

COLLOID STABILITY AS A DYNAMIC PHENOMENON

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Abstract - The interaction between two hydrophobic colloid particles is analyzed from a dynamic point of view. Rates of adjustment of the Gouy-layer, the Stern-layer and the surface layer are estimated on the basis of both theoretical considerations and new experimental facts and are then compared with the rate of approach during a Brownian encounter. The AgI-system is used as a model system. The combined evidence indicates that, for this system, interaction takes place at constant total surface charge on the particles. The transfer of ions between the Stern-layer and the diffuse layer may be fast. Some consequences will be discussed.

INTRODUCTION

Traditionally, most colloid stability studies, including those of coagulation kinetics, treat particle interaction as if the overlapping electrical double layers are continuously equilibrated. Typically, the Gibbs energy of interaction is calculated, using methods of classical thermodynamics (which is virtually thermostatics) rather than those of the thermodynamics of irreversible processes. The assumption, either tacitly made or not, is that double layers adjust themselves completely during a collision. In other words, the double layers are assumed to be relaxed throughout the process of interaction.

Verwey and Overbeek (Ref. 1.), in their monograph, paid some attention to this issue. They distinguished two extreme cases: a) the interacting double layers are always completely relaxed and b) they do not relax at all. In their picture, case (a) is the constant potential case: the surface potential ϕ_0 is determined by the (fully relaxed) adsorption equilibrium of the potential determining (p.d.) ions; ϕ_0 is constant because the concentration (c_{pd}) of p.d. ions in bulk is invariant. The theory then predicts a reduction of the surface charge σ_0 if the particles approach each other. Desorption of p.d. ions was taken to be responsible for this reduction. In the opposite case (b), σ_0 is assumed to remain constant. This will occur if no mechanism is available to discharge the surface during a Brownian collision. The latter case is the constant charge case, in which ϕ_0 has to increase during interaction. There is no relation between ϕ_0 and c_{pd} in this case.

At a later stage, Frens (Ref.2) realized that even for systems such as AgI-sols, traditionally considered as a notorious example of constant potential interaction, σ_0 would not adjust itself during a particle encounter because the required exchange rate of p.d. ions would be too slow. This consideration introduces the relaxation time of the double layer and compares it with the time scale of particle interaction. Several authors have since then elaborated on the constant potential vs. constant charge issue, see e.g. (Ref.3). However, the mechanism of interaction remains obscure in many cases due to both the lack of significant experimental information available on the several types of double layer relaxation and because the double layer models to date have been too simple.

It is the purpose of the present paper to contribute to the solution of this problem by considering the dynamics of the interaction in more detail. The main improvements with respect to earlier work are the following:

- i) It is explicitly taken into account that, under conditions of fast coagulation, double layers are mainly non-diffuse. For instance, for AgI-sols at $pI=4$, $\phi_0 \sim -390mV$ but $\sigma_0 \sim 10$ to $20mV$, hence $\geq 95\%$ of the potential decay takes place in the Stern-layer. For the charge distribution the situation is less extreme, but even for such simple counterions as Na^+ or K^+ the Stern charge σ_s may amount to 65% of σ_0 (Ref.4). All of this means that we must not only analyse the relaxation of the diffuse part of the double layer but also that of the Stern-layer.
- ii) As an immediate consequence of (i) it should be realised that double layers are characterized by more than one relaxation time. Which of these relaxation times is relevant depends on the nature of the experiment, especially with respect to its time scale.
- iii) We consider the "constant potential" and "constant charge" cases as extremes, the actual situation being determined by the relaxation rates of the various parts

of the double layer.

- iv) New experimental data are presented which help to unravel the various relaxation processes and estimate their time scales.

In this paper some basic ideas will be set forth and followed by a semiquantitative interpretation. It is hoped to work this matter out in detail in a later paper with van Leeuwen.

RELAXATION PROCESSES UPON INTERACTION

In fig. 1 a sketch is presented of possible charge transfer processes that may take place due to the approach of a second particle. For the time being, we ignore the complementary polarization of the second particle.

First there is relaxation of the diffuse part of the double layer. It is a three-dimensional process, determined by diffusion and/or conductance.

Second, charge transfer, both of potential determining and inert ions may take place between the diffuse layer and the Stern-layer, with a rate determined by σ_s , σ_d and some energy of activation.

