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Some Applications of a Useful Theorem in Double Layer Theory*

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The mechanisms whereby a solid-solution interface acquires a charge are outlined and the Grahame Model of the double layer, frequently used to interpret such phenomena is critically reviewed. An alternative thermodynamic approach based on a recently derived theorem is forwarded. This approach utilises the concept of an outer Stern plane but does not require any other electrostatic concepts inherent in the Grahame model (including the wall potential ψ_0). The thermodynamic approach leads to simple tests for the specific adsorption of non-potential determining species and provides a general method for estimating the amounts adsorbed of more than one species from electrokinetic data alone. It also leads to a general method for estimating, the electro-chemical contribution to the interaction between like or unlike plates given that appropriate experimental data for the two isolated interfaces is available. For surfaces fairly close to their isoelectric point where amounts adsorbed are small expressions for the chemical potentials of adsorbed species in terms of amounts adsorbed are obtained from consideration of the expected behaviour of the surface pressure π. These expresions are very similar in form to the corresponding expressions used with the Grahame model but are arguably more soundly based. When used to interpret electrokinetic studies of surfactant adsorption on solids they give excellent agreement with experiment.

1. INTRODUCTION

The occurrence of electrical double layers at the solid solution interface is a widespread phenomenon of considerable scientific interest and technical importance. Several mechanisms for this phenomenon may be distinguished; for instance —

a) For some crystals such as $BaSO_4$ Ba^{++} and SO_4^{--} ions may dissolve unequally.

b) Ionisable groups on the surface such as CO_2H and NH_2 may loose or gain H^+ ions. Many oxides probably acquire their charge in this way as do materials such as cotton, nylon and latex particles.

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c) Ions from solution, especially surfactant ions, but also in some cases non potential determining ions may adsorb.

The charges and potentials that result from these mechanisms are strongly dependent on the concentrations of potential determining species in solution (Ba^{++} and SO_4^{--} for mechanism a, H^+ or OH^- for mechanism b). They are also influenced by the concentration of supporting electrolyte, the adsorption of other ions and the adsorption of uncharged species such as nonionic surfactants. It is usual to assume that the potentials at the solid surface which arise via mechanism a are governed by the Nernst equation. However, this is generally not the case for mechanisms b and c.

Of the methods used to study these phenomena two of the most important are potentiometric titration and electrokinetic studies. Potentiometric titration leads directly to changes in amounts of potential determining species adsorbed. Electrokinetic studies lead to estimates of the zeta potential, ζ, which is the potential relative to the bulk solution at the plane of shear. It is often assumed that this plane coincides with the boundary between the inner regions of the double layer and the diffuse region.

This paper is concerned particularly with the interpretation and use of electrokinetic data but potentiometric titration data are also considered where appropriate. We begin by reviewing critically the Grahame model of the double layer, which is the model traditionally used to interpret such data, and continue by outlining an alternative thermodynamic approach. The basis of this new approach is a recently derived theorem[1] which is stated but not proved. A number of applications of this theorem are outlined and illustrated by experimental data where appropriate.

2. THE GRAHAME OF THE DOUBLE LAYER

The conventional approach for interpreting potentiometric and electrokinetic data on solids, particularly the latter, is the Grahame model of the double layer[2]. The significance of the various quantities and concepts which form the basis of this model are shown in figure 1 and may be summarised as follows.

The double layer is divided into an inner region and a diffuse region by a plane referred to as the auter Stern plane (OSP). It is supposed that the Poisson-Boltzmann equation holds in the diffuse region but not in the inner region. The inner region is supposed to have an integral capacity K and is itself sub-divided into two regions by the so called inner Stern plane (ISP), which corresponds to the adsorption plane of specifically adsorbed ions from the supporting electrolyte. The integral capacitances of these two inner regions are denoted by K_1 and K_2 · ψ_o, ψ_β and ψ_d respectively refer to the electrical potentials relative to the bulk solution at the solid surface, the ISP and the OSP. σ_o refers to the charge per unit area at the solid surface, σ_β refers to the charge per unit area located at the ISP. σ_d refers to the total charge per unit area beyond the OSP. The plane of shear to which the zeta potential, ζ, refers may coincide with the OSP and it is often supposed that it does, however it will in general be displaced from the OSP by a distance Δ[3].

