Electrical Double Layer Interactions under Regulation by Surface Ionization Equilibria—Dissimilar Amphoteric Surfaces

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The electrostatic interaction between similar and dissimilar double layers under regulated approach is considered. During the interaction the surface potentials and charges are regulated by the association and dissociation of ionizable groups at each surface. A new method, similar to the method of isodynamic curves, is developed to study this problem. This method can provide a qualitative description of the salient features of the surface charge, the surface potential and the pressure between the surfaces as a function of separation without first having to obtain an exact solution of the problem. This qualitative and the accompanying exact solution are presented in terms of the Gouy–Chapman approximation as an illustration of the role of surface regulation during interaction.

1. INTRODUCTION

In a variety of situations that involve particles of colloidal dimensions, for instance, in fibrous bed filtration of emulsions [1,2] mineral flotation,[3] it is necessary to understand the interaction between dissimilarly charged particles.

In the classical Gouy–Chapman theory of electrical double layers, it has been usual to assume, as boundary conditions for the electrostatic problem, that constant charge or constant potential is maintained on either or both surfaces throughout the interaction. For certain surfaces, where the charge is due, for example, to strong acid sites, the constant charge assumption may indeed be correct at $pH \gg pK_a$. However, there are as yet no criteria for determining the extent to which such an assumption is valid, nor are there criteria for selecting *a priori* whether interaction under constant charge or constant potential is more appropriate for many other important colloidal systems. The problem of interacting dissimilar double layers has been considered by a number of authors.[4-16] In all instances, the constant charge or constant potential boundary condition was employed. It has been recognised for some time that these boundary conditions lead to infinitely large surface potential or surface charge, as the case may be, at small interparticle separations. This difficulty can, of course, be avoided by invoking some minimum cut-off in the

separation,[17] or, perhaps more satisfactorily, by a proper consideration of the chemical potential of adsorbed ionic species at the surface.[18-20]

In a previous paper,[24] (I), we have considered in detail the electrical double layer interaction between two identically charged planar surfaces where the surface potential is regulated by those equilibria at the surface that are responsible for the development of the surface charge.[25] At each interparticle separation, the surface charge density which determines the potential distribution in the diffuse layer is itself given as a self-consistent function of the surface potential.

Using the notions developed in (I), we consider the double layer interaction between two dissimilar amphoteric planar surfaces. Although we are dealing specifically with amphoteric surfaces, the analysis which follows also applies to surfaces which bear only acidic or basic groups. In the next section, by a consideration of the dissociation of surface groups, we shall briefly recapitulate the relation which governs the regulation of surface charge and potential. The formulation of the potential distribution, assumed to be given by the Poisson–Boltzmann (PB) equation, and also the pressure, as a function of distance will be derived. From the first integral of the PB equation and the boundary conditions, we can predict qualitatively the behaviour of the repulsive pressure, surface potential and surface charge as a function of the separation. Our analysis is analogous to the method of isodynamic curves due to Deryaguin.[4] The interaction between surfaces having like signs at infinity (but different magnitudes in charge and potential) is described in Section 3; that between unlike surfaces in Section 4. The method of quantitative solution of the interaction for all cases is considered in Section 5.

2. FORMULATION

As in (I), we adopt the concept that each surface develops a surface charge via dissociation equilibria of amphoteric surface groups. The reactions may be written as:

$$AH_2^+ \rightleftharpoons AH + H^+ \qquad (2.1)$$

$$AH \rightleftharpoons A^- + H^+. \qquad (2.2)$$

Although the discussion is independent of the type of PDI, we shall assume they are hydrogen ions as, for example, in hydrous metal oxides, and that for each reaction, the ratios of the concentration of surface species are given by surface dissociation constants, viz.,

$$\frac{[AH][H^+]_s}{[AH_2^+]} = K_+ \qquad (2.3)$$

$$\frac{[A^-][H^+]_s}{[AH]} = K_-. \qquad (2.4)$$

The dissociation constants K_+, K_- are assumed to be functions only of temperature and pressure. The validity of eqn (2.3) and (2.4) has been discussed in detail in (I).

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

$$\sigma = eN_s \frac{[AH_2^+] - [A^-]}{[AH] + [AH_2^+] + [A^-]} \equiv eN_s\alpha. \qquad (2.5)$$

The fraction, α, defined by eqn (2.5), can assume any value between plus and minus one.

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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 ψ is measured with respect to the value at the reservoir (taken to be zero). In particular, the surface concentration of PDI is:

$$[H^+]_s = H \exp(-e\psi_s/kT) \qquad (2.6)$$

where H is the bulk concentration of PDI and ψ_s is the surface potential. Combining eqn (2.3), (2.4) and (2.6) the surface charge can be written as:

$$\sigma = eN_s \frac{(H/K_+)\exp(-e\psi_s/kT)-(K_-/H)\exp(e\psi_s/kT)}{1+(H/K_+)\exp(-e\psi_s/kT)+(K_-/H)\exp(e\psi_s/kT)}. \qquad (2.7)$$

Given the dissociation constants, K_+ and K_-, which characterize the surface, and the bulk concentration of PDI, eqn (2.7) represents a canonical relationship between the values of the surface charge and the surface potential. It is used in place of the constant charge or potential boundary condition for solving the Poisson-Boltzmann (PB) equation that governs the distribution of the diffuse layer. If during the interaction the surface potential changes from ψ_s to ψ_s', the surface charge will change from σ', where (ψ_s,σ) and (ψ_s',σ') must satisfy eqn (2.7) which is thus an " equation of state " of the surface. It specifies all possible values of the " coordinate " (ψ_s,σ).

It is instructive to rewrite eqn (2.7) in the form:

$$\sigma = eN_s \frac{\delta \sinh\left[e(\psi_N-\psi_s)/kT\right]}{1+\delta \cosh\left[e(\psi_N-\psi_s)/kT\right]} \equiv eN_s\alpha \qquad (2.8)$$

where

$$\delta = 2\times 10^{-\Delta pK/2} = 2[K_-/K_+]^{\frac{1}{2}} \qquad (2.9)$$

and

$$\Delta pK = pK_- - pK_+. \qquad (2.10)$$

We shall call the potential:

$$\psi_N = \frac{kT}{e}2.303(pH_0-pH) \qquad (2.11)$$

the Nernst potential since it is related to the point-of-zero-charge (pzc)

$$pH_0 = \tfrac{1}{2}(pK_+ + pK_-) \qquad (2.12)$$

by the Nernst eqn (2.11). We note from eqn (2.8) that $\sigma \gtrless 0$ if $\psi_s \lessgtr \psi_N$ and $\sigma = 0$ when $\psi_s = \psi_N$. When the surface potential is far away from the Nernst value, the surface charge attains the saturation values $\pm eN_s$. In view of eqn (2.10) to (2.12), the surface equation of state can be completely specified by the pzc (pH_0) and ΔpK together with the bulk pH, or equivalently the Nernst potential. A detailed study of the non-Nernstian behaviour of amphoteric oxides, based on eqn (2.8), is given elsewhere.[26] We can now proceed to study the potential distribution and the pressure between two amphoteric surfaces.

Consider the general Poisson–Boltzmann (PB) equation that governs the electrostatic potential ψ in an electrolyte:

$$\nabla^2\psi = -\frac{4\pi e}{\varepsilon}\sum_i n_i v_i \exp\left(-ev_i\psi/kT\right). \qquad (2.13)$$

In eqn (2.13) n_i is the bulk number density of ion types having valence v_i and ε is the dielectric constant of the solvent. For the one-dimensional problem of two

charged flat surfaces at $z = 0$ (hereafter referred to as surface 1) and at $z = L$ (surface 2) interacting across the electrolyte, eqn (2.13) can be written as :

$$\frac{d^2\psi}{dz^2} = -\frac{4\pi e}{\varepsilon} \sum_i n_i v_i \exp{(-ev_i\psi/kT)}. \qquad (2.14)$$

This has to be solved with the usual boundary conditions

$$\frac{d\psi}{dz}\bigg|_{z=0} = -\frac{4\pi}{\varepsilon}\sigma_1(\psi_1) \qquad (2.15)$$

$$\frac{d\psi}{dz}\bigg|_{z=L} = \frac{4\pi}{\varepsilon}\sigma_2(\psi_2). \qquad (2.16)$$

According to eqn (2.7) the surface charges σ_1, σ_2 are functions of the surface potentials ψ_1, ψ_2 when we have dissociation equilibrium at the surface. The exact forms of the functions are determined by the dissociation constants of each surface and the bulk concentration of PDI.

