

## COLLOIDAL BEHAVIOUR OF MATERIALS WITH IONIZABLE GROUP SURFACES

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**Abstract** - Classic DLVO descriptions of coagulation are cast in terms of mean interfacial potentials developed in self-consistent physical terms by a general surface charge. An alternative approach is to begin by identifying an array of well defined, chemically distinguishable surface groups. The charging of such groups is controlled through equilibrium constants by bulk aqueous solution parameters. Subsequent definition of the mean potential of the array of ionizable groups is then a first approximation towards the more difficult task of defining local potentials. Nevertheless, the combination of specific group charge plus a mean potential allows new approaches to be made towards understanding interaction of biological surfaces and model (eg, latex) colloids, particularly in concentrated suspensions.

### INTRODUCTION

The recent Discussion of the Faraday Society on Colloidal Stability (1) recognised the 30th anniversary of the first formal presentation of the DLVO theory of the stability of lyophobic colloids. Derjaguin, Landau, Verwey and Overbeek made a contribution that has been of lasting value and served to raise colloid science to the level of a quantitative science, a progress begun by Irving Langmuir and others (2) almost fifty years ago.

The essential structure of the DLVO theory has stood the test of time, *viz.*, that interaction between approaching surfaces can be expressed as a sum of two independent interactions of attraction due to van der Waals forces and repulsion due to electrostatic (screened Coulomb) forces. The current models (3) of the attractive van der Waals component are now more sophisticated and acceptable than those used in 1948 and include, for example, analyses of the dependence of the van der Waals attraction on the electrostatics of the intervening solvent medium between the approaching surfaces. The essential correctness of the theory of van der Waals forces has indeed been verified experimentally by Tabor *et al.* (4,5).

The application of DLVO theory to the kinetics of Brownian coagulation of colloidal particles was perhaps the earliest test of the theory, and general agreement between theory and experiment was obtained. More recently, the known relaxation processes that must occur during collision have been considered, both experimentally and theoretically, and new advances or modification of the DLVO theory in this area are imminent (6).

Ironically it is in the theory of electrostatic repulsion where relatively little modification has been made to the DLVO model. In most instances we still calculate the repulsion by the techniques of classical electrostatics with the interacting surfaces being considered as planes of smeared-out charge surrounded by atmospheres (diffuse layers) of equal and opposite charge density. This mean field approach, enshrined in the Gouy-Chapman and Debye-Hückel theories is, with very few modifications, the basis of all theories of double layer repulsion.

We imagine, with increasing scepticism, that this model is an adequate representation of interacting mercury drops, silver halide particles and polymer latex colloidal particles! The latter, we well know, have surfaces with chemically identifiable ( $-\text{COO}^-$  or  $-\text{NH}_3^+$ , etc) groups set in a sea of, say, polystyrene. While such synthetic surfaces cannot be seen as planes of smeared-out charge, it is possible, however, with adjustment of parameters, to understand some of the general features of latex colloid stability in terms of the traditional DLVO theory. Fortunately, the complacent stance of colloid scientists has been disturbed in the past few years by Israelachvili (7) and Ottewill (8), and others, who produce more and more direct measurements of the forces between surfaces separated by aqueous

electrolyte solutions. These brilliant experimental studies are now of a precision where subtleties in the force-distance curve can be detected and real quantitative tests of interaction theory are possible.

If we consider biosurfaces, we are again forced to recognise that they too are arrays of identifiable ionizable groups set in a matrix of more or less hydrophobic or at least non-ionic material, the overall form of which may or may not be deformable! May we suggest that it is too easy to say that such biosurfaces are just too difficult to consider; such an apology for the general lack of impact of DLVO theory on biology is, we believe, facile. Biological systems and processes abound in "interacting surfaces" and yet the essential and well-tried theory of colloid science has been almost spectacularly absent from the field. Perhaps this assessment is overstated, but doing so forces colloid chemists to re-examine some of the tenets of their much beloved theory to see where one might begin to better model biosurfaces and biosystems in general.

## REGULATION

### General aspects

One possible way is to recognise that most surfaces of interest to the colloid chemist are composed of arrays of specific chemical groups that can and will ionize to generate "a surface charge". The aim of the present paper is to review zeroth and first order theories of interaction that are based on just such surface structures with a view to contrasting the results of such models with conventional DLVO theory, ie, mean field theory.

Before considering interaction between surfaces, it is important to distinguish the conventional DLVO models for the calculation of double layer interaction, viz., constant potential or constant charge interaction. This is shown schematically in Figure 1, where we consider two identical surfaces that have surface potential and surface charge values of  $\psi_0$  and  $\sigma_0$  respectively at infinite separation.