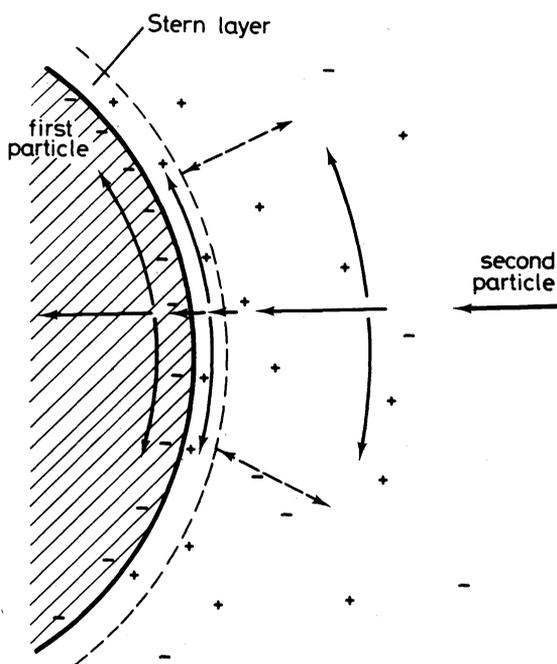


Fig. 1. Schematic representation of possible relaxation processes in double layers upon interaction.

Stern-layers, in turn can relax either by transfer of potential determining ions into the solid or by lateral flow, determined by surface diffusion and/or surface conductance. The latter two are typically two-dimensional processes.

Charges, accumulating at the surface of the particle can leak away by diffusion and/or conductance in the solid. This is again a three-dimensional process. In the case of AgI, where the electrical conductance is solely connected with the movement of interstitial silver ions, this leaking process is analogous to the adjustment of the diffuse double layer within the solid. For non-conducting particles it may be entirely absent.

Finally, fig. 1 contains dashed arrows. These account for the likelihood of ion exchange between Stern-layer and Gouy-layer at some distance from the approaching second particle, because the two-dimensional tangential flux in the Stern-layer and the tangential component of the three-dimensional flux in the Gouy-layer are normally different, so that double layer polarization ensues.

A holistic dynamic approach to colloid stability, encompassing all of these processes is still to be developed, but some constituent parts are fairly well understood, at least as regards the order of magnitude of their relaxation times τ . We shall discuss some

of them, mostly with the AgI-system as the example. In passing, we note that the relative contributions of the various processes depend also on the macro- and microheterogeneity of the surface, but this complication will be disregarded here.

THE TIME SCALE OF A BROWNIAN ENCOUNTER

If two particles approach each other by free diffusion, the interaction distance $2\kappa^{-1}$ is covered in

$$\tau_{Br} \sim \frac{(2\kappa^{-1})^2}{2D_p} = \frac{12\pi\eta a}{\kappa^2 kT} \quad (1)$$

where D_p is the coefficient of free diffusion of the particle and a is the particle radius. For rather coarse particles in a AgI-sol, $a \sim 500$ nm, in 10^{-1} M solutions of (1-1) electrolytes i.e. the order of magnitude of the critical coagulation concentration $c_{c,\kappa} \sim 10^7$. Taking the usual values for the viscosity η , the Boltzmann constant k and the temperature, we obtain $\tau_{Br} \sim 10^{-5}$ s.

For particles of other radii and/or c_c , this value changes accordingly.

However, diffusion is not entirely free. If the two particles come very close, their approach is slowed down because of hydrodynamic interaction. This matter has been dealt with by several authors (Ref. 5-7). Honig et. al. (Ref.6) give a useful simplified analytical expression, relating the actual value of the diffusion coefficient at distance H between the particle surfaces $D(H/a)$ to D_p :

$$D(H/a) = \frac{D_p}{\beta(H/a)} = D_p \cdot \frac{1 + 2a/3H}{1 + 13a/6H + a^2/3H^2} \quad (2)$$

For an interaction distance down to $H = 2\kappa^{-1} = 2$ nm and $a = 500$ nm, $D(H/a)$ is a factor 12.5 lower than D_p ; for large H and smaller a the difference is less. The precise order of magnitude of the retardation is difficult to assess because the particle motion is not uniform. Perhaps it is safe to conclude that the corrected Brownian interaction time τ_{Br} (corr) $\lesssim 10^{-4}$ s.

RELAXATION OF PARTS OF DIFFUSE ATMOSPHERES

Local ionic space charge excesses relax very rapidly. If relaxation proceeds by diffusion, eq. (1) can be used but now with the diffusion coefficient of ions instead of D_p . For this case $\tau \sim 10^{-8}$ s so that obviously $\tau \ll \tau_{Br}$. If the excess charge relaxes through conductance only (Maxwell), the relaxation time τ_{DC} is given by

$$\tau_{DC} = \frac{\epsilon \epsilon_0}{\kappa_{cond}} \quad (3)$$

where κ_{cond} is the specific conductivity of the solution and ϵ its relative dielectric constant. For 10^{-1} M solutions of (1-1) electrolytes, $\kappa_{cond} \sim 1.5 \times 10^4 \Omega^{-1}m^{-1}$, $\epsilon = 80$, $\epsilon_0 = 9 \times 10^{-12} CV^{-1}m^{-1}$ and $\tau_{DC} \sim 5 \times 10^{-8}$ s which is of the same order of magnitude as the diffusion controlled diffuse layer relaxation.

