

# Colloid Stability in Aqueous and Non-Aqueous Media

## INTRODUCTORY PAPER

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Colloid stability is determined by the interaction between particles during a (Brownian) encounter. The forces playing a role in encounters (van der Waals forces, double-layer interaction, interaction between adsorbed molecules, such as surfactants, polymers and small molecules) are discussed with emphasis on unsolved problems. It is pointed out in which of the papers of this Discussion the different problems are treated.

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### GENERAL ASPECT OF COLLOID STABILITY

Since colloidal particles dispersed in a liquid are always subject to Brownian motion, encounters between the particles occur frequently and the fate of the colloidal dispersion is determined by the interaction between particles during such an encounter. When attraction predominates the particles will adhere more or less permanently and the dispersion will coagulate; in the case of predominant repulsion the system will remain in the dispersed state.

Van der Waals forces are always present, whatever the composition of the system, and it has been proved that such forces always result in attraction between particles of the same material. Therefore, a colloidal suspension can only be stable if a sufficiently strong repulsion counteracts the van der Waals attraction. This repulsion may be based on the interaction of electrical double layers—mainly but not exclusively important in aqueous systems—or on the interaction of layers of adsorbed uncharged molecules, including the solvent molecules themselves, a mechanism which may act in any solvent.

The interaction between particles and adsorbed molecules does not necessarily lead to repulsion. Especially, if the adsorbed molecules are polymeric, one molecule may be attached to two particles and thus form a bridge between the particles, enhancing the attraction rather than the repulsion, and leading to sensitized flocculation.

Qualitatively our picture of colloid stability is well established and for several of the factors entering the picture quantitative or semi-quantitative theories exist. At present we are at a stage of refinement of our understanding and control of colloid stability, but much refinement has still to be done before the situation is satisfactory. In this introductory paper, I shall treat the main interaction forces one by one and try to indicate in each case what critical experiments or improvements in the theory should be made.

Težak's contribution to this Discussion, in which he gives a systematic description of all states between the homogeneous solution and the macrocrystal, with a strong emphasis on the variability of the phenomena, has a wider scope than most of the other contributions. It includes and rather stresses such aspects as complex formation, nucleation and crystal growth and reserves only a modest place for colloidal stability in the more restricted sense.

## THE ELECTRICAL DOUBLE LAYER

The structure of the electrical double layer is relatively well established, not in the sense that the value of the surface charge or the surface potential can be predicted from first principles, but that the relation between charge and potential and the spatial extension of the double layer and the repulsion between overlapping double layers are fairly well known—fairly well, but possibly not well enough. Colloid stability is governed by the difference between repulsion and attraction and a relatively small error in one of the two may make our estimate of the stability grossly wrong.

The relation between charge and potential difference between the two phases is dealt with by Levine and Bell, who will discuss a number of refinements to the Poisson-Boltzmann equation, such as the influence of ion-size, dielectric saturation, discreteness of charge, cavity potential, etc. They will also show the influence of these refinements on the interaction of double layers and on colloid stability. Težak lays great stress on the interaction between individual ions, as opposed to the collective behaviour of ions in double layers. Lyklema has obtained data on charge and potential difference at the AgI/water interface at elevated temperatures. Since he finds a more simple, more “Gouy-like” structure of the double layer and a correspondingly simpler behaviour in coagulation, high temperature may well become an important tool in double-layer research.

Instead of the potential difference between the two phases the zeta-potential is often used. It has the advantages that it can be determined in practically all cases of interest, at practically any electrolyte concentration, and that it gives information on the diffuse part of the double layer. The disadvantage is that the theoretical relation between zeta-potential and electrokinetics is far from simple, and as yet there is no good understanding of where the slipping plane (if it is a plane) is situated with respect to the phase boundary. Nevertheless in at least eight of the papers presented at this discussion (Watillon and Mrs. Joseph-Petit, Hall, Ottewill and Shaw, Matijevic, Kratochvil and Stryker, McGown and Parfitt, Romo, Težak and Micale, Lui and Zettlemoyer) the zeta-potential is used for information on the double layer, three being about suspensions in non-aqueous media. In the papers by Romo and by Micale, Lui and Zettlemoyer the influence of trace amounts of water on the zeta-potential is stressed.

The above information deals mainly with single double layers. Direct experimental information on the interaction of double layers is much scarcer. I would like to cite the classical work of Bergmann, Löw-Beer and Zocher<sup>1</sup> on Schiller layers, and mention the modern work on black soap films (see Overbeek<sup>2</sup>) of which a good example obtained with a new technique is presented here by Mysels and Jones, who find a quite acceptable agreement with the theory for the interaction of diffuse double layers.