A first integral of (2.14) yields :

$$\left(\frac{d\psi}{dz}\right)^2 = \frac{8\pi kT}{\varepsilon} \sum_i n_i \left[\exp{(-ev_i\psi/kT)}+C\right]. \qquad (2.17)$$

Applying the boundary conditions, we get two equations for the surface potentials ψ_1, ψ_2 and the constant of integration C :

$$\sigma_1^2 (\psi_1) = \left(\frac{\varepsilon}{4\pi}\right)^2 \left\{\frac{8\pi kT}{\varepsilon} \sum_i n_i \left[\exp(-ev_i\psi_1/kT)+C\right]\right\} \qquad (2.18)$$

$$\sigma_2^2 (\psi_2) = \left(\frac{\varepsilon}{4\pi}\right)^2 \left\{\frac{8\pi kT}{\varepsilon} \sum_i n_i \left[\exp(-ev_i\psi_2/kT)+C\right]\right\}. \qquad (2.19)$$

We observe that if electrical neutrality were to be preserved in the limit of small separations we must either have $\sigma_1 = -\sigma_2$ or $\sigma_1 = 0 = \sigma_2$ as $L\to 0$. In either case, both surface potentials must become the same in this limit. Further if both $\sigma_1 \sigma_2 \to 0$ as $L\to 0$ both surface potentials must approach their own Nernst values [eqn (2.8)], and this is only possible when both surfaces have the same pzc (pH$_0$) but different ΔpK's (to remain as dissimilar surfaces at infinity).

The repulsive pressure between the plates ($P > 0$ implies repulsion) can be written in the physically perspicuous form :

$$P = kT \sum_i n_i[\exp{(-ev_i\psi/kT)}-1] - \frac{\varepsilon}{8\pi}\left(\frac{d\psi}{dz}\right)^2. \qquad (2.20)$$

We can now use eqn (2.17) giving :

$$P = -2nkT(C+1) \qquad (2.21)$$

where

$$n = \tfrac{1}{2}\sum_i n_i. \qquad (2.22)$$

It is well known* that the second integration of the PB equation requires a knowledge of whether

(i) $C < -1$ (*i.e.*, $P > 0$ repulsive)   (2.23)

(ii) $|C| < 1$ (*i.e.*, $P < 0$ attractive)   (2.24)

or (iii) $C > 1$ (*i.e.*, $P < 0$ attractive)   (2.25)

* see for example ref. (4), (5), (10), (12) and (15).

because the integration procedure is different for each case. Therefore, a third relation between ψ_1, ψ_2 and C can be obtained. This, together with eqn (2.18) and (2.19) would enable us to obtain a complete solution of the problem.

Before proceeding further, we shall make one simplifying assumption by considering only the case of a $1:1$ electrolyte. The PB eqn (2.14) now takes on the simpler form:

$$\frac{d^2\psi}{dz^2} = \frac{8\pi ne}{\varepsilon} \sinh(e\psi/kT).\tag{2.26}$$

A moment's reflection will reveal that only the three types of solution illustrated in table 1 are allowed. These results will be useful in later discussions.

TABLE 1.—EXAMPLES SHOWING THE THREE TYPES OF SOLUTIONS ALLOWED BY THE POISSON–BOLTZMANN EQUATION TOGETHER WITH SOME GENERAL RELATIONS BETWEEN σ AND ψ

I. *Like charges and like potentials*

If $|\sigma_1| \gtrless |\sigma_2|$ then $|\psi_1| \gtrless |\psi_2|$ and vice versa.
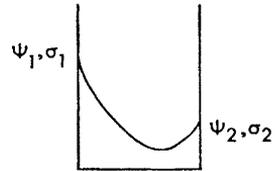
II. *Unlike charges and like potentials*

If $|\sigma_1| \gtrless |\sigma_2|$ then $|\psi_1| \gtrless |\psi_2|$ and vice versa.
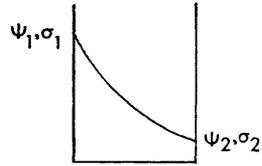
III. *Unlike charges and unlike potentials*

At $\psi = \dfrac{d^2\psi}{dx^2} = 0.$
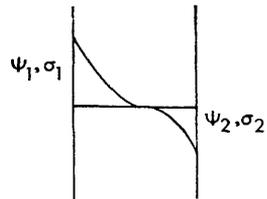
For notational convenience, we introduce the reduced potential

$$y = e\psi/kT \tag{2.27}$$

the Debye screening parameter

$$\kappa = \left(\frac{8\pi ne^2}{\varepsilon kT}\right)^{\frac{1}{2}} \tag{2.28}$$

the dimensionless constant

$$\gamma_i = \frac{\kappa N_{si}}{4n}, \qquad i = 1, 2 \tag{2.29}$$

with

$$n = \frac{NI}{1000}$$

where I is the ionic strength in mol dm^{-1} and N is Avogadro's number. The subscripts 1,2 will refer, as before, to surface 1 and 2. Eqn (2.18) and (2.19) can now be written in the form:

$$\eta_1(y_1) \equiv -\tfrac{1}{2}(C+1) = \tfrac{1}{2}(\cosh y_1 - 1) - \gamma_1^2\alpha_1^2(y_1^2) = \sinh^2(y_1/2) - \gamma_1^2\alpha_1^2(y_1) \quad (2.30)$$

$$\eta_2(y_2) \equiv -\tfrac{1}{2}(C+1) = \sinh^2(y_2/2) - \gamma_2^2\alpha_2^2(y_2) \quad (2.31)$$

where [cf. eqn (2.5) and (2.8)]

$$\alpha_i(y_i) = \frac{\delta_i \sinh (y_{N_i} - y_i)}{1 + \delta_i \cosh (y_{N_i} - y_i)}, \quad i = 1, 2. \quad (2.32)$$

Since the pressure must be the same on both surfaces, the relation

$$\eta_1(y_1) = \eta_2(y_2) \quad (2.33)$$

must hold for the functions η_1, η_2 defined by the above equations.

The key to solving the problem of interacting dissimilar amphoteric surfaces lies in understanding the interplay between the curve $\sinh^2(y/2)$ and the charge curves $\gamma^2\alpha^2(y)$, of each surface. Therefore, it is important that we systematically characterize the manner in which these curves intersect each other. To begin with, let us plot $\sinh^2(y/2)$ and $\gamma^2\alpha^2(y)$ as a function of the *surface* potential y. [Subscripts 1 and 2 will be suppressed when we are considering a general surface. The *surface* potential y under consideration should not be confused with the potential at some general position $y = y(z)$.] This is shown schematically in fig. 1. We have shown, without
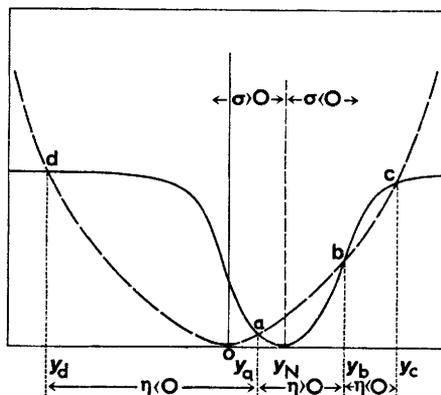
Fig. 1.—A schematic plot of the functions $\sinh^2(y/2)$ (broken curve) and $\gamma^2\alpha^2(y)$ (solid curve) showing the points of interaction between these curves, and the regions where the function $\eta(y)$ and the surface charge σ is positive or negative.

loss of generality, values of the concentration of PDI such that the Nernst potential, y_N, is positive and we observe that the quantity ΔpK [eqn (2.10)] is a measure of the width of the charge curve. For ease of later discussions, it is useful to adopt the following nomenclature. Since $\eta(y)$ and hence the pressure is the (vertical) difference between the two curves, we can delineate regions where $\eta > 0, 0 > \eta > -1, \eta < -1$ corresponding to cases (i), (ii) and (iii) in eqn (2.33) to (2.25). We label the points

of intersection between the two curves (where $\eta = 0$) as a, b, c and d with the corresponding potentials y_a, y_b, y_c and y_d. The point a is defined as the intersection where y_a falls between the origin and the Nernst potential y_N. Points b and c are the intersections where y_b and y_c have the same sign as y_N. Under some circumstances there may be no intersections b and c or the points b and c may coincide. The point of intersection on the opposite side of the origin to y_N is labelled d.