The quantities referred to above are related by the following equations which are obtained from electrostatic considerations and a first integration of the Poisson-Boltzmann equation.

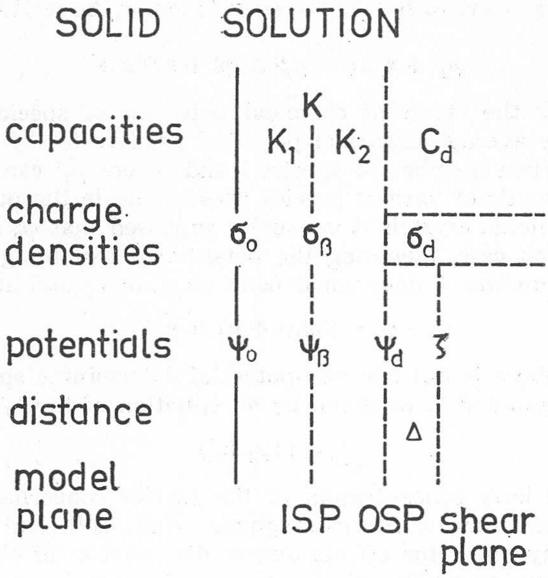

Figure 1. Double layer model.

$$\frac{1}{K} = \frac{1}{K_1} + \frac{1}{K_2} \qquad (1)$$

$$\sigma_o + \sigma_\beta + \sigma_d = 0 \qquad (2)$$

$$\psi_o - \psi_\beta = \frac{\sigma_o}{K_1} \qquad (3)$$

$$\psi_\beta - \psi_d = \frac{-\sigma_d}{K_2} \qquad (4)$$

$$(\sigma_d)^2 = \frac{\varepsilon\, kT}{2\,\pi} \sum_i n_i^b \left[\exp\left(-\nu_i\, e\, \psi_d/kT\right) - 1\right] \qquad (5)$$

where e is the charge of a proton, ε is the permittivity of the pure solvent, n_i^b is the bulk concentration of species i, ν_i is ionic valence including the sign and the summation extends over all ionic species in solution. When $\frac{\nu_i\, e\, \psi_d}{kT} \ll 1$ we note that

$$\zeta = \psi_d \exp\left(-\varkappa\, \Delta\right) \qquad (6)$$

where

$$\varkappa^2 = \frac{4\,\pi\, e^2}{\varepsilon\, kT} \sum_i n_i^b\, \nu_i^2 \qquad (7)$$

In order to apply the model, even when $\Delta = 0$, additional expressions relating the potentials ψ_o and ψ_β to the bulk concentrations through the amounts adsorbed are required. These equations may be written in the general form —

$$\mu_i^\sigma + \nu_i e \psi = \mu_i^\ominus (T, p) + kT \ln n_i^b \tag{8}$$

Where $\mu_i^\ominus$ is the standard chemical potential of species i in the bulk solution, ψ is the average electrical potential relative to the bulk solution as seen by an adsorbed member of species i and where μ_i^σ can be expressed in terms of the amounts of various species present inside the outer Stern plane. For example, for ionic crystals it is usually supposed that ψ_o obeys the Nernst equation. In which case, (denoting the potential determining species by subscript 1) μ_1^o in equation 8 does not depend on σ_o or σ_β and at constant T & p

$$\psi_o = \text{Const} + kT \ln n_i^b \tag{9}$$

Also, when there is but one non-potential determining species specifically adsorbed, σ_β is supposed to be given by an equation of the type

$$\sigma_\beta = f(\psi_\beta, n_2^b) \tag{10}$$

where n_2^b is the bulk concentration of the species concerned and f is some function obtained from a Stern-Langmuir type isotherm[4] or some other theory which may allow for effects due to discreteness of charge[5].

Of the various quantities K, K_1, K_2, ψ_o, ψ_β, ψ_d, σ_o, σ_β and σ_d we have above at most only seven equations relating them. Two of the quantities, ψ_d and σ_o, may be estimated from electrokinetic and potentiometric titration experiments. Even so it is clear that the use of the Grahame model to characterise a solid solution interface is hardly a simple procedure. There are also two other difficulties.