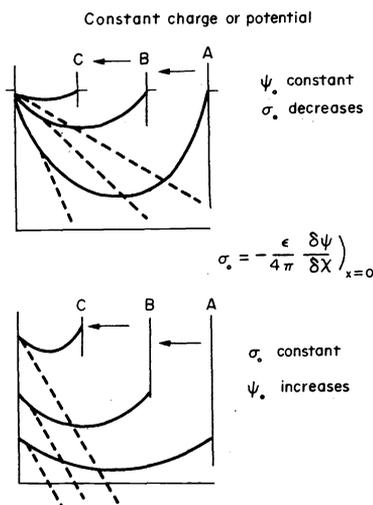


Figure 1. Schematic representation of the potential-distance profiles during double layer overlap under conditions of constant potential (upper) or constant charge (lower). One surface is moved from A to B to C.

Since  $\sigma_0$  is given by the negative of the slope of potential ( $\psi$ ) versus distance ( $x$ ) at  $x = 0$ , the constant potential approximation yields decreasing charge until  $\sigma_0 = 0$  at  $x = 0$ . Again, if  $\sigma_0$  must remain constant, then the potential at  $x = 0$ ,  $\psi_0$ , increases as the separation decreases.

Interaction between surfaces composed of arrays of ionizable groups is a modification of DLVO theory and is clearly composed of many elements of the conventional theory. In the present paper, consideration will be given to the electrostatic component of interaction, which is necessarily repulsive, between identical non-zero charge surfaces, and may be repulsive or attractive if dissimilar surfaces are considered.

The model is best described as 'Regulated Interaction' or interaction under charge regulation, following the pioneering work of Ninham and Parsegian (9). The essence of general regulated interaction is that during the progress of approach the surfaces communicate with each other,

adjusting their surface charges, shapes or adsorption densities to ensure at all times that the system is as little displaced from equilibrium as possible during interaction. Alternatively, the system of interacting surfaces adjust itself to minimize the total free energy. The mechanism whereby the two interacting surfaces "see" each other or communicate with each other resides in sets of equations that define the system and which sets contain explicit relationships which link the free energy of the interacting double layer system to the state of the interfaces and bulk solution.

A useful conceptual example involves two identical liquid (say oil) drops approaching each other in an aqueous solution. If the drops are stabilized by a layer of strongly adsorbed, charged surfactant species, then as the double layers overlap, repulsion is observed. The system can minimize the repulsion by allowing the two drops to flatten in the region of contact but at the expense of creating regions of more curved interface at the flat-curve surface confluence. Again, the detergent molecules could migrate to the rear of the drops to decrease the surface charge per unit area in the region of contact but at the expense of creating a surface tension gradient around the drop circumference and, possibly, internal circulation within the drop. All these very complex processes serve to minimize the repulsion during approach at the price of disturbing the total structure of the two drops from their equilibrium, infinite separation structure.

If by responding in these ways the net free energy of the system is decreased during interaction, then the system will so respond. More generally, processes will operate such that the total free energy of the system is minimized at each separation.

If one considers two bioparticles during approach, again one can see an array of regulation processes that may or may not contribute. Consider two cells that approach each other with each cell surrounded by a lipoprotein membrane. As the protein-protein interaction sets in, repulsion may be minimized by changes in tertiary structure of the proteins, which will in turn influence the packing of the lipids, which will in turn influence the shape of the membrane and its permeability; a train of subsequent events will operate to accommodate these changes, which will in turn communicate themselves back to the secondary and tertiary structure of the proteins. The dynamics of such interactions will be complex to the extent that biosystems are themselves complex sets of interactions and reactions.

We can begin to retain some of the communication processes that will regulate interaction by using simple colloidal systems composed of polymer latex particles or metal oxide particles. Essentially, we thereby eliminate "deformation" as a regulatory process and concentrate on charge regulation associated with the interacting electrical double layers.

In the following section, a model is presented for two interacting surfaces that have identifiable ionizable surface groups. The formalisms of previous papers (10,11) on regulation have been retained, although the reader is directed specifically to an elegant alternative formalism due to Radke and Everett (12). The aim in the present paper is to explore the conclusions of charge regulation for some simple but real systems of interacting particles and to explore the use of charge regulation in considering the concentrated suspensions or close-packed arrays of colloidal particles.

#### CHARGE REGULATION - An Outline of the Model

The original Ninham and Parsegian (9) (NP) model considered two surfaces, each containing an array of discrete carboxyl ( $-\text{COOH}/-\text{COO}^-$ ) groups. The surface charge ( $\sigma_0$ ) is given by the number of  $-\text{COO}^-$  groups and we seek an expression for the surface potential ( $\psi_0$ ). In principle, we should operate in terms of local or micropotentials (13) and indeed, seek to obtain the profile of potential over the surface (14). At present, the essential physics of charge regulation is lost if we attempt to include these necessary sophistications and for the moment we restrict ourselves to considerations that rely on obvious approximations. Thus we shall identify a mean potential,  $\psi_0$ , of the surface which we shall couple to a net charge,  $\sigma_0$ . [The nature of this approximation is discussed in detail elsewhere (15).]