For a single surface in equilibrium with a bulk solution containing a given concentration of PDI, there is no net force exerted on the surface. Therefore the pressure P is identically zero, that is, $\eta = -\frac{1}{2}(C+1) = 0$. Of the four points where $\eta = 0$, only point a, where the surface charge and the surface potential have the same sign, satisfies the PB equation. [This multiplicity of solution does not arise if we realize that since $(C+1) = 0$, we can take the appropriate square root of eqn (2.30), say, and the resultant expression then only has one root.] Thus we obtain the general result that the surface potential of an isolated amphoteric surface always lies between zero and the Nernst potential. The only occasion when y_a equals zero is when the Nernst potential is zero. That is, the concentration of PDI is at the point-of-zero-charge, $pH = pH_0$ and $\sigma = 0$.

To study the electrostatic interaction between two dissimilar amphoteric surfaces, we need to examine the functions $\eta_1(y_1)$ and $\eta_2(y_2)$ given in eqn (2.30) and (2.31). This is best accomplished by plotting (schematically) the two charge curves $\gamma_1^2\alpha_1^2(y)$, $\gamma_2^2\alpha_2^2(y)$ and the function $\sinh^2(y/2)$ on the same graph. See for example fig. 2 (a) and (b). We define y^* to be the potential corresponding to that point of intersection of the two charge curves which falls *in between* the Nernst potentials y_{N_1} and y_{N_2}.

(a)   (b)
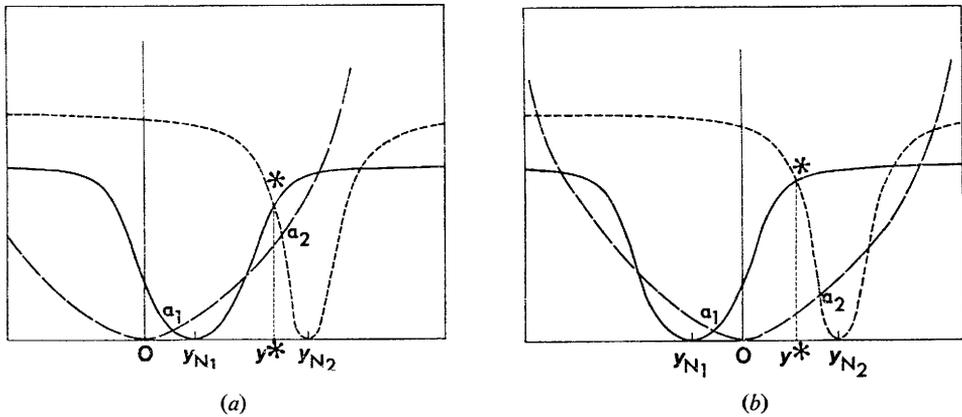
FIG. 2.—Typical arrangements of charge curves for like (a) and unlike (b) surfaces.

The state of surface i ($i = 1,2$) can be identified with the coordinate (y_i, σ_i). However, the values of the surface potential $\psi_i = kTy_i/e$ and the surface charge σ_i cannot vary independently as they are related by eqn (1.7) or (1.8). In other words, the state of each surface must correspond to some point (y, σ) on its own charge curve $\gamma^2\alpha^2(y)$. As the surfaces approach each other, changes in the charge and potential at each surface due to the interaction can be envisaged as movements of these points along their own charge curves. Since the surfaces are interacting, the *loci* of these two points must be correlated. Firstly, the movement of these points must ensure that eqn (2.33) [cf. eqn (2.30) and (2.31)] is satisfied. Secondly, the values of y_1 and y_2 must satisfy the PB equation. That is, the relationship between

the charge and potential at each surface and between surfaces must fall within one of the three types listed in table 1. Thus it is possible to obtain a description of the behaviour of the repulsive pressure, surface potential and charges as a function of separation by considering the charge curves $\gamma_1^2\alpha_1^2(y)$, $\gamma_2^2\alpha_2^2(y)$ and the function $\sinh^2(y/2)$. Most of the results we are about to describe can be deduced from the fact that $\sinh^2(y/2)$ increases monotonically as $|y|$ increases and that the charge curves $\gamma^2\alpha^2(y)$ have an absolute minimum at $y = y_N$.

Before proceeding to an analysis of the interaction between like and unlike surfaces it is important to note that the preceding formulation makes no comment on the rate at which surfaces can regulate when H^+ and OH^- or any other ions are involved in surface equilibria. It is, however, directly applicable to increasing numbers of direct measurements of interaction where the surfaces are brought together very slowly and/or where assemblages of particles are forced together slowly in compression experiments. As to whether H^+/OH^- equilibria can readjust in the time of Brownian collision awaits more experimental testing.[17]

3. THE INTERACTION BETWEEN LIKE SURFACES

We have already shown in Section 2 that the surface potential of a single surface in isolation falls between zero and the Nernst value. Here we consider only those values of the bulk concentration of PDI where the Nernst potentials of each surface have the same signs. That is, both surfaces have the same sign of the charge at infinite separation. For the purpose of this analysis, we can assume without loss of generality that the surfaces are both positive and that surface 1 has a lower Nernst potential, *i.e.*, $y_{N_i} < y_{N_2}$. (In fact, by reversing the sign of the Nernst potentials, negative surfaces can be " transformed " into positive ones and the following analysis will be applicable.)

For the interaction of surfaces having like signs of infinity, there are three distinct cases classified by the number of times that the repulsive pressure curve changes sign. Each is in turn determined by the position of y^* as follows (with L designating like surfaces):

$$\text{case L1}: y^* \leqslant y_{b_1}$$

$$\text{case L2}: y_{b_1} \leqslant y^* \leqslant y_{c_1}$$

$$\text{case L3}: y_{c_1} \leqslant y^*.$$

We shall consider each of these separately.

3a. CASE L1

The appropriate charge curves for this case are given in fig. 3 (*a*) and (*b*). The characteristic feature of these sets of curves is that y^* (the potential corresponding to the intersection of the two charge curves that falls in between the Nernst potentials) is $< y_{b_1}$. This case also includes the situation where surface 1 (defined to be the one with the lower Nernst potential) does not have the intersection points b_1 and c_1.

Since the arguments involved in deducing the behaviour of the surfaces are rather tedious, we shall first summarize the results. The (schematic) variations with separation for the repulsive pressure P, surface charge and potential of each surface are given in fig. 4 (*a*) and (*b*).

(i) In case L1, the interaction is always repulsive, $P > 0$.
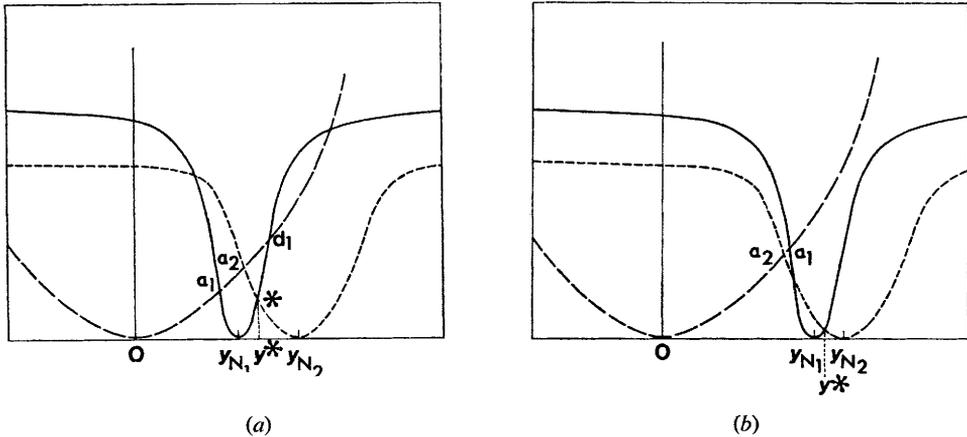
FIG. 3.—(a), (b) Arrangements of charge curves between like surfaces [surface 1—solid curve, surface 2—dotted curve, and $\sinh^2 (y/2)$—dashed curve] that correspond to Case L1.