1) It is usual to suppose that K_1 and K_2 are independent of σ_o and σ_β. To what extent this assumption can be expected to hold in practice is unclear.

2) The form of equation 8 adopted for the potential determining species is dictated by the mechanism whereby the double layer is supposed to form. For ionic crystals it is assumed in effect that μ_i^σ is independent of the amount adsorbed. For surfaces with dissociable groups it has been *assumed*[3,6] that μ_1^σ can be described by an equation of the kind that applies to the adsorption of an uncharged species, such as a Langmuir isotherm. Although such an assumption may appear reasonable and may lead to a useful description of experimental data we suggest that the theoretical basis of equation 8 is far from secure. The only situation we are aware of in which such an assumption has been justified by theory is the hypothetical case of a partially ionised monolayer of eg a carboxylic acid, for which the Poisson Boltzmann equation is valid right up to the plane at which the primary charge is located[7]. Even in this case it is assumed in effect that this primary charge, σ_o ,is non-discrete. For the more complex situations to which the Grahame model is applied no rigorous justification of equation 8 has been given as far as we know.

It appears then that the Grahame model has two major drawbacks. It is cumbersome to apply in some situations and it involves assumptions whose theoretical status is not secure.

The alternative approach to be described also utilises the concept of an outer Stern plane with its associated potential ψ_d and assumes that ψ_d is related to σ_d by the Poisson-Boltzmann equation. However, it does not require any other electrostatic concepts inherent in the Grahame model, including ψ_o.

Nor does it involve any prior knowledge of the mechanism whereby a surface acquires its charge. This approach is based on a recently derived theorem[1] which we will now state but not prove.

3. STATEMENT OF THE THEOREM

We consider a solid surface in contact with an electrolyte solution and suppose that there is a surface S beyond which the ion distribution is described by the Poisson-Boltzmann equation.

The theorem states that dL given by

$$\mathrm{d}L = \sum_{\mathrm{i}} \Gamma_{\mathrm{i}}\, \mathrm{d}\mu_{\mathrm{i}} \tag{11}$$

is an exact differential where

1) The summation extends over all independent solute species (ionic or nonionic) found on both sides of S.

2) $$\Gamma_{\mathrm{i}} = \Gamma_{\mathrm{i}}{}^* - \frac{n_{\mathrm{i}}{}^{\mathrm{b}}}{n_{\mathrm{o}}{}^{\mathrm{b}}}\, \Gamma_{\mathrm{o}}{}^* \tag{12}$$

where $\Gamma_{\mathrm{i}}{}^*$ is the total amount of i found on the solid side of S minus what would be there if the bulk solid was uniform right up to S, $\Gamma_{\mathrm{o}}{}^*$ is the corresponding quantity for solvent (species o) and $n_{\mathrm{o}}{}^{\mathrm{b}}$ is the bulk number density of solvent.

3) $$\mu_{\mathrm{i}} = \mu_{\mathrm{i}}{}^{\mathrm{b}} - \nu_{\mathrm{i}}\, e\, \psi_{\mathrm{d}} \tag{13}$$

where $\mu_{\mathrm{i}}{}^{\mathrm{b}}$ is the chemical potential of i in the bulk solution and ψ_{d} is the electrical potential relative to the bulk solution at the surface S. For ionic species the $\mu_{\mathrm{i}}{}^{\mathrm{b}}$ are assumed to be given by —

$$\mu_{\mathrm{i}}{}^{\mathrm{b}} = \mu_{\mathrm{i}}{}^{\ominus}(T, p) + kT \ln n_{\mathrm{i}}{}^{\mathrm{b}} \tag{14}$$

Sometimes there may be a choice available as to which species in the system may be regarded as independent (eg. H^+, COO^- and COOH are not all independent). Whenever possible this choice is made in such a way that —

$$\sum_{\mathrm{i}} \Gamma_{\mathrm{i}}\, \nu_{\mathrm{i}}\, e = -\sigma_{\mathrm{d}} \tag{15}$$

where σ_{d} is the total charge per unit area found on the solution side of S.