To close my remarks about the double layer I should say that accurate data of charge and potential difference for a variety of interfaces especially at low electrolyte concentrations are still greatly needed and that experiments, in which the double layer repulsion is determined as free as possible from other interactions, such as those mentioned above on Schiller layers or soap films, are extremely valuable.

## VAN DER WAALS FORCES

Since Kallmann and Willstaetter<sup>3</sup> suggested that van der Waals forces are responsible for the attraction between colloid particles, much work, both theoretical and experimental, has been done on these forces. The earlier theories (Tomlinson,<sup>4</sup>

Bradley,<sup>5</sup> de Boer,<sup>6</sup> Hamaker<sup>7</sup>) treated the forces between atoms or molecules as strictly additive and did not take into account that the forces might be modified by passage through a dense medium. Lifshitz,<sup>8</sup> basing his treatment on electromagnetic fluctuations in a dense medium, derived an exact expression for the attraction between macroscopic objects (consisting of many atoms or molecules) in terms of the macroscopic dielectric constant and dielectric loss factor, which had to be known over the complete frequency range of dispersion. This treatment has been extended (Dzyaloshinskii, Lifshitz and Pitaevskii<sup>9</sup>) to include even the interaction between two flat plates of different composition separated by a dense medium. At low densities, Lifshitz' treatment is equivalent to the earlier treatment based on additivity of the forces between pairs of molecules.

Unfortunately, the necessary dielectric data are not yet known with sufficient accuracy to be able to apply Lifshitz' theory directly. Only for the retarded attraction forces, effective at "large" distances (e.g.,  $> 1000 \text{ \AA}$ ) between the objects, the situation is more favourable, since in this case only the "static" dielectric constant (square of the refractive index extrapolated to long wavelengths) has to be known. But, although the retarded force may play a role in some colloidal phenomena, the non-retarded force is much more important. Independent measurements of the van der Waals forces of some accuracy exist only in the retarded region, whereas measurements in the non-retarded range are still highly inaccurate (for a review see Overbeek and Van Silfhout,<sup>10</sup> Van Silfhout<sup>11</sup>). In the present situation the best source of information on van der Waals forces are flocculation experiments and experiments on thin liquid films, but to a certain extent this is begging the question.

In this Discussion the papers by Watillon and Mrs. Joseph-Petit and by Ottewill and Shaw show how the stability of polystyrene latex dispersions can be used to derive values for the van der Waals attraction. Use is made of the variation of the stability with particle size, particle charge and electrolyte content, but the resulting values for the van der Waals attraction are not yet internally consistent. The following factors should be considered in the search for an explanation of this discrepancy.

(i) The electrostatic repulsion may have been incorrectly estimated. The influence of this uncertainty can be minimized by comparing sols with different particle sizes, but with identical surface charge or potential (at flocculation).

(ii) An incorrect estimate of the distance between the phase boundary (where the van der Waals constant changes its value) and the plane of the surface charge (from where the distance of repulsion is calculated). Quite often these planes are supposed to coincide, but this is almost certainly incorrect. It might be advisable to introduce the distance between these planes as a parameter in the theory.

(iii) Neglecting the influence of transmission of the van der Waals force through a medium may be a more serious error than is usually assumed. A first estimate could be obtained by using Lifshitz' theory with relatively simple models for the dispersion curves. In this connection it is also important to develop Lifshitz' method for more complicated geometrics (spheres, spheres surrounded by layers of different composition).

Further work on the direct measurement of non-retarded van der Waals forces, if possible between objects in a dense medium, is highly desirable. Optical data should be obtained especially in the far ultra-violet to be used in Lifshitz' equations. Continued work on the stability of isodispersed sols with careful control of the surface charge and wide variation of conditions is desirable. Work on thin films (equilibrium thickness under pressure, light scattering, rate of drainage, etc.) ought to lead to important information.

## PROTECTION AGAINST COAGULATION BY ADSORPTION OF NEUTRAL MOLECULES

Protective action of hydrophilic colloids on hydrophobic ones has been recognized early in the history of colloid science. It was interpreted as the envelopment of hydrophobic particles by a layer of the hydrophilic colloid making the particles as stable against coagulation as the hydrophilic colloid. The particles of a gold sol protected by gelatin behave as "gelatin particles with a golden heart".

