NERNSTIAN AND NON-NERNSTIAN POTENTIAL DIFFERENCES AT AQUEOUS INTERFACES

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ABSTRACT

A simplified general formalism of the physics of the charge-potential interdependence of the electrical double layer at ionisable group surfaces is presented. The equilibrium total double layer potential is obtained graphically and analytically for surfaces with acidic and basic sites, with amphoteric sites and with single acid sites. The deviations from Nernstian behaviour are given as a function of the acid ionization constants of the surface groups.

INTRODUCTION

The potential difference $(\mathrm{d}E)$ across the Ag/AgI-electrolyte interface, and other reversible electrode systems, is given by

$$\mathrm{d}E = (kT/e) \, \mathrm{d} \ln a_{\mathrm{pdi}} \tag{1}$$

where a_{pdi} is the solution activity of potential determining ions (pdi), $(\mathrm{Ag}^+, \mathrm{I}^-$ for AgI). There are sound thermodynamic grounds and unequivocal experimental evidence that eqn. (1), the Nernst equation, is obeyed at reversible electrode-electrolyte interfaces where there is a thermodynamic connection between bulk solid and bulk electrolyte phases.

The potential difference $\mathrm{d}E$ is conventionally split into an outer potential due to ionic contributions and an independent dipole component, such that in eqn. (1),

$$\mathrm{d}\psi_0 = (kT/e) \, \mathrm{d} \ln a_{\mathrm{pdi}} \tag{2}$$

where ψ_0 is identified as the ionic contribution to the total double layer potential difference across the electrical double layer at the AgI-electrolyte interface.

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When the material is not an electrode but an isolated particle of an aqueous colloidal dispersion or when the material is an insulator such as SiO_2 or a clay particle, or when the solid part of the interface is a monolayer of ionic surfactants or a membrane with exposed ionizable groups, then the validity of the electrochemical approach to interface potentials is not certain. These non-electrode systems can be characterised experimentally as surfaces for which H^+ and OH^- are the usual pdi, and *by analogy* it is conventional to write that

$$d\psi_0 = (kT/e) \, d \ln a_{H^+}$$

or for ψ_0 in mV at $25°C$,

$$\psi_0 = 59.2(pH_0 - pH) \tag{3}$$

where pH_0 is the pH of the bulk solution corresponding to zero surface charge and/or the pH of zero zeta potential if indifferent ions only are present. If ψ_0 is defined exactly, as the potential of the plane at which the surface charge of the non-electrode system is located then there is no a priori thermodynamic or experimental reason [1—3] to expect that such non-electrode systems are Nernstian as defined by eqn. (3).

Alternatively, the surface charge of these non-electrode systems can be considered as arising from dissociation of chemically identifiable groups on the surface or from dissociation of surface complexes identified by analogy with bulk complexes. Levine and Smith [2], Smith [3] and Yates et al. [4] have now developed such surface ionization models of the oxide, latex, clay, membrane, etc., double layers and a quantitative basis for Nernstian or non-Nernstian behaviour is emerging.

The aim of the present paper is to present a simplified analysis of potentials and charges at ionizable group interfaces to show the effect of the ionization model chosen, and to give a graphical method of identifying the expected deviation from Nernstian behaviour of a given interface.

THEORY

(1) Amphoteric site model

Consider a surface bearing ionizable amphoteric surface groups in equilibirum with a 1 : 1 electrolyte which contains a specified concentration of potential determining ions. Each surface group can become positively or negatively charged by one of the following general surface dissociation reactions:

$$AH_2^+ \rightleftharpoons AH + H^+ \tag{1.1}$$

$$AH \rightleftharpoons A^- + H^+ \tag{1.2}$$
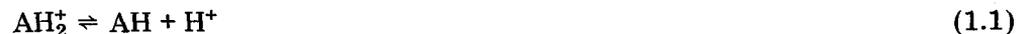
The inorganic oxides, SiO_2, TiO_2, Fe_2O_3, etc., appear to be well represented by such an amphoteric surface. Although H^+ are taken to be pdi, the following analysis is completely general and is valid for any other types of pdi. The ratios between the relative concentrations of positive (AH_2^+), negative (A^-) and neutral (AH) sites and the activity of hydrogen ions at the surface $(a_{H^+})_s$ are given by two effective surface dissociation constants

$$(AH) \cdot (a_{H^+})_s / (AH_2^+) = K_+ \tag{1.3}$$

$$(A^-) \cdot (a_{H^+})_s/(AH) = K_- \tag{1.4}$$

The validity of eqns. (1.3) and (1.4) has been discussed in detail elsewhere [2,6].

