensoid particles remaining the same, however. But does not this repulsive force become smaller because the lyophilic particles partly shield the charge of the suspensoid particles?

Mr. Overbeek answers:

ad 1. De Smet investigated the behaviour of carbon suspensions with $\text{Ca}(\text{OH})_2$ and CaCl_2 . He did not find any indication that the Ca^{++} ion may effect a reversal of the charge of the suspension.

ad 2. I only maintained, that before the addition of electrolyte to a sensitized system, the repulsive force must be strong enough to keep the hydrophobic particles apart. This repulsive force may be smaller than it was in the original sol.

Dr. de Boer remarks: Is the following hypothesis permissible in explanation of sensitization? If the hydrophile substance is strongly bound by its hydrophile groups (for example the $\text{CO}-\text{NH}$ -groups in gelatin) to the surface of the hydrophobe particles, and thereby pushes aside ions of the double layer, a condition might be reached where, (with very small amounts of hydrophile substance which may be entirely bound in the above manner), the hydrophile character is not yet able to manifest itself, while at the same points a double layer capable of repulsion is no longer present, and the particles may attach themselves. Upon addition of more hydrophile substance, it will also be added at these points but now with the hydrophile groups outermost, so that a shielding action is obtained. The charge of the hydrophile substance is then indeed of no importance, but only the hydrophile groups.

Mr. Overbeek answers: It seems rather improbable, that, at the interface water-X (a hydrophobic substance) a hydrophil particle should turn its hydrophilic groups to X rather than to the water.

Apart from this, the picture, Dr. de Boer suggests of a sensitized flocculation does not differ very much from the one given by me. In both cases the hydrophobic particles are held together by hydrophilic ones.

In my theory this linkage is effected by one hydrophilic particle, in Dr. de Boer's theory by two.

It seems to be premature to enter into such details as long as experimental data in this field are still scarce (exp. data concerning the amount of hydrophilic substance carried down by the flocculating sol are almost completely lacking).

Mr. Nanninga asks: With this explanation of sensitization can you account for the phenomenon first observed by Rideal in a hydrogenation process²¹⁾ and verified by me in the decomposition of H_2O_2 , that the catalytic activity of a platinum sol increases, when very small quantities of gelatin (e. g. 0.00075 % with a 0.02 % sol) are added?

Prof. Kruyt says: As the heterogeneous catalysis is located at the "Lockerstellen" (Taylor), Rideal's results, as mentioned by Mr. Nanninga would suggest, that the lyophilic colloid is not bound at those spots but just the contrary at the flat faces.

Dr. Boasson wants to draw attention to a group of sensitization-phenomena, which are as remarkable as those discussed here in as far as they occur between two hydrophilic colloids (especially proteins) with charges of the same sign. I mean the sensitization-phenomena well known in serology and immunology. For this case Marrack²²⁾ has already given the picture used by Overbeek for the flocculation of a sensitized sol (fig. 6). Moreover it has been found that here, too, the phenomena are largely governed by the laws of complex coacervation²³⁾.

Disregarding the marked specificity of serological reactions, an analogy with the system silver iodide-gum arabic seems to be well established. Would it be possible to use the latter system as a model for serological flocculations?

Mr. Overbeek answers: If serological flocculations are hampered by large concentrations of electrolyte there seems to be no advantage in using the sensitization of AgI by gum arabic as a model, as in this system no stability zone is found at higher salt concentrations.

After the conclusion of this paper Dr. van der Minne was called upon by the chairman to present two subsequent papers, a more general and a more specialized one.

General remarks on emulsions *)

by

J. L. van der Minne (Amsterdam).

In the last two decades emulsions have been studied very intensively and a mass of literature has grown up on the subject. This being so, however conscientiously I might attempt to summarize it, my resumé could be no more than an extract of the findings elaborated by many different authors. I therefore propose instead to concentrate here on a few important points relating to the emulsification and stability of emulsions, with special reference to the physico-chemical principles.

We give the term "emulsion" to a system of two

²¹⁾ Rideal, J. Am. Chem. Soc. 42, 749 (1920).

²²⁾ J. L. Marrack, The Chemistry of Antigens and Antibodies, London, 1934 (page 106).

²³⁾ E. H. Boasson, Dissertation, Utrecht, 1937, and J. Immunology, in press.

*) For collective literature on emulsions see:

W. Clayton, The theory of emulsions and their technical treatment, London, 1935, 3rd ed.; O. Lange, Technik der Emulsionen, Berlin, 1929; Brit. Section Intern. Soc. Leather Trades' Chem., Technical aspects of emulsions, London, 1935; in Dutch: Van der Minne, „Over emulsies", Thesis, Utrecht, 1928.