It is, however, useful to begin with a charge regulation model that is more general than the single site NP system. Thus we shall consider a surface made up of  $\text{AH}_2^+$  sites that ionize to  $\text{AH}$  and  $\text{A}^-$  sites, ie, a so-called amphoteric surface or zwitterionic surface. In subsequent sections we shall detail the results of charge regulation for two-site surfaces, the detailed discussion of which is presented elsewhere (15).

#### CHARGE REGULATION - Formalism

Consider a surface which develops a surface charge via dissociation equilibria of a surface (amphoteric) group,  $\text{AH}$ .



Here, hydrogen ions act as potential determining ions and  $K_+$  and  $K_-$  are surface dissociation constants defined in terms of surface concentrations of sites and protons as:

$$\frac{[\text{AH}][\text{H}^+]_s}{[\text{AH}_2^+]} = K_+ \quad (3)$$

$$\frac{[\text{A}^-][\text{H}^+]_s}{[\text{AH}]} = K_- \quad (4)$$

The dissociation constants,  $K_+, K_-$ , are assumed to be only functions of temperature and pressure. The validity of equations (3) and (4) has been discussed elsewhere (15).

For  $N_s$  surface groups per unit area, the net surface charge density is ( $e$  = protonic charge)

$$\sigma_o = eN_s \frac{[\text{AH}_2^+] - [\text{A}^-]}{[\text{AH}] + [\text{AH}_2^+] + [\text{A}^-]} = eN_s \alpha \quad (5)$$

The fraction  $\alpha$  defined by equation (5) can assume any value between plus and minus one.

In the Gouy-Chapman approximation, which we shall adopt, the concentration of ionic species at any point is related to the bulk value by the Boltzmann factor  $\exp(e\psi/kT)$ . The electrostatic potential,  $\psi$ , is measured with respect to the value at the reservoir (taken to be zero). In particular, the surface concentration of PDI is:

$$[\text{H}^+]_s = H \exp(-e\psi_o/kT), \quad (6)$$

where  $H$  is the bulk concentration of PDI and  $\psi_o$  is the surface potential. Combining equations (3), (4) and (6), the surface charge can be written as:

$$\sigma_o = eN_s \frac{(H/K_+) \exp(-e\psi_o/kT) - (K_-/H) \exp(e\psi_o/kT)}{1 + (H/K_+) \exp(-e\psi_o/kT) + (K_-/H) \exp(e\psi_o/kT)}. \quad (7)$$

This is an "equation of state" of the surface. It specifies all possible values of the "co-ordinate",  $(\psi_o, \sigma_o)$ .

It is instructive to rewrite equation (7) in the form:

$$\sigma_o = eN_s \frac{\delta \sinh[e(\psi_N - \psi_o)/kT]}{1 + \delta \cosh[e(\psi_N - \psi_o)/kT]} = eN_s \alpha, \quad (8)$$

where

$$\delta = 2 \times 10^{-\Delta pK/2} = 2 \left( \frac{K_-}{K_+} \right)^{1/2} \quad (9)$$

and

$$\Delta pK = pK_- - pK_+. \quad (10)$$

We shall call the potential,

$$\psi_N = \frac{kT}{e} 2.303 (pH_o - pH), \quad (11)$$

the Nernst potential, since it is related to the pH of the point-of-zero-charge ( $pH_o$ ) (pzc) of the surface composed of amphoteric AH groups,

$$pH_o = \frac{1}{2}(pK_+ + pK_-). \quad (12)$$

Equation (8) can be further simplified in notation by introducing reduced variables,

$$y_0 = \frac{e\psi_0}{kT} \quad \text{and} \quad y_N = \frac{e\psi_N}{kT},$$

such that

$$\sigma_0/eN_s = \alpha = \frac{\delta \sinh(y_N - y_0)}{1 + \delta \cosh(y_N - y_0)}. \quad (13)$$

Thus the charge, or fractional charge,  $\alpha$ , is expressed in terms of the potential,  $y_0$ , for any pair of surface dissociation constants.

Before we let two identical surfaces, described by equation (13), interact, we need first to describe the diffuse layer charge,  $\sigma_d$ , that in a simple Gouy-Chapman first approximation is equal and opposite to  $\sigma_0$ , i.e.,

$$\sigma_d = - \frac{\epsilon \kappa kT}{2 \pi e} \sinh y_0/2. \quad (14)$$

Since, in this simple model,

$$\sigma_0 + \sigma_d = 0, \quad (15)$$

then from equations (13), (14), (15),

$$\gamma^{-1} \sinh y_0/2 = \alpha, \quad (16)$$

where

$$\gamma = 10^3 \kappa N_s / 4N_0 e. \quad (17)$$

where  $\gamma$  is the Debye length and  $N_0$  is Avogadro's number.