In the absence of site binding by "indifferent" ions the net surface charge and, in this case, the titratable surface charge, can be written as

$$\sigma_0 = eN_s([AH_2^+] - [A^-])/([AH] + [AH_2^+] + [A^-]) \tag{1.5}$$

where N_s is the number of surface groups per unit area of the surface. The activity of hydrogen ions at the surface, where the macroscopic electrostatic potential is ψ_0, is then related to the bulk activity H by

$$(a_{H^+})_s = H \exp(-e\psi_0/kT) \tag{1.6}$$

From eqns. (1.5) and (1.6) it follows that the net fractional charge is

$$\frac{\sigma_0}{eN_s} = \alpha_A = \frac{(H/K_+) \exp(-e\psi_0/kT) - (K_-/H) \exp(e\psi_0/kT)}{1 + (H/K_+) \exp(-e\psi_0/kT) + (K_-/H) \exp(e\psi_0/kT)} \tag{1.7}$$

Implicit in the use of eqn. (1.6) is the neglect of discreteness-of-charge effects for the pdi. Equation (1.7) is a relation between the (normalised) surface charge and the surface potential. This condition should now be used in place of the more usual "constant" potential (that given by the Nernst equation) boundary condition in determining the distribution of the diffuse layer in the electrolyte.

Equation (1.7) can be rewritten as

$$\frac{\sigma_0}{eN_s} = \alpha_A = \frac{\delta \sinh(y_N - y_0)}{1 + \delta \cosh(y_N - y_0)} \tag{1.8}$$

Here it is convenient to introduce the variables

$$y_0 = e\psi_0/kT \tag{1.9}$$

$$\Delta pK = pK_- - pK_+ \tag{1.10}$$

$$pH_0 = \tfrac{1}{2}(pK_+ + pK_-) \tag{1.11}$$

such that the constant δ is defined by

$$\delta = 2 \times 10^{-\Delta pK/2} \tag{1.12}$$

The potential ψ_N (in mV at 25°C) is

$$\psi_N = (kT/e)y_N = (kT/e) \, 2.303(pH_0 - pH) = 59.6 \, \Delta pH \tag{1.13}$$

and will hereafter be called the "Nernst potential". In the absence of specific binding of indifferent ions, pH_0 will correspond to the bulk concentration of pdi at the point-of-zero-charge (p.z.c.).

To assess the effect of the choice of the surface dissociation model on the deviations from Nernstian behaviour, it is necessary to introduce a model of the diffuse double layer. In general the choice of model will affect the magnitude of the deviations but not the basic characteristics, as will be discussed later. For simplicity we have chosen the Gouy-Chapman model *. Thus if the total double

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* However, it can be shown [6] that this model does give a reasonable fit to the charge-potential relationships for many oxides and polymer latices in simple electrolyte solutions.

TABLE 1

Ranges of values of δ, the ΔpK parameter of the present formalism and $\tilde{\theta}_0$ of Levine and Smith [2]

ΔpK	δ	$\tilde{\theta}_0$
−4	2×10^2	4.98×10^{-1}
−2	2×10^1	4.76×10^{-1}
0	2	3.33×10^{-1}
2	2×10^{-1}	8.33×10^{-2}
4	2×10^{-2}	9.80×10^{-3}
6	2×10^{-3}	1.00×10^{-3}
8	2×10^{-4}	1.00×10^{-4}

layer potential is ψ_0 $(= (kT/e)y_0)$ then according to the Gouy-Chapman theory, this would give rise to a diffuse double layer charge

$$\sigma_d = -(2\epsilon\, 10^{-3} N_0 ckT/\pi)^{1/2} \sinh y_0/2 \qquad (1.14)$$

Here c is the bulk electrolyte concentration in mol dm^{-3}, N_0 is Avogadro's number and ϵ is the dielectric constant of the solvent. The condition of electrical neutrality,

$$\sigma_0 + \sigma_d = 0 \qquad (1.15)$$

yields a self-consistent value for the double layer potential ψ_0. From eqns. (1.8) and (1.14) this gives

$$\sinh(y_0/2) = \gamma\delta\, \sinh(y_N - y_0)/[1 + \delta\, \cosh(y_N - y_0)] \qquad (1.16)$$

where the dimensionless constant γ is given by

$$\gamma = 10^3 \kappa N_s/4N_0 c \qquad (1.17)$$

with κ as the usual Debye screening parameter.