Later, it was found that the phenomenon is not restricted to aqueous systems and that protective agents need not necessarily be polymeric. The work of Van der Waarden, Mackor and van der Waals<sup>12-14</sup> on the stabilization of carbon black suspensions in a liquid hydrocarbon by adsorbed mixed aromatic-aliphatic molecules of modest mass is a good example.

In non-aqueous and in particular non-polar systems repulsion between particles by electric charge is usually of minor importance. Non-aqueous suspensions, therefore, have to be stabilized by some variant of protective action. Given the tremendous technical importance of non-aqueous suspensions (paints, inks, pigments for synthetic polymers, etc.) it is no wonder that in this Discussion much attention is given to protected colloid systems. Crowl and Malati and Walbridge and Waters give some pure examples of stabilization of suspensions in hydrocarbons by polymeric surfactants. Clayfield and Lumb treat the case of separating carbon from metal by a polymeric surfactant. In McGown and Parfitt's work on the dispersion of rutile in p-xylene by aerosol OT obviously electric charge plays a role. There is no indication that the simple presence of an adsorbed layer of uncharged surfactant molecules contributes to the protection. Glazman stresses the fact of protection in aqueous media by non-ionic surfactants of low and intermediate molar mass. Mrs. Taylor and Haydon point out the parallel between the stability of thin hydrocarbon films in water and colloid stability in non-aqueous media. They confirm the essential correctness of Mackor and van der Waals ideas, which predict a very steep repulsion for a film thickness equal to twice the length of the stabilizing chains.

It is striking that in so many of these cases polymers are used as protective agents. They are obviously favourable in several respects. Their standard free energy of adsorption is proportionally larger than that of a small molecule of similar chemical nature. Therefore they are more easily adsorbed. Simply on account of their size they are expected to form thicker layers, keeping the particles more widely separated. Nevertheless, they should not be adsorbed too strongly, i.e., at too many points, because then the layer formed will be thin and the protection inadequate.

The detailed chemistry of the adsorption process becomes a point of major interest in this field as pointed out by Slater and Kitchener in their paper on the closely related field of flocculation caused by small amounts of polymers.

The theory of protective action is still in a rather primitive state. Mackor and van der Waals<sup>14</sup> introduced the notion "entropic repulsion", because the loss of translational freedom of the "wriggling tails" of the adsorbed molecules when the layers interpenetrate, leads to a loss of entropy and thus to repulsion. This theory has only been worked out for very simple cases.

We should try to reach a more complete force-distance relation, using more complete statistics for the interpenetrating chains, taking into account that polymer molecules may have several points of attachment to the particles and that the adsorption density itself decreases when the layers interpenetrate. Such a theory would also be very helpful for a more complete understanding of sensitization.

## SENSITIZATION OF LYOPHOBIC SUSPENSIONS BY SMALL AMOUNTS OF POLYMERS

A polymer molecule, having many points of possible attachment to a surface, can in principle as easily form loops between adsorption sites on one particle as form bridges between sites on different particles. In the last mentioned case, agglomerates are formed and flocculation occurs. A low concentration of polymer and a high concentration of particles will promote this sensitization.

Sensitized flocculation cannot simply be treated as an interplay between attractive and repulsive force between the particles. The elementary step in this case is not the approach of two particles (which, in a stable sol, may be prohibited by an activation energy of  $30 kT$  or more), but the formation of a single adsorption contact (which, even when the adsorbed group is charged, would only have an activation energy of a few times  $kT$ ). Once the polymer bridge is made between two particles with single adsorption contacts on each of them, it can be strengthened and made virtually irreversible by occupying more adsorption sites on each particle. This lack of reversibility does not permit the particles to find the closest packing by sliding along each other and explains the openness of the flocculate.

It is evident that the quantitative theory of sensitized flocculation should have many points in common with the theory of protective action, including considerations on the specificity and on the thermodynamics of adsorption of polymer molecules. However, as indicated above, for sensitization also kinetic factors and energies of activation, both for adsorption and desorption, are essential.

Several papers in this Discussion deal with sensitized flocculation. In the first place we should mention the paper by La Mer, who stresses the different nature of flocculation by polyelectrolytes and that by small ions, and offers the rate of refiltration through the flocculate as a tool to distinguish the two types of aggregation. La Mer also proposes to keep the terms coagulation and flocculation sharply separated, the former for precipitation by electrolytes (forming dense flocs), the latter for precipitation by polyelectrolytes (open flocs). It might be useful to spend some time of the Discussion on this point of nomenclature.