This confirms earlier statements that the diffuse part of the double layer is always completely relaxed during particle encounter. It implies also that the exchange currents, represented by the dashed arrows in fig. 1 are determined only by the lagging behind of the non-diffuse double layer part, if any.

RELAXATION OF THE NON-DIFFUSE DOUBLE LAYER PARTS

This is a more difficult matter, partly because the various charge transfer processes are only incompletely understood and partly for want of sufficiently precise numerical data on conductivities, diffusivities etc. Exchange current densities i_0 can vary drastically from one system to the other. For instance Overbeek (Ref.3) takes 10^{-10} and 1 Acm $^{-2}$ as the lower and upper limit. If we assume reasonable interfacial capacitance values of 10^{-5} F cm $^{-2}$ and use the relationship

$$\tau_{SE} = \frac{RTC}{nFi_0} \quad (4)$$

these exchange current densities correspond with relaxation times of 2.500 s to 0.25 μ s, i.e. these processes could either be much faster or much slower than a Brownian collision. Obviously more precise data are needed.

Lateral diffusion in the Stern-layer has a time scale that will again be determined by an equation of type (1)

$$\tau_{SD} \sim \frac{a^2}{2D^S} \quad (5)$$

where D^S is the surface coefficient of diffusion and a the particle radius. Eq (5) assumes that the entire Stern-layer of the particle relaxes, but this is not necessarily the case. Anyway, as a trend, under conditions of coagulation $a \geq \kappa^{-1}$, $D^S < D^{\text{bulk}}$, hence it is likely that the Stern-layer relaxes more slowly by lateral diffusion than diffuse double layers do. Similar reasoning applies to lateral relaxation by conduction. The ratio between lateral conductivity over a surface and three-dimensional conductance in bulk is on the order of

$$\frac{\kappa_{\text{cond}}^S a^2}{\kappa_{\text{cond}}^{\text{bulk}} a^3} = \frac{\kappa_{\text{cond}}^S}{\kappa_{\text{cond}}^{\text{bulk}} a} \quad (6)$$

where κ_{cond}^S is the surface conductivity. For $\kappa_{\text{cond}}^S \sim 10^{-8}$ to $10^{-9} \Omega^{-1}$, $\kappa_{\text{cond}}^{\text{bulk}} \sim 1,5 \times 10^4 \Omega^{-1} \text{ m}^{-1}$, as before, and $a = 5 \times 10^{-7} \text{ m}$, this ratio is much less than unity.

The conclusion is that it is likely that Stern-layers relax more slowly than diffuse double layers do, but this possibility definitely demands a more quantitative footing before it is useful. Besides all of this, there is the possibility that charge transfer between the diffuse layer and the Stern-layer is so fast that a "short-circuit" through the diffuse layer is possible. Theoretically, the situation is not very promising. However we have relevant experimental data available that take us further.

EXPERIMENTAL APPROACH TO THE RELAXATION IN NON-DIFFUSE DOUBLE LAYERS

In our laboratory, a fast pulse technique has been developed to measure the relaxation of a Ag/AgI electrode in aqueous solutions. The basic principle is that an electrode is very rapidly ($\sim 10^{-6}$ s) disequibrated by a coulstatic impulse (i.e. by a charge impulse). After cessation of this impulse, the double layer relaxes and the overpotential ΔE is obtained as a function of time, using some transient recording system. The $\Delta E(t)$ curves are analysed via Laplace transformation and yield (one or more) relaxation times (Ref. 8,9 10).

It is necessary to stress that such relaxation experiments produce only part of the solution of our problem. For one thing, AgI-film electrodes are flat and the entire surface becomes homogeneously polarized during the disequilibrium; consequently in this case no lateral surface conductivity takes place. Secondly, polarization of a double layer by a charge injection compared with that due to a second particle may well be different phenomena. On the other hand, the method is applicable over a large range of pAg-values and salt concentrations: in particular it can be applied under coagulation conditions, say pAg 11 to 12, at $c_{\text{salt}} \sim 10^{-1} \text{ M}$. Moreover, it is possible to assign a capacitance value to each relaxation step, using a so-called Randles circuit; these capacitances can be compared with those obtained experimentally on AgI-electrodes (Ref. 11,12) or on dispersed AgI (Ref. 13); this is an important step in the identification of the measured relaxation times.