In the next section the solution of eqn. (1.16) for the surface potential y_0 $(= e\psi_0/kT)$ will be considered in detail. However, before proceeding it is instructive to test typical values of the constants δ and γ and the quantity $\tilde{\theta}_0$ used by Levine and Smith [2] and defined by them as the fraction of positive or

TABLE 2

Typical range of values of the electrolyte concentration — maximum surface site density parameter γ

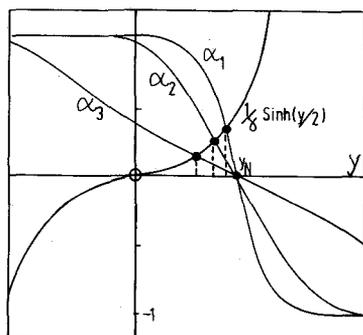| c/mol dm^{-3} \ N_s/sites cm^{-2}	5×10^{14} (20 Å^2/site)	5×10^{13} (200 Å^2/site)	5×10^{12} (2000 Å^2/site)
10^{-5}	2000	200	20
10^{-3}	200	20	2.0
10^{-1}	20	2	0.2

Fig. 1. Variation of the charge parameter (α_A) and the potential parameter ($\gamma^{-1} \sinh(y/2)$) with reduced potential (y) for amphoretic surfaces of different ΔpK; $\Delta pK_3 > \Delta pK_2 > \Delta pK_1$. All K's correspond to α_3, α_2 and α_1, respectively. All other variables are fixed.

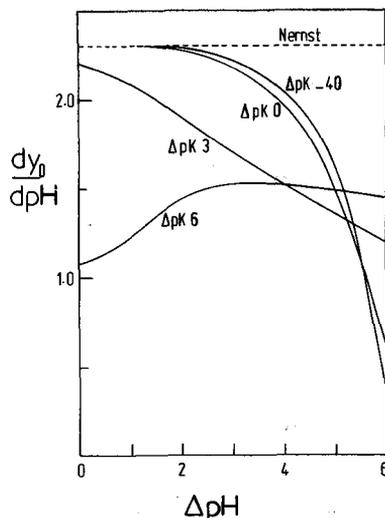Fig. 2. Variation of the potential gradient parameter with ΔpH for various ΔpK values at 10^{-3} M supporting electrolyte.

negative sites at the p.z.c., i.e.,

$$\tilde{\theta}_0 = \tfrac{1}{2}\delta/(1 + \delta) \tag{1.18}$$

A simple graphical method is available for locating the potential of the interface. Thus if α_A, defined by eqn. (1.8) and $(1/\gamma) \sinh(y_0/2)$ are both plotted as functions of y_0, then from eqn. (1.16) the point of intersection yields the equilibrium value of the total double layer potential for the surface. This is shown in Fig. 1 for various values of δ (i.e., ΔpK). It is immediately apparent that for pH $<$ pH$_0$, the surface potential y_0 *always* falls between zero and the Nernst potential y_N. A similar consideration will show that for pH $>$ pH$_0$, $y_N < y_0 < 0$. Secondly, the equilibrium value of y_0 is displaced further and further from the Nernst value y_N as pK is increased.

The effect of the double layer model also may be demonstrated on such a graph. Any model predicting a lower fractional surface charge at a particular potential will have a lower intersection with the ionization α—y curve. Hence the deviation from the Nernst potential will be lower. Correspondingly, a double layer model giving higher fractional charges than the Gouy-Chapman theory will produce larger deviations from the Nernst potential.

For further comparison of how an amphoteric surface with surface dissociation equilibrium differs from a Nernstian surface, it is instructive to examine the quantities y_0 and dy_0/dpH, (i.e., $d\psi_0/dpH$) as a function of pH. Differentiation of eqn. (1.16) yields

$$\frac{\partial y_0}{\partial pH} = \left(\frac{\partial y_N}{\partial pH}\right)\left(\frac{2\gamma\delta}{\cosh(y_0/2) + \delta[2\gamma + \cosh(y_0/2)\cosh(y_N - y_0)]}\right) \tag{1.19}$$

Near the p.z.c., i.e., $\Delta pH \ll 1$ or $y_0 < y_N < 1$,

$$\frac{\partial y_0}{\partial pH} \simeq \frac{\partial y_N}{\partial pH} \left(1 + \frac{1+\delta}{2\gamma\delta}\right)^{-1} \qquad (1.20)$$

since both $\cosh(y_N - y_0)$ and $\cosh(y_0/2)$ approach unity.