The potential of the interface ( $y_0$ ) can thus be obtained graphically to illustrate the operation of equation (16), which is central to charge regulation. As shown in Figure 2, we have plotted the potential term ( $\gamma^{-1} \sinh y/2$ ) and the charge term  $\alpha$  as functions of the reduced potential,  $y$ ,

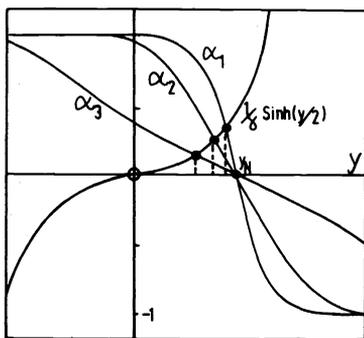


Figure 2. Schematic plot of both the variation of the charge parameter  $\alpha$  and the potential parameter  $[\gamma^{-1} \sinh(y/2)]$  with the reduced potential  $y$  for different values of  $\Delta pK$ ;  $\alpha_3$ ,  $\alpha_2$  and  $\alpha_1$  refer to increasing values of  $\Delta pK$ .

such that the intersection is  $y_0$  for that system. The three  $\alpha$  curves plotted are for increasing  $\Delta pK$  with the result that  $y_0$ , which is always less than or equal to  $y_N$ , becomes further removed from  $y_N$  as  $\Delta pK$  increases. Surfaces are more and more Nernstian as the number of uncharged groups at the point-of-zero-charge increases (15,16). As the number of uncharged groups approaches zero then  $y_0 \rightarrow y_N$ , the value of the potential for a truly Nernstian amphoteric surface.

Emphasis on whether or not a surface, ie, an isolated surface, is Nernstian is important, since it determines, amongst other things, whether or not the usual DLVO approximation of constant potential is realistic or not for any given system.

If we now let two surfaces interact, each given by Equation (16), we can describe the potential and charge on each wall at any separation and both charge and potential will adjust ie, regulate during the interaction.

The electrostatic free energy of interaction for two plates, each at -50 mV at infinite separation, for a bulk electrolyte concentration of  $10^{-3}$  mol dm $^{-3}$  is calculated in Figure 3 via the conventional constant charge and constant potential approximations.

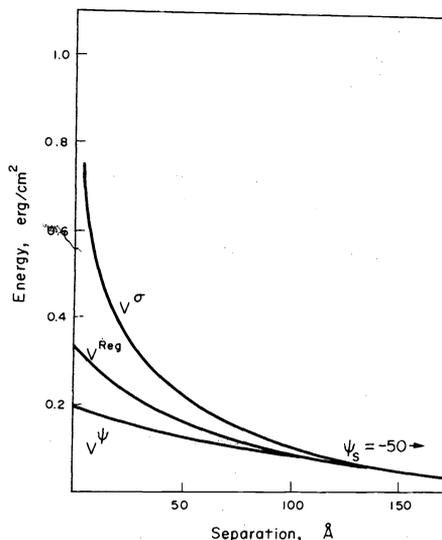


Figure 3. Comparison of the electrostatic free energy of interaction ( $V_R$ ) as a function of separation for interaction at constant charge ( $V^\sigma$ ), constant potential ( $V^\psi$ ) and under charge regulation ( $V^{\text{Reg}}$ ) for  $\Delta\text{pK} = 6$  and pH 7 and  $10^{-3}$  mol dm $^{-3}$  supporting 1:1 electrolyte.

For comparison, regulated interaction is also included for a surface of point-of-zero-charge at pH 7 and a  $\Delta\text{pK}$  of 6. Notice that  $V^{\text{Reg}}$  is much less than  $V^\sigma$  and is closer to  $V^\psi$ .

The feedback element of regulation is summarized as follows for a positive surface and fixed bulk pH.

1. Allow small overlap of double layers.
2. The mid-plane potential increases, and the potential at all separations increases.
3. Thus  $\psi_0$  increases, and since
 
$$[H_S^+] = H \exp(-e\psi_0/kT),$$
4.  $H_S^+$  decreases, and since
 
$$K_+ = [AH] H_S^+ / [AH_2^+],$$
5.  $[AH_2^+]$  sites decreases by dissociation and since  $\sigma_0$  is given by  $\sigma_0 = e([AH_2^+] - [A^-])$ ,  $\sigma_0$  decreases and since  $\sigma_0$  is related to  $\psi_0$  via equation (7), then
7.  $\psi_0$  decreases.

Regulation minimizes changes in  $\psi_0$  during interaction and it works best as  $\Delta\text{pK}$  decreases.