(ii) If the function $\eta_1(y_1)$ has a maximum in the range $y_{a_1} \leqslant y_1 \leqslant y^*$, then the pressure has a maximum (P^{max}) at $y_1 = \bar{y}_1$ say, where $\bar{y}_1 \geqslant y_{N_1}$ [fig. 4 (a)]; otherwise the pressure increases monotonically from zero at infinite separation to the final value P^* at zero separation [fig. 4 (b)].

(iii) At zero separation, the surface potentials are equal and the surface charges are equal in magnitude but opposite in sign (*cf.* discussion in Section 2).

The results summarized in fig. 4 can be deduced from fig. 3 if we bear in mind the discussion in Section 2 regarding the charge curves. We shall briefly summarize the main points :

(A) The surface charge and potential of each surface is related to each other by eqn (2.7) or (2.8). A state of the surface, *i.e.*, (y, σ), can be represented by a point on the charge curve $\gamma^2\alpha^2(y)$.

(B) Changes in the surface charge and potential due to interaction are described by the movement of this point along the charge curve.

(C) The *loci* of the points for each surface must together satisfy eqn (2.33) and the PB equation (*cf.* table 1).

(D) The function $\sinh^2(y/2)$ increases monotonically as $|y|$ increases and similarly $\gamma^2\alpha^2(y)$ is a monotonic increasing function of $|y_N - y|$.

Using (A)-(D) above we now demonstrate how the results from fig. 4 (a) can be deduced from fig. 3 (a) and (b). When the surfaces are far apart, we have already shown in Section 2 the potentials of surface 1 and 2 are y_{a_1} and y_{a_2} respectively. Referring to the charge curves, we say surface 1 is at the point a_1 and surface 2 is at a_2. We first consider the case shown in fig. 3 (a) where $y_{a_2} > y_{a_1}$. We define

$$\sigma^* = \sigma_2(y^*) = -\sigma_1(y^*) \tag{3.1}$$

and observe that the surface charges at infinite separation $\sigma_1(y_{a_1})$, $\sigma_2(y_{a_2})$, obey the relations

$$\sigma_2(y_{a_2}) > \sigma^*, \sigma_1(y_{a_1}) \tag{3.2}$$

but $\sigma_1(y_{a_1})$ can be $>$ or $<\sigma^*$.

As the surfaces approach each other and just begin to interact, we know, by the overlap approximation that the surface potentials must increase and the interaction

is repulsive. That is $P > 0$, $\eta_1(y_1) = \eta_2(y_2) > 0$ [cf. eqn (2.21), (2.30)–(2.33)]. Therefore, each surface would move along its own charge curve towards its respective Nernst potential. While the surface potentials increase, the surface charges decrease. This minimizes the interaction energy. As the surfaces approach the rate of change of the charge and potential of each surface with separation (i.e., the velocities along the charge curves) must of necessity be different since the equality $\eta_1(y_1) = \eta_2(y_2)$ must be maintained at all times.
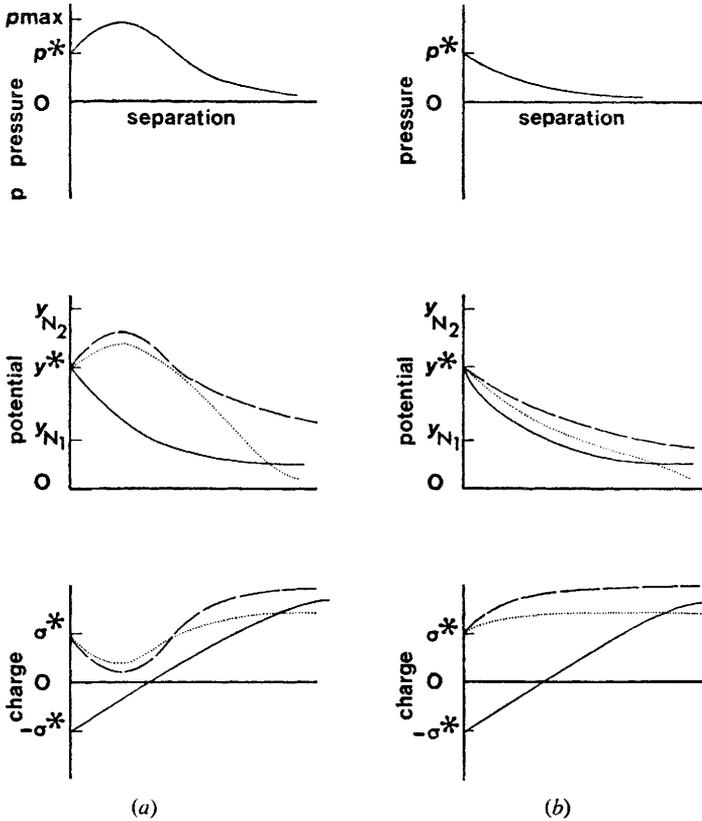
FIG. 4.—(a), (b) Schematic results showing the different possible variations of the repulsive pressure, surface potentials and surface charges with plate separation for Case L1 (surface 1—solid curves, surface 2—dashed curves).

We assume that the function $\eta_1(y_1)$ has a maximum between y_{a_1} and $y^*(y_{a_1} \leqslant y_1 \leqslant y^*)$; at $\bar{y}_1$ say. It is clear from point (D) above that $\bar{y}_1$ is between y_{N_1} and y^* ($y_{N_1} \leqslant \bar{y} \leqslant y^*$). Now, as the separation between the surfaces decreases, both surfaces would move closer to their Nernst potentials. When surface 1, which has the lower Nernst potential, reaches y_{N_1} where its charge has decreased to zero, surface 2 is still below its Nernst value with a finite and positive surface charge.

As the separation further decreases, the potential of surface 1 continues to increase beyond y_{N_1}, but with a surface charge of opposite sign to that at infinity (cf. fig. 1). When surface 1 reaches $\bar{y}_1$ where $\eta_1(y_1)$ has a maximum, surface 2 is at $\bar{y}_2$ where $\eta_1(\bar{y}_1) = \eta_2(\bar{y}_2)$. Again from point (D) we can deduce that

$$y^* \leqslant \bar{y}_2 \leqslant y_{N_2}.$$

As surface 1 proceeds beyond $\bar{y}_1$ towards y^*, $\eta_1(y_1)$ can only decrease. Hence surface 2 must retrace its path along the charge curve from $\bar{y}_2$ and approach y^* from above. Therefore surface 2, which has the higher Nernst potential, never reaches y_{N_2} and so its surface charge always retain the same sign as that at infinite separation.

Now both surfaces must reach y^* at the same time because $\eta_1(y^*) = \eta_2(y^*)$. Here we have $\gamma_1^2 \alpha_1^2(y^*) = \gamma_2^2 \alpha_2^2(y^*)$ and the potentials are equal but the charges are equal and opposite. The surfaces cannot proceed beyond y^* as this would violate the PB equation (*cf.* type II, table 1). Clearly, the boundary conditions $y_1 = y_2$, $\sigma_1 = -\sigma_2$ can only be attained when the separation between the surfaces is zero.

The above results are summarized in fig. 4 (*a*). The variations with separation of the charge and potential of surface 1 are given in solid lines, and those of surface 2 in dashed lines.

It will be shown that:

(iv) for interactions between surfaces having like signs at infinity, the surface with the *lower* Nernst potential would *always* reach its Nernst potential and reverses the sign of its surface charge while the other surface never changes sign.

Obviously, this excludes the degenerate case where both surfaces have the same Nernst potential. In this instance, neither surface charge changes sign.

Now it is possible for surface 2, which by definition has the higher Nernst potential, to have a lower surface potential than surface 1 when they are far apart [see fig. 3 (*b*)]. It is clear from the figure that the surface charges at infinity obey the inequalities

$$\sigma_1(y_{a_1}) > \sigma_2(y_{a_2}) > \sigma^*.$$

If $\eta_1(y_1)$ has a maximum in $y_{a_1} \leqslant y_1 \leqslant y^*$, the results for surface 2 are given in dotted lines in fig. 4 (*a*). These can be derived using the arguments given above. The only noticeable differences between this case ($y_{a_2} < y_{a_1}$) and the previous case ($y_{a_2} > y_{a_1}$) are the cross-over points between the charge and potential curves. These must occur when both σ_1 and σ_2 are greater than σ^*. The behaviour of the repulsive pressure and the properties of surface 1 remain essentially the same for both cases.