From eqn. (1.19) it is clear that near the p.z.c. of an amphoteric surface, Nernstian behaviour is observed if

$$(1 + \delta)/2\gamma\delta \ll 1$$

i.e., if

$$\tilde{\theta}_0 \gg \tfrac{1}{4}$$

or if $\Delta pK < 2 \log_{10}[2(2\gamma + 1)]$ \qquad (1.21)

On the other hand, at pH values far from the p.z.c. deviations from Nernstian behaviour are always significant.

The results described above are summarized in Figs. 2 and 3. In Fig. 2 dy/dpH is given as a function of ΔpH and in Fig. 3, y_0 (for $\Delta pH = 3$) is given as a function of ionic strength. It is interesting to note that at $\Delta pK = 6$, there is indeed quite a region where the function dy_0/dpH is constant over a fairly large range of pH and ionic strength, and further the constant of circa 39.7 compared to 59.2 agrees very well with the constant non-Nernstian factor used by Hunter and Wright [1] and others [5] for analysis of experimental zeta potentials for the SiO_2-electrolyte interface. The marked deviation of the surface potential from Nernstian behaviour as the ionic strength is increased *and* as ΔpK is increased is also shown in Fig. 3.
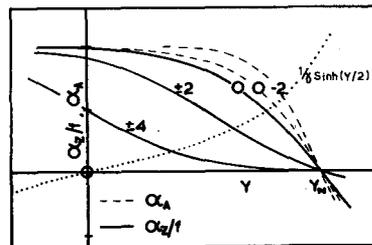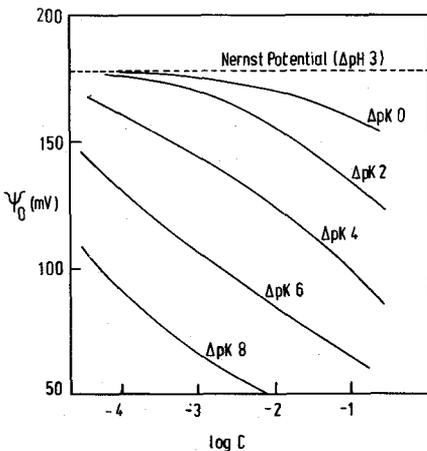

Fig. 3. Variation of surface potential (ψ_0) with ionic strength at fixed ΔpH of 3 for various ΔpK values.

Fig. 4. Variation of the charge parameter (α_z/f) with reduced potential (y) for zwitterionic surfaces of different ΔpK. Some analogous curves of α_A as a function of y for amphoteric surfaces are included for comparison. For $\Delta pK = 4$ and 2, the α_A—y curves are identical with α_z/f—y curves for $\Delta pK = \pm4$ and ±2 and have been omitted for clarity. The curves are for $f = 1/2$ and $\Delta pH = 2$.

(2) Zwitterionic surface model

The second surface we shall consider is one with two types of groups in equilibrium with electrolyte and pdi. One type can easily ionize to become negative and the other to become positive. The surface equilibria are represented by acid dissociations (i.e., H^+, OH^- are pdi), as

$$AH \rightleftharpoons A^- + H^+ \tag{2.1}$$

$$BH^+ \rightleftharpoons B + H^+ \tag{2.2}$$

This zwitterionic surface model will be shown to exhibit large deviations from the Nernst equation. It is the appropriate model for biological surfaces with amine and carboxyl groups and also is probably applicable to inorganic oxides where more than one type of surface hydroxyl groups has been identified [7].

The surface equilibria are controlled by two effective surface dissociation constants

$$K_- = (H^-)(a_{H^+})_s/(AH) \tag{2.3}$$

$$K_+ = (B)(a_{H^+})_s/(BH^+) \tag{2.4}$$

Following an analogous derivation to the one detailed in section 1, the surface charge is given by

$$\sigma_0 = e \frac{[N_B(H/K_+)\,e^{-y_0} + N_B(K_-/K_+) - N_A(K_-/H)\,e^{y_0} - N_A(K_-/K_+)]}{1 + (H/K_+)\,e^{-y_0} + (K_-/H)\,e^{y_0} + K_-/K_+} \tag{2.5}$$

where N_A and N_B are the number of acidic and basic surface groups per unit area of the surface. Alternatively the net fractional charge is

$$\alpha_z = \frac{\sigma_0}{eN_s} = \frac{f(H/K_+)\,e^{-y_0} + (2f-1)K_-/K_+ - (1-f)(K_-/H)\,e^{y_0}}{1 + K_-/K_+ + (H/K_+)\,e^{-y_0} + (K_-/H)\,e^{y_0}} \tag{2.6}$$