#### REGULATION - A More General Approach

The previous methodology is, with the wisdom of hindsight, rather restrictive. It is more useful to express the electrostatic energy of interaction between any two surfaces 1 and 2 distance  $L$  apart in terms of the pressure in the system. Thus,

$$P = P_{el} + P_{OS} - P_\infty, \quad (18)$$

where the pressure in the system of overlapping double layers is split into an osmotic and electrostatic term, ie,

$$P = 2n_0 kT \left[ -\left(\frac{\partial y}{\partial x}\right)^2 + (\text{coshy} - 1) \right] \quad (19)$$

where  $n_0$  is the bulk electrolyte concentration and, again,  $y$  is the reduced potential;  $L$  is plate separation and is related to the distance ( $x$ ) from one plate by

$$x = \kappa L,$$

where  $\kappa^{-1}$  is Debye length, ie,

$$P = -2n_0 kT(C + 1), \quad (20)$$

where

$$C = \frac{1}{2} \left(\frac{\partial y}{\partial x}\right)^2 - \text{coshy}. \quad (21)$$

$C$  is a function of potential ( $\psi$ ) separation ( $L$ ) and ionic strength ( $\kappa$ ), and is a constant anywhere in the system for a given set of conditions.

By evaluating  $C$  at each surface (1,2), we obtain

$$C + 1 = \frac{1}{2} \alpha_1^2 \gamma_1^2 - (\text{coshy}_1 - 1) \quad (22)$$

and

$$C + 1 = \frac{1}{2} \alpha_2^2 \gamma_2^2 - (\text{coshy}_2 - 1). \quad (23)$$

As before, for each surface we have a charge term ( $\frac{1}{2}\alpha^2 \gamma^2$ ) and a potential term ( $\text{coshy} - 1$ ), both of which are greater than or equal to zero.

If the charge term is greater than the potential term,  $(C + 1)$  is positive, which corresponds to attraction or a negative pressure. Similarly, if the charge term is less than the potential term, repulsion or positive pressure is observed.

In the equations (22) and (23) above, it can be seen that  $C \rightarrow -1$  at  $L \rightarrow \infty$ , which corresponds to zero pressure at infinite separation.

Combining the charge and potential curves gives us the value of surface charges and potentials at any separation. For identical surfaces (ie, two  $\frac{1}{2} \alpha^2 \gamma^2$  curves that superimpose) the form of the solution is shown in Figure 4. We have chosen a positive surface

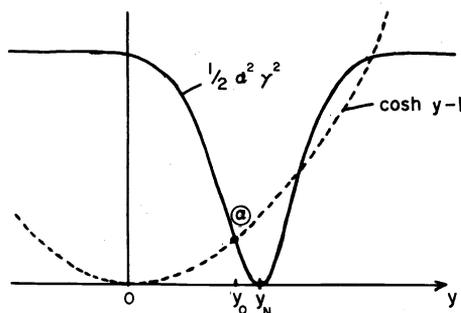


Figure 4. A schematic plot of the charge parameter ( $\frac{1}{2} \alpha^2 \gamma^2$ ) and potential parameter ( $\text{coshy} - 1$ ) for a positive surface ( $y_N > 0$ ) as a function of the reduced potential,  $y$ .

and a particular  $\Delta pK$  (ie, a particular  $\frac{1}{2} \alpha^2 \gamma^2$  curve) to yield four crossing points or four solutions. Since  $C + 1$  must be zero at infinite separation, and since  $y_0 \ll y_N$ , only point a is acceptable. In Figure 5, the region around point a is enlarged to identify the movement of  $y_0$ , the surface potential and  $\alpha$ , the surface charge, during approach of the two surfaces.

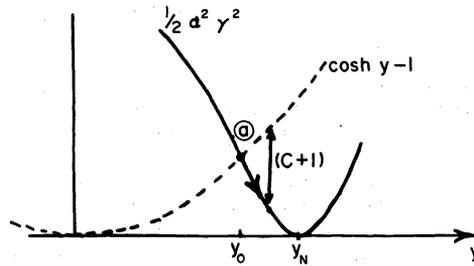


Figure 5. An expansion of the region of the intersection of the charge and potential curves of Figure 4. As  $L \rightarrow 0$ , the system moves along the charge curve as shown by the arrow.

Note that for such a case of identical surfaces, the pressure must be repulsive at all separations and that  $y_0 \rightarrow y_N$  as  $L \rightarrow 0$  and  $\alpha$  (or  $\frac{1}{2} \alpha^2 \gamma^2$ )  $\rightarrow 0$  as  $L \rightarrow 0$ .