If $\eta_1(y_1)$ does not have a maximum in the range $y_{a_1} \leqslant y_1 \leqslant y^*$, the interaction is still repulsive but there are no turning points in the pressure, potential and charge curve [fig. 4 (*b*)]. The arguments needed to deduce these results follow along the line of those given above. The results pertaining to surface 1 are given in solid curves.

If $y_{a_2} > y_{a_1}$ ($y_{N_2} > y_{N_1}$) the charges at infinite separation satisfy

$$\sigma_2(y_{a_2}) > \sigma^*, \sigma_1(y_{a_1})$$

but $\sigma_1(y_{a_1})$ can be greater or less than σ^*. The charge and potential for surface 2 for this case are given in dashed lines.

If $y_{a_2} < y_{a_1}$ ($y_{N_2} < y_{N_1}$) the results for surface 2 are given in dotted lines. Here $\sigma_1(y_{a_1}) > \sigma_2(y_{a_2}) > \sigma^*$ and the cross-over points in the potential and charge must occur when the charges of surfaces 1 and 2 are $> \sigma^*$.

When the Nernst potentials are very far apart [fig. 3 (*a*)], the pressure may exhibit a local minimum after the maximum. However, the pressure still remains positive for all separation. The charges and potentials will have corresponding maxima and minima.

In the degenerate case where the surfaces have the same Nernst potential (*i.e.*, the same pzc), *e.g.*, identical surfaces, then $y^* = y_{N_1} = y_{N_2}$ and neither surface changes sign. The surface potentials start off at y_{a_1} and y_{a_2}, and increases monotonically towards their Nernst values. The surface charges decrease monotonically to zero. At zero separation, both potentials are equal and surface charges are reduced to zero.

It is important to note that significant changes in the pressure *etc.* only occur when the separation is within the Debye screening length $1/\kappa$.

This completes the discussion on the various possible types of behaviour under case L1.

3b. CASE L2

The appropriate charge curves for this case are shown in fig. 5 (a). The characteristic feature of this set of curves is that:

$$y_{b_1} < y^* < y_{c_1}.$$

The variations with separation of the repulsive pressure P, surface potentials and charge of each surface are given in fig. 5 (b), (c).

(a)

(b)   (c)
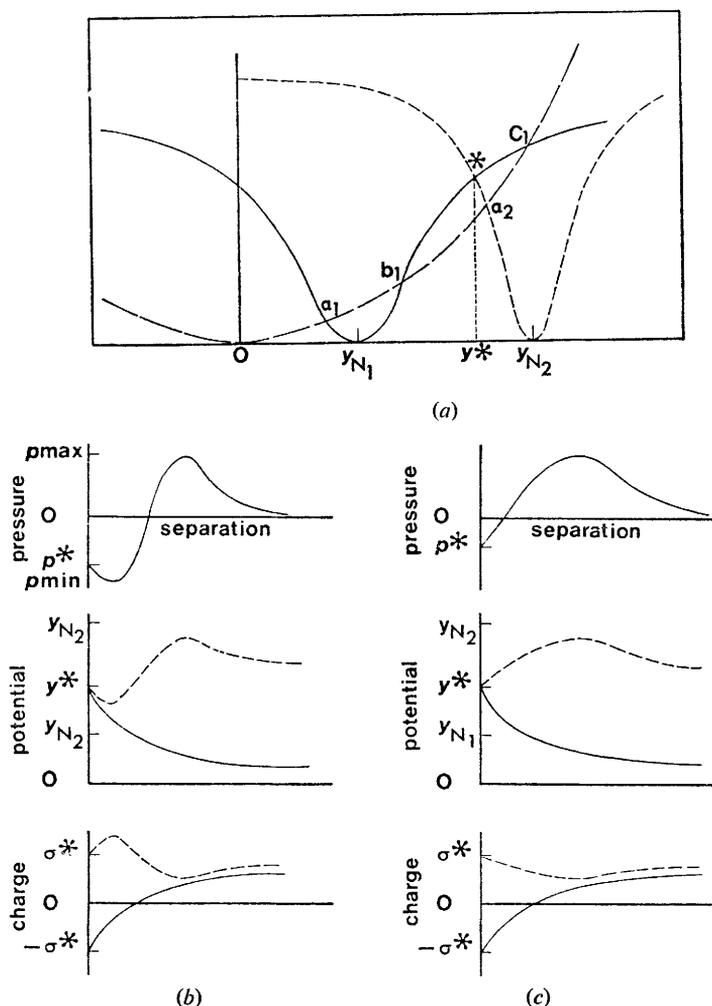
FIG. 5—(a) The arrangement of the charge curves for like surfaces Case L2 (surface 1—solid curve, surface 2—dotted curve, $\sinh^2(y/2)$—dashed curve); (b), (c) schematic results showing the possible ways which the repulsive pressure, surface potentials and charges can vary with separation (surface 1—solid curves, surface 2—dashed curves).

In case L2 the interaction is initially repulsive $(P > 0)$ but becomes attractive $(P < 0)$ at smaller separations. If $\eta_1(y_1)$ has a minimum between y_{b_1} and y^* then the pressure has a local minimum $P^{\min} < 0$ at $y_1 = \bar{\bar{y}}_1$ and $y_2 = \bar{\bar{y}}_2$ say, where $\bar{\bar{y}}_2 \leqslant y^*$.

Let us now deduce the results from the charge curves in fig. 5. As with case L1, surfaces 1 and 2 start at a_1 and a_2 respectively, and move along their charge curves towards their Nernst potentials as the surfaces approach. Clearly $\eta_1(y_1)$ has a maximum at some $\bar{y}_1$ where $y_{N_1} \leqslant \bar{y}_1 \leqslant y_{b_1}$. This maximum corresponds to the maximum in the repulsive pressure. Thus as the potential of surface 1 increases from y_{a_1} to y_{N_1} and then onto $\bar{y}_1$, its surface charge decreases to zero at $y_1 = y_{N_1}$ and changes sign between y_{N_1} and $\bar{y}_1$. Meanwhile the potential of surface 2 increases steadily from y_{a_2} to $\bar{y}_2$ where $\eta_2(\bar{y}_2) = \eta_1(\bar{y}_1)$ while the charge decreases from $\sigma_2(y_{a_2})$ to $\sigma_2(\bar{y}_2)$. Since $\bar{y}_2 < y_{N_2}$, the sign of the charge on surface 2 does not change.

As surface 1 now moves from $\bar{y}_1$ to y_{b_1}, $\eta_1(y_1)$ can only decrease; therefore surface 2 must return along its charge curve towards y_{a_2} increasing the charge and decreasing the potential. When surface 1 reaches the point b_1, surface 2 reaches a_2 whereby $\eta_1(y_{b_1}) = 0 = \eta_2(y_{a_2})$ and the pressure is zero at this point.

Between y_{b_1} and y^*, $\eta_1 = \eta_2$ is negative which corresponds to attraction. Now
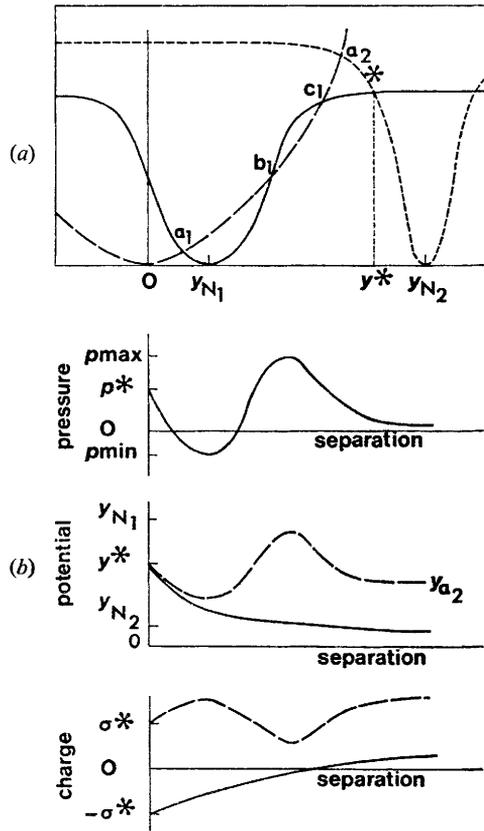
FIG. 6.—(a) The arrangement of the charge curves for surfaces having like signs at infinity, Case L3 (surface 1—solid curve, surface 2—dotted curve, $\sinh^2(y/2)$—dashed curve); (b) schematic results of the variation of pressure surface potentials and charges with separation (surface 1—solid curves, surface 2—dashed curves).