where N_s is the total number of ionizable groups per unit area and f is the fraction which is basic, i.e.,

$$N_s = N_A + N_B$$
$$f = N_B/N_s \tag{2.7}$$

Equation (2.6) is comparable to (1.7), the analogous equation for the amphoteric site model. Firstly, it should be noted that α_z is not quite equivalent to the α_A in eqn. (1.7) because in the zwitterionic model the maximum charge corresponds to complete ionization of only one type of group rather than all of the groups. In general, α_z ranges from f to $-(1-f)$ compared with α_A, which has limits of ± 1. To remove this difference from the comparison of α_z and α_A, it is best to compare α_A with α_z/f (or $\alpha_z/(1-f)$ for negative surfaces). This is equivalent to using σ_0/maximum σ_0, which is the usual form of experimental values. In Fig. 4, α_z/f calculated from eqn. (2.6) is shown as a function of y_0 for various ΔpK values and compared with some corresponding curves for α_A. The curves have the same general form, and in fact are identical for large positive values of ΔpK, but they become very different as ΔpK goes to negative values.

Since the point of intersection with the $\gamma^{-1} \sinh(y_0/2)$ curve gives the equilibrium value of the reduced surface potential y_0 (as discussed in section 1), it can be seen that the zwitterionic model gives large deviations from the Nernst potential for negative ΔpK values. This contrasts with the amphoteric model which yields its smallest deviations for negative ΔpK. This difference between the two surface models is shown more clearly in Fig. 5, where the deviations from the Nernst potential are compared as a function of ΔpK.

In Fig. 6, the surface charge and potential are shown as a function of pH — pH_0 ($pH_0 = \frac{1}{2}(pK_+ + pK_-)$) for the amphoteric and zwitterionic cases. This type of plot is useful for comparison with experimental determinations of surface charge and potential as functions of pH [5].

The effects of varying the electrolyte concentration and ΔpH on the zwitterionic surface potential are similar to those discussed above for amphoteric surfaces. This is because these effects arise in the double layer model and *not* in the surface ionization model.

(3) Single site model

The final surface we shall consider is one with only one type of ionizable group, again in equilibrium with electrolyte and pdi. If this group is of the acid type, i.e., H^+, OH^- are pdi, then the surface equilibrium is represented by

$$AH \rightleftharpoons A^- + H^+ \tag{3.1}$$

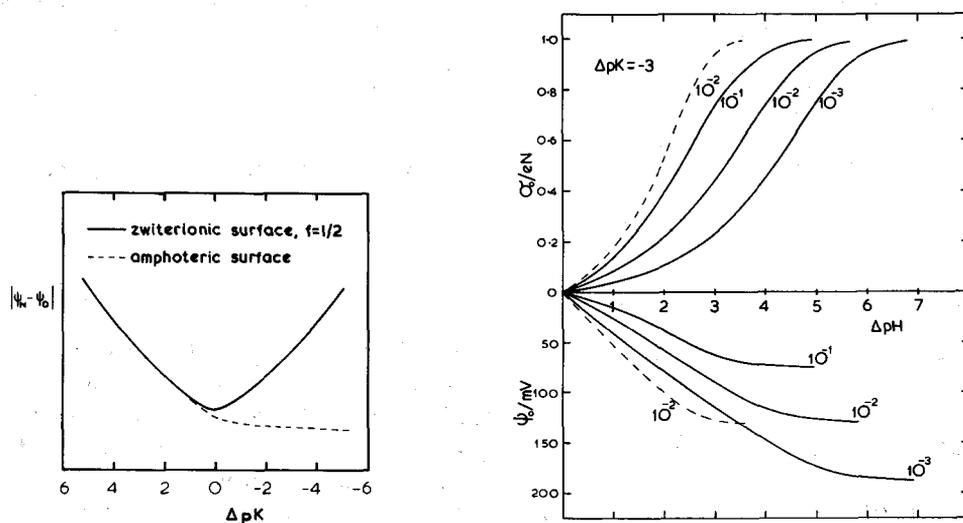Polymer latices with surface charges due to ionization of carboxyl or sulphate

Fig. 5. Variation of the deviation of the surface potential from the Nernst potential with ΔpK for the amphoteric and zwitterionic surface models.