Slater and Kitchener also discuss flocculation of aqueous suspensions by polymers. Since their theoretical treatment of the phenomenon differs from that by La Mer in essential points, we may expect an interesting discussion. La Mer and Slater and Kitchener both stress the importance of the specific chemical aspects in the interactions leading to sensitization.

In La Mer's paper, in that of Hall on the interaction of clay with hydrolyzed aluminium solutions and, although perhaps somewhat less clearly, in the paper by Matijevic, Kratochvil and Stryker, we see the possibility that hydrolyzed polyvalent ions form polymers and that charge reversal and flocculation by "polyvalent ions", as already pointed out by Troelstra and Kruyt,<sup>15, 16</sup> is more akin to sensitization than to flocculation by simple compression of the double layer.

## THE ROLE OF THE SOLVENT AS A PROTECTIVE AGENT

Undoubtedly, the structure of a liquid near an interface deviates from its structure in bulk. There is no doubt either that the special structure of water near the interface with particles dispersed in it will affect their stability by influencing the structure of the electrical double layer and possibly even by modifying the van der Waals forces. But it is further conceivable that this layer of modified solvent affects the stability in a more direct way, e.g., by increasing the viscosity in the neighbourhood of the particles or by acting as a protective, impenetrable layer.

An example of such an influence of small neutral molecules can be found in a hitherto unpublished observation by Mackor. During his work on the influence of acetone on the electrical double layer at the interface AgI/water<sup>17</sup> he found that acetone changed the coagulation of AgI by electrolyte in a qualitative way. If AgI is coagulated in water by the addition of simple salts it has a rather voluminous open structure and is not easily peptized by washing away the precipitant electrolyte. In the presence of 5-98 % (vol/vol) of acetone the coagulate is more compact and sandy and can be easily and completely re-peptized by dilution, which suggests that acetone is firmly bound to the surface of the AgI particles and prevents an actual AgI—AgI contact.

Whether such an influence of the solvent itself, e.g., of water, occurs more or less generally is still an open question. The arguments for such a role of the solvent derive on the one hand from the lack of agreement between experiments and a theory based exclusively on van der Waals forces and double layer interaction ("there must be some additional factor"), and on the other hand on determinations of properties of the solvent near an interface such as increased viscosity, nuclear magnetic resonance, certain interpretations of electrokinetics, etc. Unfortunately, the whole situation is still somewhat ambiguous. The theories of van der Waals + double layer interactions may in themselves be inaccurate. The "additional factor" may be just a necessary refinement of these theories.

Stigter<sup>18</sup> has calculated from the viscosity of micellar solutions that there is not a layer of increased viscosity around each micelle. Lyklema, Scholten and Mysels<sup>19</sup> concluded from the rates of drainage of soap films that the whole inner core of a soap film has the same viscosity as bulk water. On the other hand, Derjaguin<sup>20</sup> has given examples of changes of viscosity of liquids near interfaces to a very great depth and he pointed out that the thickness of black soap films<sup>21</sup> frequently remains thicker than can be explained by double layer repulsion alone.

In this Discussion the paper by Derjaguin on the effect of lyophile surfaces on the properties of boundary liquid films and that by Johnson, Lecchini, Smith, Clifford and Pethica on the stability of polyvinylacetate sols and on the nuclear magnetic resonance of water in these sols relate to this problem and may hopefully initiate an interesting exchange of ideas.

The most desirable advance in this field would be a theory which explains the protective action of the solvent in a mechanistic way and on the other hand more accurate experiments connecting stability with "structure" or "adsorption" of the solvent.

#### THIN FILMS

It will be clear from some of the above remarks that thin detergent films are an important source of information for several of the finer points of colloid theories. The combination of a small thickness determined by the interactions, in which we are interested, with a relatively large area, which makes optical and other observations easy and the applicability of straightforward thermodynamics, are advantages. It is fortunate that several papers in this Discussion on colloid stability are devoted to thin film work. The papers by Mrs. Taylor and Haydon, by Mysels and Jones, and by Derjaguin have been cited earlier. I should also mention here Vrij's paper on fluctuations in the thickness of soap films which may lead to rupture (the equivalent of coalescence in emulsions) and the paper by Corkill, Clunie and Goodman who obtain consistent values for the thickness of the films using a variety of techniques and find from their measurements that a water layer of about 20 Å thickness is tenaciously held between the two surfactant layers.

## CONCLUSION

The general framework in which colloid stability can be interpreted appears to be well established. There are sufficient uncertainties in the quantitative aspects of the theory and in the detailed interpretation of certain observations, to expect a lively and fruitful discussion.

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