Although there is in principle no restriction on the position of the surface S, provided that the Poisson-Boltzmann equation holds beyond it, in practice it makes sense to suppose that it is as close to the solid surface as this restriction permits (i. e. to identify S with ithe Outer Stern Plane). One reason for this is that when applying the theorem it is convenient and sometimes necessary to suppose that at least one ionic species in the bulk solution, usually an indifferent co-ion, is effectively absent from the solid side of S. Under these circumstances all the μ_{i} in equation 11 may be varied independently at equilibrium. Such a supposition is often reasonable, for if a species is effectively absent from the inner regions of the double layer at the zero point of charge or the isoelectric point, it is hardly likely to be found in significant amounts when the charge on the surface is such as to repel it. It is also convenient to assume that ζ can be identified with ψ_{d}.

A proof of the above theorem is given in ref. (1). We now proceed to applications.

4. TESTS FOR THE SPECIFIC ADSORPTION OF SUPPORTING ELECTROLYTE IONS

In this section we consider the situation in which there is but one potential determining species (species 1) and in which the region between the solid surface and the outer Stern plane is effectively devoid of counterions and co-ions.

In this case equation (11) becomes

$$\mathrm{d}L = \Gamma_1 \, \mathrm{d}\mu_1 \tag{16}$$

from which it is clear that $\mu_1 = \mu_1 (\Gamma_1)$ and vice-versa. Since in this case —

$$\sigma_\mathrm{d} = \nu_1 e \Gamma_1 \tag{17}$$

and

$$\mu_1 = \mu_1^\ominus (T, p) + kT \ln n_1^\mathrm{b} - \nu_1 e \psi_\mathrm{d} \tag{18}$$

It follows that —

1) at constant σ_d, ψ_d vs $kT \ln n_1^\mathrm{b}/\nu_1 e$ should be linear with unit slope,

2) graphs of σ_d vs $[kT \ln n_1^\mathrm{b} - \nu_1 e \psi_\mathrm{d}]$ for different ionic strengths should superimpose.

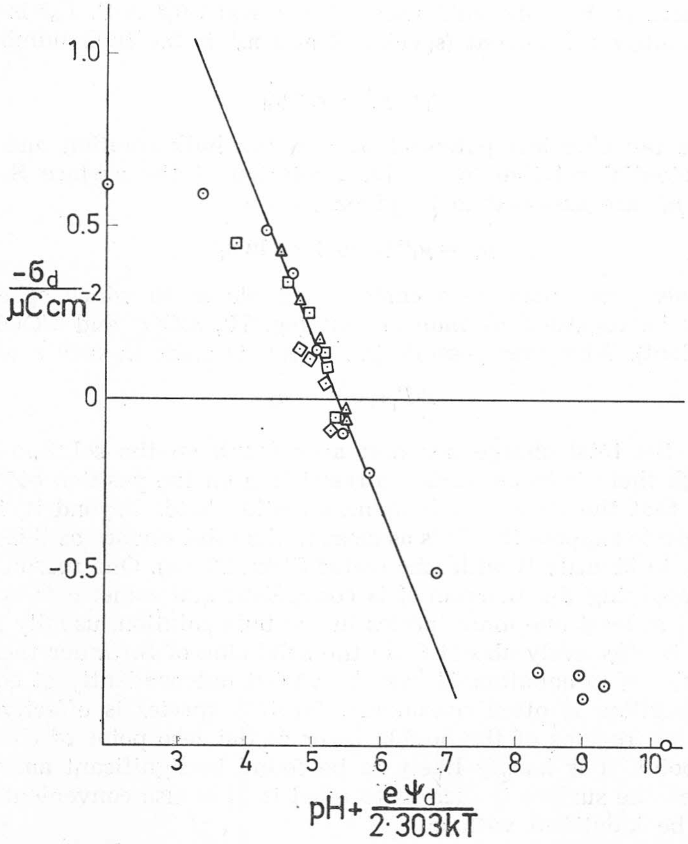

Figure 2. »Congruence plot« for nylon sol, — σ_d vs $[\mathrm{pH} + e\,\psi_\mathrm{d}/2.303\;kT]$ at various ionic strengths ○ = 10^{-3} mpl, △ = 10^{-2} mpl, □ = 5×10^{-2} mpl, diamond = 10^{-1} mpl