For dissimilar surfaces the solution is a little more complex. Consider two surfaces, shown in Figure 6, that are both negative at infinite separation, ie,  $y_{01}$  and  $y_{02}$  respectively,

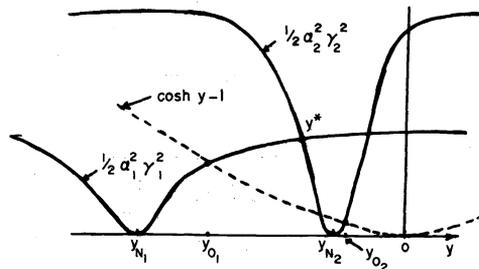


Figure 6. Charge and potential curves for two dissimilar surfaces, both negative at infinite separation.

and let  $|y_{N2}| < |y_{N1}|$ , *ie*,  $pH_0$  for surface 2 is less than  $pH_0$  for surface 1. We shall also let  $\gamma_2 > \gamma_1$ , *ie*, surface 2 has more surface sites than 1. Further, let  $\Delta pK$  for surface 1 be greater than  $\Delta pK$  for surface 2. This makes the charge curve for surface 2 somewhat "flatter" than that of surface 1; surface 1 is more nearly Nernstian. This example could be, say,  $pH\ 6.3$  and  $10^{-2}$  mol  $dm^{-3}$  for

|           |                  |                     |                                  |
|-----------|------------------|---------------------|----------------------------------|
| Surface 1 | SiO <sub>2</sub> | (pzc $pH_0 = 3$ )   | $N_s = 5$ sites/nm <sup>2</sup>  |
| Surface 2 | TiO <sub>2</sub> | (pzc $pH_0 = 5.8$ ) | $N_s = 12$ sites/nm <sup>2</sup> |

For this condition the Nernst potentials given by Equation (11) are  $-195.4$  and  $-29.6$  mV for SiO<sub>2</sub> and TiO<sub>2</sub> respectively. As we proceed to solve the electrostatics of this system in terms of charge regulation, Figure 6 can be used to highlight the physically significant steps that emerge, *ie*:

- The infinite separation values of the potentials on each surface ( $y_{01}$  - SiO<sub>2</sub> and  $y_{02}$  - TiO<sub>2</sub>) must both lie below their respective  $y_N$  values and for the above system are  $-115.6$  and  $-29.1$  mV for SiO<sub>2</sub> and TiO<sub>2</sub> respectively.
- The zero separation value ( $y^*$ ) for both surfaces must be the same, *viz.*,  $-57.2$  mV, and both surfaces have negative surface charges.
- At zero separation the charge on the SiO<sub>2</sub> is negative since in magnitude  $y^*$  falls below the  $y_0$  and  $y_N$  values of SiO<sub>2</sub>.
- At zero separation the charge on the TiO<sub>2</sub> is positive since in magnitude  $y^*$  lies above the  $y_N$  value for TiO<sub>2</sub>.
- At large separation the pressure is first repulsive so that the potential of both surfaces must move towards their  $y_N$  values.
- Since the difference between the (coshy - 1) and both the ( $\frac{1}{2}\gamma^2\alpha^2$ ) curves must remain the same at each separation, at a particular separation the TiO<sub>2</sub> surface moves to its Nernst value, through it, and then moves such that there is zero pressure in the system.
- Beyond this point, as both  $y_0$  values move towards  $y^*$ , we are at points along the charge curves which lie above the (coshy - 1) curve, *ie*, attraction.

These qualitative predictions can be determined quantitatively, as in Figure 7.

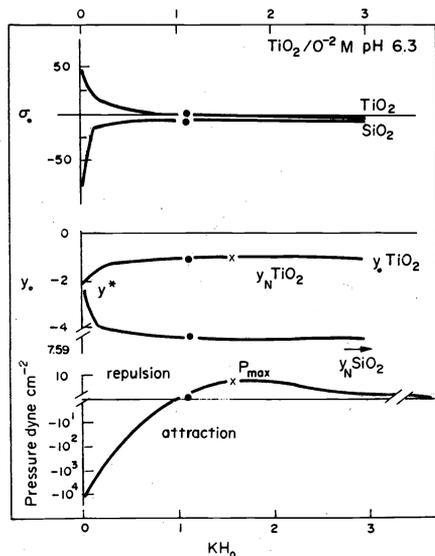


Figure 7. Quantitative variation of the charge and potential on TiO<sub>2</sub> and SiO<sub>2</sub> surfaces during interaction (for details see text above). The pressure in the system derived from the charge regulation is shown in dyne  $cm^{-2}$  as a function of reduced distance. (Note the arbitrary truncation of the pressure scale around zero pressure for display purposes.)

For the parameters above and a Hamaker constant of approximately  $4 \cdot 10^{-13}$  ergs, sphere-sphere ( $a = 100$  nm) interaction produces a barrier to coagulation of approximately 50 kT at a reduced distance of approximately 0.5 ( $\kappa^{-1}$ ). At constant potential the barrier under such conditions is essentially zero, and is very, very large for constant charge interaction.