$\eta_1(y_1)$ may have a minimum (*i.e.*, $|\eta_1(y_1)|$ a maximum) for $y_{b_1} \leqslant y_1 \leqslant y^*$. If this is indeed the case, the pressure will have a minimum turning point [see fig. 5 (*b*)]. Corresponding to this, the potential of surface 2 will decrease below y^* and finally approaches y^* from below. There will be a similar turning point for the charge on surface 2.

If $\eta_1(y_1)$ does not have a minimum in $y_{b_1} \leqslant y_1 \leqslant y^*$ the pressure just decreases monotonically after turning attractive [see fig. 5 (*c*)]. Similarly the extra turning points in y_2 and σ_2 would not occur.

From fig. 5 we obtain the following inequalities which hold for all separations:

$$y_2 > y_1, \sigma_2 > \sigma_1$$

and when the surfaces are far apart:

$$y_{a_2} > y^* > y_{a_1}$$
$$\sigma^* > \sigma_2(y_{a_2}) > \sigma_1(y_{a_1}).$$

3*c*. CASE L3

The charge curves pertaining to this case are given in fig. 6. They are characterized by the inequality $y^* > y_{c_1}$. The variations with separation of the repulsive pressure, surface potential and charge of each surface are given the same in fig. 6 (*b*). These results can be derived from the charge curves by a similar consideration to that given in the previous two cases.

In case L3 the interaction is initially repulsive ($P > 0$), then it turns attractive ($P < 0$) and finally becomes repulsive again as the separation decreases from infinity to zero.

We note that if $P^{\mathrm{max}} < P^*$ then the potential (charge) curve of surface 2 would not extend above (below) y^* (σ^*) at the corresponding turning point.

4. THE INTERACTION BETWEEN UNLIKE SURFACES

In this section we consider those values of the bulk concentration of PDI where the signs of the Nernst potentials are different. This means that when the surfaces are far apart, the surfaces have different signs. Given two unlike surfaces, we can always make a transformation (*e.g.*, reversing the signs of the potentials) so that surface 1 (y_{a_1}) is initially negative, surface 2 (y_{a_2}) is positive *and* that y^* is also positive as well. [See for example fig. 2 (*b*)].

First let us define the nomenclature useful in describing how the charge curve of surface 1 (the negative surface) intersects with the curve of $\sinh^2(y/2)$. This is done in fig. 7. Depending on the value of y_{N_1} and ΔpK of surface 1 it is possible that only one of the points d_1, e_1 and f_1 exists. In this case we label this one point as d_1.

In general there are four distinct cases where the interactions are different. Again these are classified by the number of times the repulsive pressure changes sign when the separation varies from zero to infinity. These cases are determined by the position of y^* and hence by the relative position and shape of the charge curve of surface 2 (the positive surface). Each case is defined as follows (with U designating unlike surfaces):

$$\text{Case U1.} \quad 0 \leqslant y^* \leqslant y_{d_1}$$
$$\text{Case U2.} \quad y_{d_1} \leqslant y^* \leqslant y_{e_1}$$
$$\text{Case U3.} \quad y_{e_1} \leqslant y^* \leqslant y_{f_1}$$
$$\text{Case U4.} \quad y_{f_1} \leqslant y^*.$$
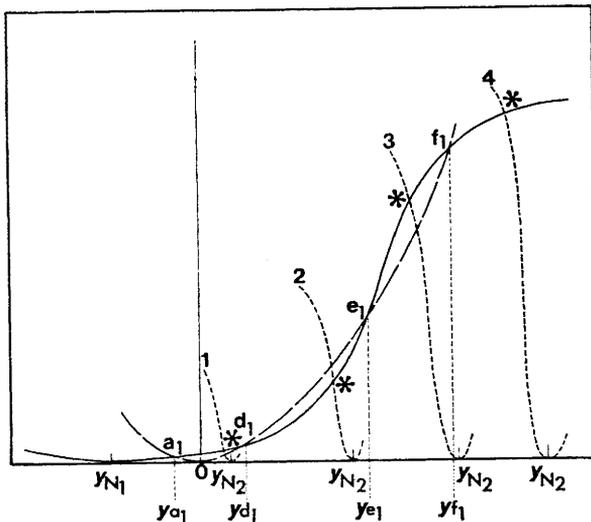
FIG. 7.—Showing the relative positions between the functions $\sinh^2$ $(y/2)$—dashed curve, the charge curve of surface 1—solid curve, and of surface 2—dotted curves, for surfaces having different signs at infinite separation. The Cases U1 to U4 are indicated.
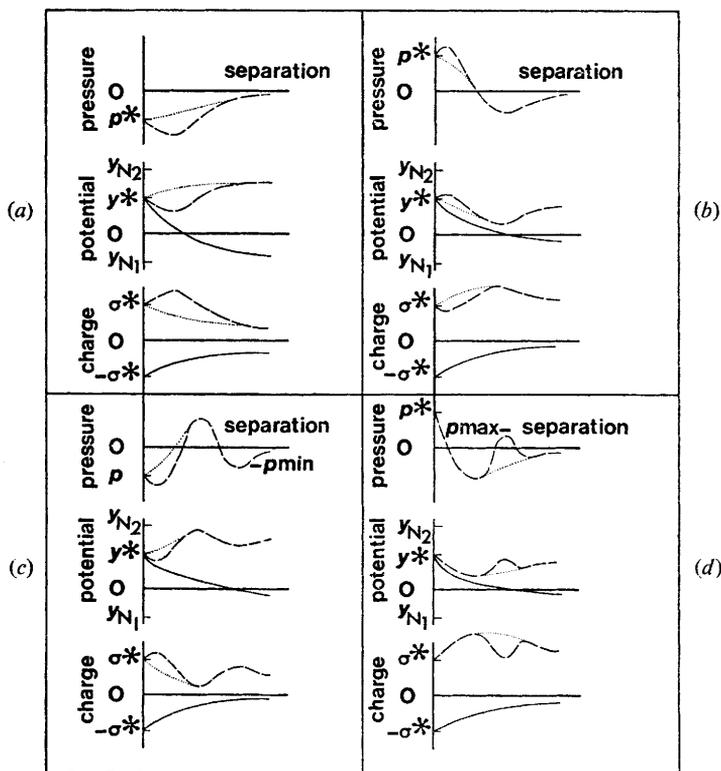
FIG. 8.—(a)-(d) Schematic results for the variation of the pressure, surface potentials and charges for curves U1 to U4 respectively (surface 1—solid curves, surface 2—dashed curves).

We shall only outline how the given results can be deduced from the charge curve for cases U1 and U2. The results of the other cases should be self-evident.

4a. CASE U1

In case U1, where $0 \leqslant y^* \leqslant y_{d_1}$, the interaction is always attractive $(P < 0)$.

The behaviour of the repulsive pressure, the surface potential and charge are summarized in fig. 8 (a). The results for surface 1 are given in solid lines, and for surface 2 in dashed and dotted lines. Referring to the curves for case U1 in fig. 7 we can deduce these results.

When the surfaces are far apart, surface 1 is at a_1 and surface 2 is at a_2. As they approach each other, we know $(e.g.,$ by the overlap approximation) that the interaction is attractive, i.e., $P < 0$, $\eta_1 = \eta_2 < 0$, and the surface potentials must decrease in magnitude. These conditions can be satisfied if both surfaces move along their charge curves towards $y = 0$. This way the interaction energy is mini-mized $(i.e.,$ maximize attraction) by making the positive surface (2) more positive and the negative surface (1) more negative.

We observe that if $\eta_1(y_1)$ has a minimum $(|\eta_1(y_1)|$ a maximum) for some $\bar{y}_1$ $(0 \leqslant \bar{y}_1 \leqslant y^*)$ then there would be a minimum in the pressure and corresponding turning points in the potential and charge of surface 2—see dashed lines in fig. 8 (a). Otherwise, all quantities are monotonic in the separation (dotted lines).