Fig. 6. Variation of surface charge and potential with pH — pH_0 for (———) zwitterionic surface and (------) amphoteric surface. Supporting electrolyte (1 : 1) concentrations are indicated in mol dm^{-3}, $\Delta pK = -3$, for the zwitterionic case $N_A = N_B = 5 \times 10^{13}$ cm^{-2} and for the amphoteric case $N_S = 5 \times 10^{13}$ cm^{-2}.
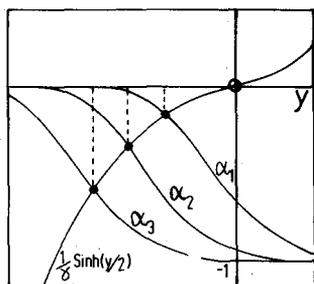
Fig. 7. Variation of the charge parameter (α) and the potential parameter ($\gamma^{-1} \sinh(y/2)$) with reduced potential (y) for monoprotic acid surfaces of different pK_a values such that $pK_{a1} > pK_{a2} > pK_{a3}$ corresponding to α_1, α_2 and α_3, respectively.
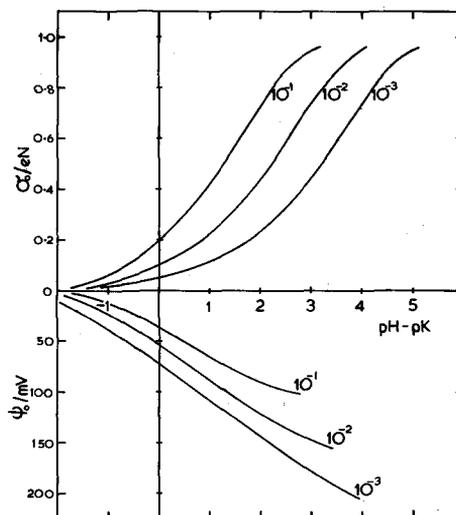
Fig. 8. Variation of surface charge and potential with pH $-$ pK for a single site surface as a function of 1 : 1 supporting electrolyte concentration indicated in mol dm^{-3}. $N_S = 1 \times 10^{14}$ cm^{-2}.

groups are good examples of this type of surface *.

Following the same method of derivation used for the previous surfaces, the net fractional charge is

$$\frac{\sigma_0}{eN_s} = \alpha_1 = \frac{-(K/H)\, e^{y_0}}{1 + (K/H)\, e^{y_0}} \tag{3.2}$$

This equation is the limiting case of eqns. (1.7) and (2.6) obtained when K_+ goes to infinity and f to zero.

Since such single site surfaces do not have a p.z.c., it is not possible to select a y_N value. However, in a formally identical manner as for the previous models, we can select a bulk pH and a pK_a for the surface group and again the intersection of the α curve with the $\gamma^{-1} \sinh(y_0/2)$ curve yields the equilibrium y_0 value for the surface at that pH. Such a construction is shown in Fig. 7 for three surfaces with groups of pK 0, 2 and 4 and $y_0(0) > y_0(2) > y_0(4)$, as expected. A typical example of the results of such constructions is shown in Fig. 8, where the surface charge and potential are given as a function of pH $-$ pK. Experimental surface charge against pH curves similar to these have been obtained recently for latices with surface carboxyl groups [8].

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* Surfaces with both sulphate and carboxylate are considered elsewhere [6].

University of Melbourne and was completed in the School of Chemistry, University of Bristol while one of us (T.W.H.) was an SRC Visiting Fellow.

REFERENCES

1 R.J. Hunter and H.J.L. Wright, J. Colloid Interface Sci., 37 (1971) 564.
2 S. Levine and A.L. Smith, Discuss. Faraday Soc., 52 (1971) 290.
3 A.L. Smith in G.D. Parfitt (Ed.), Dispersions of Powders in Liquids, Applied Science Publishers, 2nd edn., 1973, pp. 86—131.
4 D.E. Yates, S. Levine and T.W. Healy, J. Chem. Soc., Faraday Trans. I, 70 (1974) 1807.
5 G.R. Wiese, R.O. James, D.E. Yates and T.W. Healy, Electrochemistry, MTP Publications, 1975.
6 T.W. Healy and L.R. White, Advan. Colloid Interface Sci., in preparation.
7 For example: P. Jones and J.A. Hockey, Trans. Faraday Soc., 67 (1971) 2669; H.P. Boehm, Discuss. Faraday Soc., 52 (1971) 264.
8 D.E. Yates, NATO Advanced Study Institute, Polymer Colloids, University of Trondheim, 1975.