While the essential effects of charge regulation have been worked out previously, it is important to use the theory to predict interaction energies in specific real systems. By way of example, we shall consider a few systems taken from a much larger matrix to be presented elsewhere (17). The properties of five materials are summarised in Table 1 below.

TABLE 1. Summary of properties of five representative materials

| Material         | Symbol | $10^{13}$ Ha | $10^{-14}$ $N_s$ | pzc | pK <sub>-</sub> | pK <sub>+</sub> |
|------------------|--------|--------------|------------------|-----|-----------------|-----------------|
| Carboxyl latex   | CL     | 0.9          | 0.125            | -   | 4.8             | -               |
| Sulphonate latex | SL     | 0.9          | 0.125            | -   | -1              | -               |
| Amphoteric latex | AL     | 0.9          | 2.5              | 7   | 5               | 9               |
| SiO <sub>2</sub> | Si     | 1.7          | 5.0              | 3.0 | 0               | 6.0             |
| TiO <sub>2</sub> | Ti     | 3.9          | 12               | 5.8 | 3.8             | 7.8             |

#### Notes

1. The Hamaker constants, Ha, are  $A_{121}$  values in ergs.  $A_{123}$  values are computed as  $(A_{121} \cdot A_{323})^{\frac{1}{2}}$ .
2.  $N_s$  is in units of sites per  $\text{cm}^2$ .
3.  $\Delta pK$  values of 4 and 6 have been assumed for TiO<sub>2</sub> and SiO<sub>2</sub> respectively.

#### REGULATION - Some Examples

For present purposes we have used a simple site dissociation—Gouy-Chapman model of individual double layers. Addition of Stern layers, discreteness-of-charge, micropotentials, etc, will serve to improve the model. However, at this stage such sophistication is distracting while we come to terms with the role of charge regulation in any given interacting system.

It must also be stressed that our present analysis applies in the first instance to interaction of two isolated plates or spheres that come together sufficiently slowly to allow equilibrium to be attained at all separations. Coagulation and peptization (redispersion) will approximate this condition to a greater or lesser extent. But since Ottewill (8) and Israelachvili (9) now produce direct measurements of forces of interaction, clearly the regulated interaction is the only possible interaction in such cases.<sup>#</sup>

By way of example, consider the coagulation of the three latex colloids of Table 1 with carboxyl, sulphonate and carboxyl-amine surface groups, *ie*, CL, SL and AL respectively. Again, let us adjust the pH of the reservoir so that they are each separately at a surface potential of  $\psi = -25.0$  mV. The Hamaker constant is the same for each material ( $A_{121} = 0.9 \cdot 10^{-13}$  ergs) and the particle size is 1000 Å radius in each case (*ie*,  $a = 1000$  Å).

In Figure 8 are shown the total energy ( $V_T^{\text{Reg}}$ ) curves as a function of reduced distance,  $\kappa H_0$ , where  $(H + 2a)$  is the centre-to-centre distance at  $10^{-1}$  M ionic strength. We consider the case of homocoagulation of the three materials and heterocoagulation of amphoteric with carboxyl latex. From Figure 8 it can be seen that each yields a secondary minimum depth of circa 3kT with a barrier to coagulation for the carboxyl and sulphonate lattices of circa 7kT. For the amphoteric latex, the barrier is circa 0.5kT and for carboxyl-amphoteric heterocoagulation the barrier is  $\approx 2.5$ kT.

<sup>#</sup> NB If the rate of ion migration is significantly less than the rate of Brownian collision (*ie*, equilibrium cannot be attained), regulation will still operate. Its effect will be to lower the activation energy for ion migration from that observed in the absence of interacting surfaces.

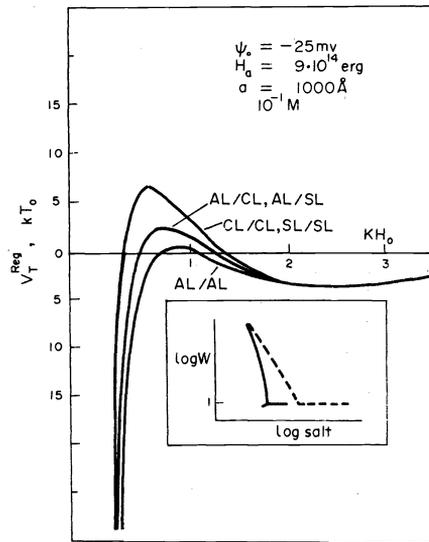


Figure 8.  $V_T^{\text{Reg}}$  total energy curves for the interaction of latex colloid spheres. CL, SL and AL refer to carboxyl, sulphonate and amphoteric latex respectively. Also shown is the CL/AL heterocoagulation case under the same conditions. (Insert - for details see text.)