We note that since $\bar{y}_2$, where $\eta_1(\bar{y}_1) = \eta_2(\bar{y}_2)$, is always positive, the potential of surface 2 never changes sign. (This is in fact true in all cases of interaction between unlike surfaces.) On the other hand, the potential of surface 1 always changes sign. It is worthwhile noting here for cases U2-U4 that y_2 cannot rise above y_{N_2}; therefore, the charge of surface 2 also retains the same sign (positive).

At zero separation, the potentials are equal

$$y_1 = y^* = y_2$$

and the charges are equal and opposite

$$\sigma_2 = \sigma^* = -\sigma_1 > 0.$$

4b. CASE U2

In case U2 $(y_{d_1} \leqslant y^* \leqslant y_{e_1})$ the interaction is initially attractive $(P < 0)$ but would eventually turn repulsive. The results are summarized in fig. 8 (b).

Initially the surfaces start at y_{a_1} and y_{a_2} and move towards $y = 0$ $(cf.$ case U1) and the interaction is attractive. Since $\eta_1(y_1)$ has a minimum for $0 \leqslant y_1 \leqslant y_{d_1}$ there will be a minimum in the pressure and a corresponding turning in the potential of surface 2. When surface 1 changes sign and reaches y_{d_1} from below, y_2 returns to y_{a_2}. Here the pressure is zero $[\eta_1(y_{d_1}) = 0 = \eta_2(y_{a_2})]$.

When surface 1 now moves from y_{d_1} to y^* the interaction becomes repulsive. If $\eta_1(y_1)$ has a maximum between y_{d_1} and y^* the potential of surface 2 will increase past y^* and then return to approach y^* from above. There will also be a similar maximum in the pressure curve (see dashed curves). If $\eta_1(y_1)$ does not have this maximum there would not be a final turning point for y_2 and P (see dotted curves).

Again at zero separation

$$y_1 = y^* = y_2 > 0$$

and

$$\sigma_2 = \sigma^* = -\sigma_1 > 0.$$

4c. CASE U3

In case U3 ($y_{e_1} \leqslant y^* \leqslant y_{f_1}$), the interaction is at first attractive, then turns repulsive and finally becomes attractive again.

The variations with separation of the potential and charge of surface 1 are given in solid lines in fig. 8 (c). If $\eta_1(y_1)$ has a minimum ($|\eta_1(y_1)|$ a maximum) for y_1 between y_{e_1} and y^* the behaviour of the pressure and the surface potential and charge of surface 2 are given the dashed lines; otherwise the results in the dotted portions would hold.

We note that if P^{min} is less than P^* then the potential (charge) of surface 2 would extend below (above) y^* (σ^*) at the corresponding turning point.

4d. CASE U4

Case U4 is characterized by the condition that $y_{f_1} \leqslant y^*$.

The behaviour of the pressure, surface charges and potentials are illustrated in fig. 8 (d)—solid lines for surface 1, dashed lines for surface 2. In the degenerate
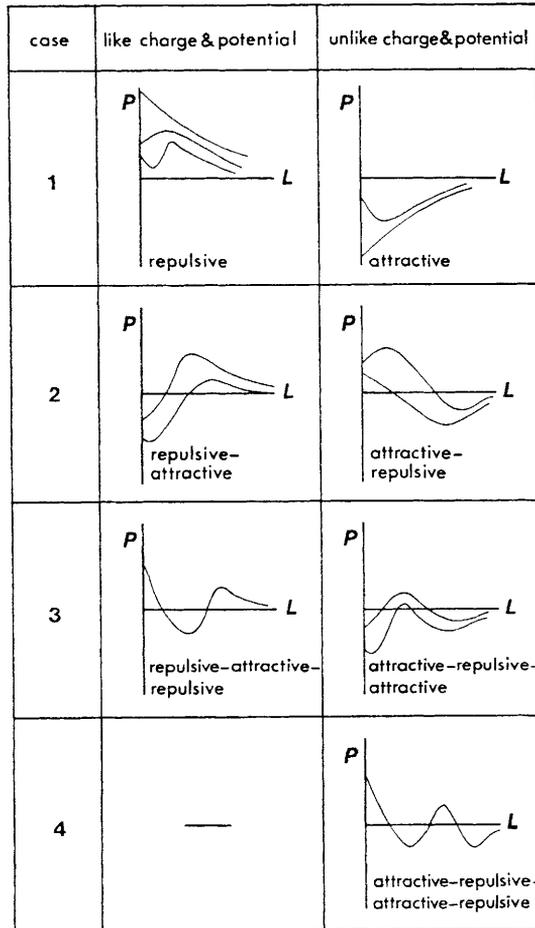
FIG. 9.—A summary of the possible variations of the pressure with separation under the different possible cases considered.

case where points e_1 and f_1 do not exist, the portions of the curves indicated by dotted lines should hold for the various quantities.

If $P^{max} > P^*$ the corresponding turning points for y_2 and σ_2 will extend beyond y^* and σ^*.

This completes the discussion of all possible types of double layer interactions between dissimilar amphoteric surfaces under regulated interaction. Although the above discussion cannot yet give the actual values of the pressure and potentials, etc., relative magnitudes of the surface potentials and charges and all the interesting features of the pressure curve can be elucidated.

Before we proceed, it is worthwhile to summarize the results discussed so far. This is accomplished in fig. 9 where all possible variations of the pressure as a function separation is given schematically for the various cases of like and unlike surfaces at infinity. Here positive pressure represents repulsion.

To obtain numerical results, we need to solve the PB equation. We show how this can be done in the next section. It is important to stress, however, that the graphical techniques that we have summarized give directly the form of the pressure–distance curve and key points on the curve (*e.g.*, zero, minimum or maximum pressure points) can also be located directly.

5. METHOD OF SOLUTION

For a 1 : 1 electrolyte, the first integral of the PB eqn (2.17) has the form

$$\frac{1}{2}\left(\frac{dy}{dz}\right)^2 = \kappa^2(\cosh y + C). \tag{5.1}$$

To obtain a second integral, we need to know the value of the constant of integration C. The solutions, in terms of Jacobi elliptic functions or elliptical integrals,[27, 28] are different, depending on whether

(i) $C < -1$, (ii) $|C| < 1$, or (iii) $C > 1$. These solutions are well known and they can be written in terms of the reduced variable

$$\phi(z) = \exp(-e|\psi(z)|/2kT). \tag{5.2}$$

(i) $C < -1$ Repulsive

$$\phi(z) = \phi_0 cd\left(\frac{\kappa(z - z_0)}{2\phi_0}; \phi_0^2\right), \tag{5.3}$$

where $\phi_0 = \phi(z_0)$ and at $z = z_0$

$$\frac{d\psi}{dz}\bigg|_{z=z_0} = 0. \tag{5.4}$$

Here z_0 can be inside or outside the range $z = 0$ to L.

(ii) $|C| < 1$ Attractive

$$\frac{1 - \phi^2(z)}{1 + \phi^2(z)} = \left(\frac{1 + C}{2}\right)^{\frac{1}{2}} sd\left(\kappa|z - z_0|; \left(\frac{1 - C}{2}\right)^{\frac{1}{2}}\right), \tag{5.5}$$

where at $z = z_0$, the potential $\psi(z_0) = 0$, that is $\phi_0 = (z_0) = 1$.

(iii) $C > 1$ Attractive

$$\phi(z) = \phi_0 sc\left(\frac{1}{2}K(\sqrt{1 - \phi_0^4}) - \frac{\kappa|z - z_0|}{\phi_0}; (1 - \phi_0^4)^{\frac{1}{2}}\right). \tag{5.6}$$

Here $K(k)$ is the complete elliptic integral of the first kind of modulus k. The constant C is given by

$$C = \tfrac{1}{2}(\phi_0^2 + \phi_0^{-2}) \tag{5.7}$$

and at $z = z_0$, $\psi(z_0) = 0$. Eqn (5.7) is suitable for $0 < z_0 < L$. For z_0 outside 0 to L, it is convenient to write the solution in the form

$$\phi(z) = \phi_0 sc\left\{ sc^{-1}\left(\frac{\phi_1}{\phi_2}\right) - \frac{\kappa z}{2\phi_0}; \sqrt{1-\phi_0^4}\right\}, \qquad z > z_0 \tag{5.8}$$

$$= \phi_0 sc\left\{ sc^{-1}\left(\frac{\phi_1}{\phi_2}\right) + \frac{\kappa z}{2\phi_0}; \sqrt{1-\phi_0^4}\right\}, \qquad z < z_0, \tag{5.9}$$

where $\phi_1 = \phi(z = 0)$. In eqn (5.3), (5.5), (5.6), (5.8) and (5.9) $cd(x;k)$, $sd(x;k)$ and $sc(x;k)$ are Jacobi elliptic functions of argument x and modulus k, sc^{-1} is the inverse function of sc with the same modulus. These solutions match up at the transition points $C = \pm 1$, as expected.