Fig. 2 is a typical example of a relaxation curve. The spectrum consists of at least two clearly distinguishable relaxation steps, one in the μ s range and one in the ms range. (There may be additional very fast relaxation processes involved with $\tau < 10^{-6}$ s but these are not detectable with the present technique.) The capacitances assigned to the fast and slow step are, in this particular experiment, 3 and 49 $\mu\text{F cm}^{-2}$ respectively.

Within some 10-30%, the slow relaxation step capacitance is equal to the experimental capacitance on powders or electrodes (Ref. 11-13). A better agreement than this may not be expected because all absolute values are subject to substantial uncertainty because of surface roughness. As under the experimental conditions (pAg = 4.26, electrolyte 10^{-1} M KNO_3) the double layer capacitance is dominated by its non-diffuse part, it can be concluded that the slow step may indeed be identified as a relaxation of the non-diffuse part of the double layer. Additional evidence stems from experiments at varying pAg: the slow step capacitance exhibits the same characteristic decrease with increasing pAg as obtained by direct measurement or titration. Fig. 3 illustrates this. On the other hand, the fast step capacitance (not shown) is insensitive to a change of pAg or, for that matter, to any change in the composition of the solution. Obviously, the fast step measures some solid phase relaxation under coagulation conditions. The exchange current density is on the order of $10^{-4} \text{ A cm}^{-2}$.

The first conclusion which may be drawn for our purpose is that the time scale of

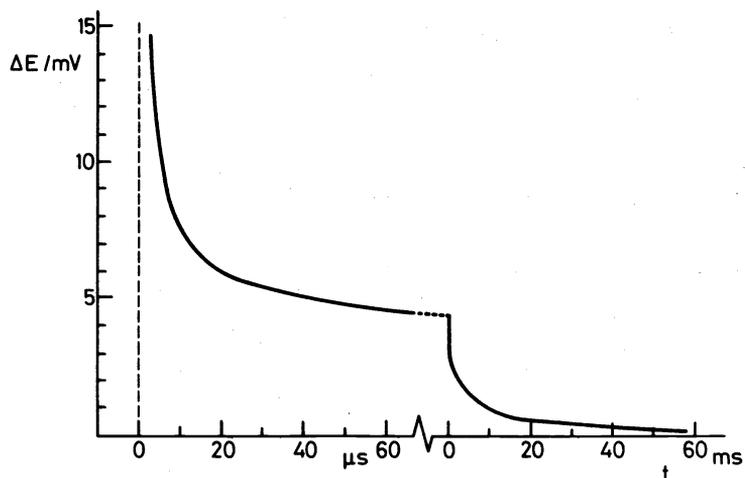


Fig. 2. Relaxation in non-diffuse double layers on AgI electrodes. Electrolyte, 10^{-1} M KNO_3 ; $\text{pAg} = 4.26$. Note the different time scales on the abscissae axis.

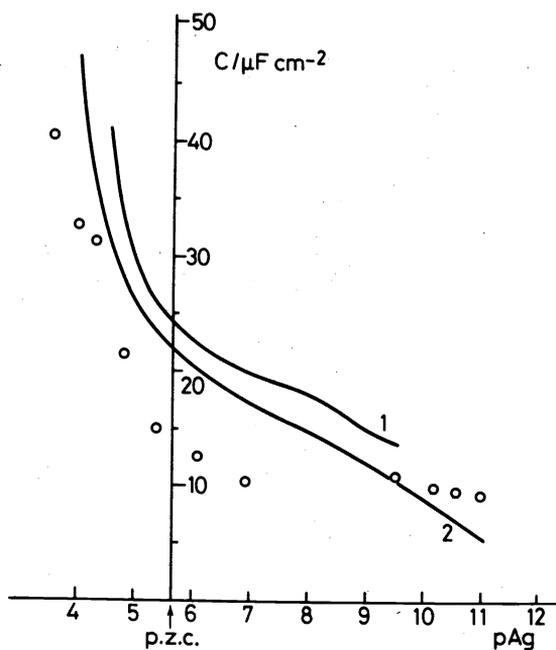


Fig. 3. Double layer capacitance of the AgI-solution interface. Comparison between the capacitance on electrodes directly measured (Ref. 11) (curve 1), the same on dispersed material (Ref. 13) (curve 2) and the capacitance assigned to the slow step of the double layer relaxation (circles) Electrolyte: 0.1 M KNO_3 (N.B. There is an absolute uncertainty of 10-30% in all these data because of surface roughness problems).