Thus for these three homo- plus one heterocoagulation systems, if we set  $5kT$  as a stable-unstable demarcation, then the carboxyl and sulphonate colloids are stable, the amphoteric and the carboxyl-amphoteric systems are unstable. The materials are of identical Hamaker constants, size and surface potential. The amphoteric latex is able to respond via charge regulation whereas the sulphonate and carboxyl latex cannot. The pH of these systems is approximately pH 7.0, compared to the  $pK_a$  values of -1 and 4.8 for these two materials. The amphoteric latex, at approximately pH 8.2, with  $pK_-$  and  $pK_+$  values at 5 and 9, is able, despite its inherently much greater charge, to regulate to oppose the electrostatic repulsion during approach. Indeed, the detailed calculation shows that at close separation the charge on the amphoteric changes from negative to positive and at zero separation is equal and opposite to the carboxyl latex charge, which changes by only 3% from infinite to zero separation.

The effect of reducing the ionic strength to  $10^{-2} \text{ M}$  and the total double layer potential to  $-17 \text{ mV}$  is shown in Figure 9, again for the homo- and heterocoagulation of carboxyl and amphoteric latex colloids. To add further emphasis to the relationship between regulated interaction and constant charge/potential interaction, we have arbitrarily departed from the data of Table 1 and chosen for both systems:

|                  |  |
|------------------|--|
| Radius           | = $1000 \text{ \AA}$   |
| Hamaker constant | = $9 \cdot 10^{-14} \text{ erg}$   |
| Concentration    | = $10^{-2} \text{ M}$  |
| $\psi_0$         | = $-17 \text{ mV}$ in <u>all</u> cases;  |
| $N_S$ (CL)       | = $2.5 \cdot 10^{12} \text{ cm}^{-2}$ ; $pK_a = 4.8$                             |
| $N_S$ (AL)       | = $N_+ = N_-$ ; $pK_+ = 9$ ; $pK_- = 5$<br>= $2.5 \cdot 10^{12} \text{ cm}^{-2}$ |

These parameters, while close to those of the real systems, are designed to make the two latex colloids as identical as possible.

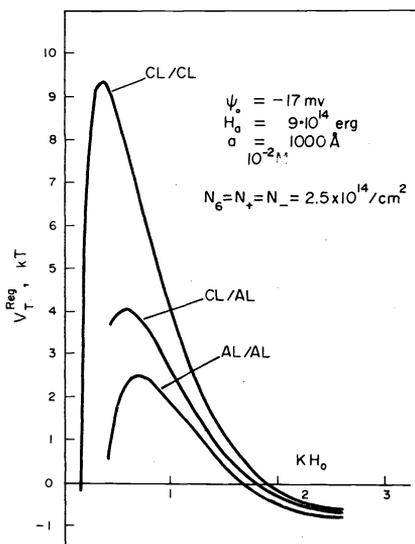


Figure 9. Total energy curves under regulated approach as a function of reduced distance ( $\kappa H_0$ ) for homo- and heterocoagulation of carboxyl (CL) and amphoteric (AL) latex colloids ( $\psi_{01} = \psi_{02} = -17$  mV).

Note again the development of a barrier to coagulation in the carboxyl homocoagulation case as a result of essentially constant charge type approach. With the amphoteric latex, regulation is able to decrease the barrier to a value of circa 2.5kT. The log W values, where W is the stability index, are 1:4:8 (approximately) for the three systems AL/AL, AL/CL and CL/CL respectively. More detailed calculations are being considered at present to see the effect of regulation on the shape of conventional log W-log salt curves. The several contribution effects are complex but may in certain cases produce non-linear log W-log salt curves, as illustrated in the insert on Figure 8.

One final example concerns the properties of concentrated dispersions, in particular, the monodispersed colloidal systems that show order-disorder behaviour (18). We consider a section of the order-disorder diagram usually plotted as volume fraction of colloid ( $\phi$ ) vs log concentration of salt in the system. Again, for purposes of illustration we consider that there is no two-phase region, or that it is very narrow.

If the volume fraction of particles at a given salt concentration is increased, the average particle-particle distance of the disordered suspension decreases until the average double layer overlap results in repulsion. The phenomenon of ordering of such a suspension is in fact a "regulation response". The system lowers the average particle-particle repulsion by changing to an ordered state.

Thus those systems that can regulate their surface charges will do so to further aid the process of minimizing the free energy of the strongly repulsive array (19). We can expect that the better the system can regulate, the larger will be the volume fraction at which disordered systems will order. Alternatively, the boundary (or region) of order-disorder will move to higher volume fractions as one compares constant charge, regulation and constant potential systems.

#### SUMMARY

Charge regulation has been shown to be a powerful mechanism in distinguishing between the stability of colloidal dispersions of materials with ionizable group surfaces. Surfaces that can regulate will in general coagulate at lower salt and order at higher volume fraction than those which cannot regulate. The use of regulated interaction instead of the usual constant charge, constant potential approximations may provide new understanding of direct force measurements and of biosystems.

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