From eqn (2.30)-(2.32) we can solve for values of the surface potentials at $C = -1$, 1, i.e., at $\eta_1 = \eta_2 = 0, -1$. Putting the appropriate values of the reduced potentials ϕ_1 and ϕ_2 at $C = -1$ ($\eta_1 = \eta_2 = 0$) into eqn (5.3) we can eliminate z_0 to give

$$(\kappa L)_{C=-1} = 2\tanh^{-1}\left(\frac{|\phi_1 - \phi_2|}{1 - \phi_1\phi_2}\right). \tag{5.10}$$

The length $(L)_{C=-1}$ is the value of the separation where the transition from $C < -1$ to $|C| < 1$ takes place, that is, where the pressure changes from positive to negative or vice versa.

Further from eqn (2.30)-(2.32) we can obtain the potential of surfaces 1 and 2 at $C = 1$ that is where $\eta_1 = -1 = \eta_2$. Using these values in eqn (5.5) and setting $C = 1$, we can eliminate z_0 to get

$$F_2 = \pm[(1-F_1^2)^{\frac{1}{2}}\sin(\kappa L) \mp F_1\cos(\kappa L)] \text{ for } L \lessgtr z, \tag{5.11}$$

where

$$F_i = \frac{1-\phi_i^2}{1+\phi_i^2}, \qquad i = 1, 2. \tag{5.12}$$

This gives us the separation where the transition from $|C| < 1$ to $C > 1$ occurs.

Hence, given the dissociation constants for each surface, the bulk concentration of PDI and the ionic strength, we know which of the types of solutions (i), (ii) or (iii) to use for a given value of the separation L. This then gives us a complete solution of the problem. The qualitative descriptions given in the previous sections will enable us to keep track of the signs and relative magnitudes of the potentials and charges. Further it also helps in determining the position of z_0, that is, whether $z_0 < 0$, $0 < z_0 < L$ or $z_0 > L$, and choose the appropriate solutions for the cases $|C| < 1$ and $C > 1$.

6. DISCUSSION

In practical situations, the dissociation constants of the surfaces are fixed, only the concentration of PDI can be varied (provided the particles do not dissolve at extreme concentrations of PDI!). In terms of the charge curves, this means that the relative positions of the two Nernst potentials are fixed. Any variations in the concentration of PDI merely shift both charge curves relative to $\sinh^2(y/2)$ by the

same amount. From the definition of the Nernst potential (assuming H^+ are the PDI)

$$y_N = 2.303 \, (pH_0 - pH) = 2.303 \, \Delta pH, \qquad (6.1)$$

we see that y_N is proportional to the change in pH. Therefore, for like (positive, say) surfaces the effect of decreasing pH can be described by the curves in fig. 10 (a), (b).

(a)   (b)

(c)   (d)
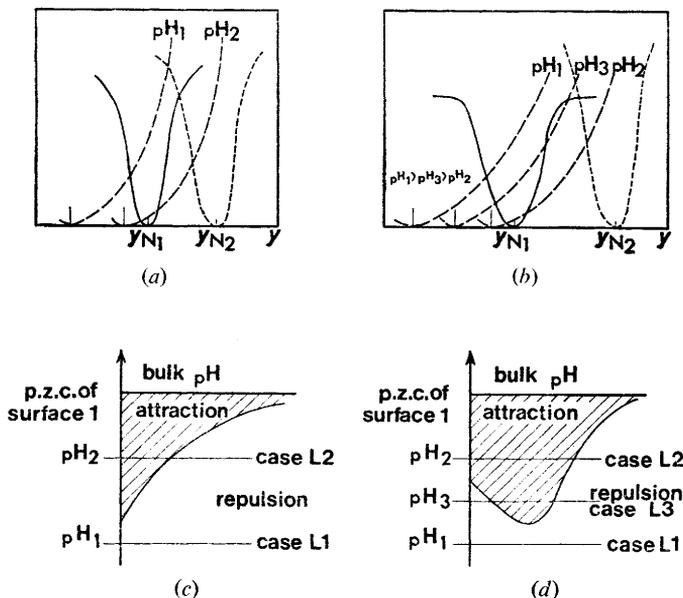
FIG. 10.—Showing the effects of bulk pH on determining the case which interaction should take place for two arrangements of the charge curves (surface 1—solid curve, surface 2—dotted curve). The effects of changes in pH is indicated as a relative displacement of the curve $\sinh^2(y/2)$ (dashed curves) with respect to the two charge curves. (See text).

In fig. 10 (a), y_{N_1} and y_{N_2} are close together. As pH increases we pass from case L1 (pH$_1$) to case L2 (pH$_2$). However, when y_{N_1} and y_{N_2} are sufficiently far apart, fig. 10 (b), we pass from case L1 (pH$_1$) to case L3 (pH$_3$) to case L2 (pH$_2$) as pH increases. Clearly we can only consider pH values smaller than the pzc of surface 1 (the surface with the lower pzc) otherwise we would not have like positive surfaces! Thus on a plot of pH against separation, we can construct regions where the interaction is attractive or repulsive. In fig. 10 (c), (d) we have constructed such diagrams corresponding to the situation in fig. 10 (a), (b). The lines delineating the attractive and repulsive regions can be obtained from eqn (5.10) for various pH values. Notice that when we are at the pzc of surface 1, the interaction is always attractive.

We have developed a method whereby we can analyse the main features of the force curve due to double layer interaction between two dissimilar amphoteric surfaces under dissociation equilibrium. The resultant free energy of interaction must of necessity be the lowest possible, since equilibrium is assumed to be maintained throughout the approach of the particles. Depending on the characteristics of each surface, it is possible to obtain force barriers and minima in the repulsive pressure from just the electrostatics alone. When combined with the contributions from van der Waals interactions (which in itself may be repulsive and/or attractive) to form the

total force curve needed in DVLO theory of colloid stability, very interesting interplay between these two contributions may be observed.

We have only used the Gouy–Chapman model for the double layer so we do not expect the present theory to be a good description of real systems. Several successful models have been proposed to describe the inner region of the double layer at amphoteric surfaces.[29-31] These models also use the concepts of surface dissociation giving rise to the surface charge. In addition, new effects such as the binding of inert ions or the existence of a gel layer have been included. These new features are in themselves charge and potential regulating. Thus by using the Gouy–Chapman model, we have embraced all the basic physical principles behind regulated interaction. The main features predicted here are essentially correct.

When the collision time is too fast for the surfaces to regulate, the constant charge approximation then becomes valid. Here the charge curves are horizontal (constant charge for all potentials). At constant charge, we expect the interaction between surfaces with

(i) like charges to be always repulsive

(ii) unlike charges to be attractive at large separations and repulsive at small separations—*except* when the surfaces have equal and opposite charges where the interaction is then always attractive.

The pressure will always diverge at small separations except for the "*equal and opposite situation*" where it remains finite.

When the regulation of potential is perfect, *i.e.*, constant potential, the charge curve is essentially an infinitely narrow "V" centred at the Nernst potential. There are no saturation plateaux when the potential is far from the Nernst value. Under constant potential interaction, surfaces (at infinity) with

(i) unlike potentials will always attract

(ii) like (but not identical) potentials will repel at large separations and attract at small separations. Identical surfaces however will always repel.

Of the various cases given for interaction between like and unlike surfaces under regulation, case L3 for like surfaces and cases U3 and U4 for unlike surfaces [fig. 6, 8 (c), (d)] cannot be predicted by the constant potential of constant charge approximation. If the equilibrium interaction is possible these cases may be observable.

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