Stern-layer relaxation is on the order of μs , which is at least a factor 10 slower than the estimated interaction time of two particles. Hence, in the AgI-system under consideration, Stern-layers do not relax during a Brownian collision.

A second relevant observation is that the exchange current density i_0 is independent of the electrolyte concentration between 10^{-2} and 1 M and independent of the nature and value of the counterion (Li^+ , K^+ , Cs^+ , Mg^{2+} , Ca^{2+} and Ba^{2+}). As the contribution of the Stern-layer increases drastically from 10^{-2} to 1 M, this may perhaps be interpreted in the following way: transfer of p.d. ions across the interface is the rate-determining step and not the interchange of charge between the diffuse and the Stern-layer. The relaxation time of the latter is then much shorter than 1 ms.

DIELECTRIC RELAXATION STUDIES

Another approach to learn more about relaxation of double layers around charged particles is to measure and analyze the dielectric increment and loss of dispersions as a function of the frequency of an applied electric field. In principle this method has the advantage that it is holistic, in that all relaxation processes of Fig. 1 participate. On the other hand it involves considerable experimental difficulties. For instance in the low frequency range polarisation of the electrodes becomes a nuisance and it is hardly possible to perform measurements at elevated salt concentrations, because of the correspondingly unfavourable loss tangent. For our purpose this implies that measurements are possible only in the region where the diffuse double layer prevails. Still, such experiments are useful, because they can be used to test the various theoretical pictures that have been developed. The most advanced theory is that by Dukhin and Shilov (Ref. 14), which may be considered as a Maxwell-Wagner type of theory, corrected for the presence of a surface charge, a Stern-layer and a diffuse layer, and allowing for radial charge exchange as envisaged in fig. 1. This theory is very complicated: about 20 equations must be simultaneously solved to obtain characteristic parameters such as the dielectric increment due to the particles and the time of relaxation.

In our laboratory, Korteweg and Springer have recently measured the dielectric properties of polystyrene latices in dilute electrolytes. For KNO_3 concentrations of 0.6×10^{-3} M they found that only one relaxation time ($\tau = 20.3 \mu\text{s}$) suffices to describe the relaxation behaviour completely. Its order of magnitude is between those of a pure diffuse layer and a Stern-layer and agrees reasonably well with the value of $37.0 \mu\text{s}$, predicted for a Gouy-Stern-layer with radial fluxes by Dukhin and Shilov (Ref. 14). In passing we note that theories by Schwarz (Ref. 15), Schurr (Ref. 16) Einolf et al. (Ref. 17) and Ballario et. al. (Ref. 18) would all give $12.4 \mu\text{s}$, but these figures must be corrected for the radial fluxes of fig. 1 and then become rather on the order of $0.3 \mu\text{s}$. With respect to our central theme, the conclusion is that a double layer that is mainly diffuse relaxes completely during a Brownian encounter, in agreement with earlier statements.

CONCLUSIONS

The main conclusion of this article is that at least for the AgI-system the diffuse part of the double layer adjusts itself rapidly to changing conditions provoked by the approach of a second particle, but that the transfer of p.d. ions through the Stern-layer is so slow that the surface charge does not noticeably alter during a Brownian encounter. Consequently, colloid stability for this system must be treated as if occurring at constant surface charge. However, the possibility of fast ion exchange between Stern-layer and diffuse layer (i.e. short circuiting of the former by the latter) in addition to the possibility of fast silver ion transport through the bulk of the particle renders an adjustment of local charge density possible, while the total charge on the particle is retained.

Various considerations on important aspects of colloid stability ensue. Some of them are:

- (i) Lyotropic sequences in coagulation concentrations are probably attributable to differences in adsorbability of different ions rather than a kinetic effect.
- (ii) As the magnitudes of tangential surface fluxes and the ensuing radial exchange fluxes depend strongly on the micro- and macrogeometry of the particle, surface heterogeneity plays perhaps a more important role in stability than is usually expected.
- (iii) As the absolute value of the surface charge density under coagulation conditions is low, say up to $4 \mu\text{C cm}^{-2}$ or one unit charge per $\sim 5 \text{ nm}^2$, the distance between charges becomes larger than κ^{-1} and it becomes necessary to take the discreteness of the charges into account. In addition, particle approach and interaction through translational diffusion must be implemented by rotational diffusion (Ref. 19,20).
- (iv) With the exception of the solid phase conductance part, which is quite low in materials such as polymer latex particles, the trends observed in this article are probably of wider applicability than just the AgI-system.

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