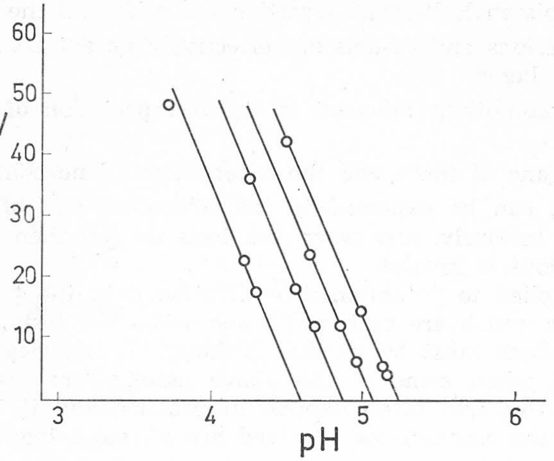

Figure 3. »Nernst plot« for nylon sol, ζ (mv) vs pH at constant σ_d, from L — R, σ_d = 0.4, 0.3, 0.2, 0.1 μC/cm² respectively.

These two tests, which we refer to as a »Nernst plot« and a »congruence plot« respectively, can be applied to either potentiometric titration data or to electrokinetic data respectively. When applied to the latter they will hold provided that the following assumptions are all valid:

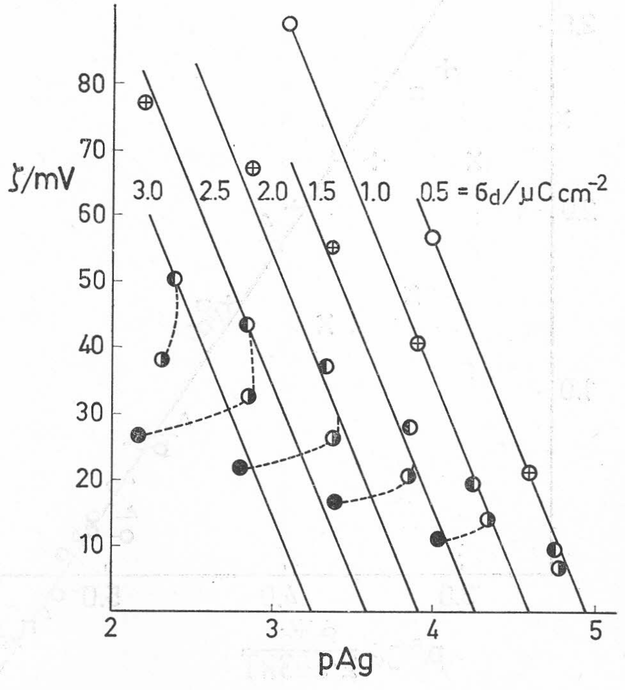

Figure 4. »Nernst plot« for AgI Sol, ζ mv vs pAg at const σ_d, from L — R, σ_d = 3.0, 2.5, 2.0, 1.5, 0.5 μC/cm² respectively. Ionic strengths ○ = 10^{-3}, circle with cross = 10^{-2}, lhs filled circle = = 5×10^{-2}, rhs filled circle = 10^{-1} ● = 1.5×10^{-1} mpl respectively.

a) The Poisson Boltzmann equation holds beyond the Outer Stern Plane.

b) Counterions and co-ions are effectively absent from the inner regions of the double layer.

c) The assumptions inherent in the interpretation of electrokinetic data are all valid.

d) The plane of shear and the outer Stern plane coincide.

The tests can be expected to fail whenever any of these assumptions breaks down seriously, and when the tests do fail then at least one of the four ossumptions is invalid.

When applied to potentiometric titration data the tests will hold when assumptions a and b are both valid, and when the tests do not hold one of these assumptions must be invalid. Although it is logically possible for the tests to hold when some of the above assumptions are invalid, it seems unikely that this will often happen in practice and it is probably safe to suppose that the assumptions involved are all valid together when the tests do hold.

The application of these ideas to experimental data is illustrated in figures 2—6.

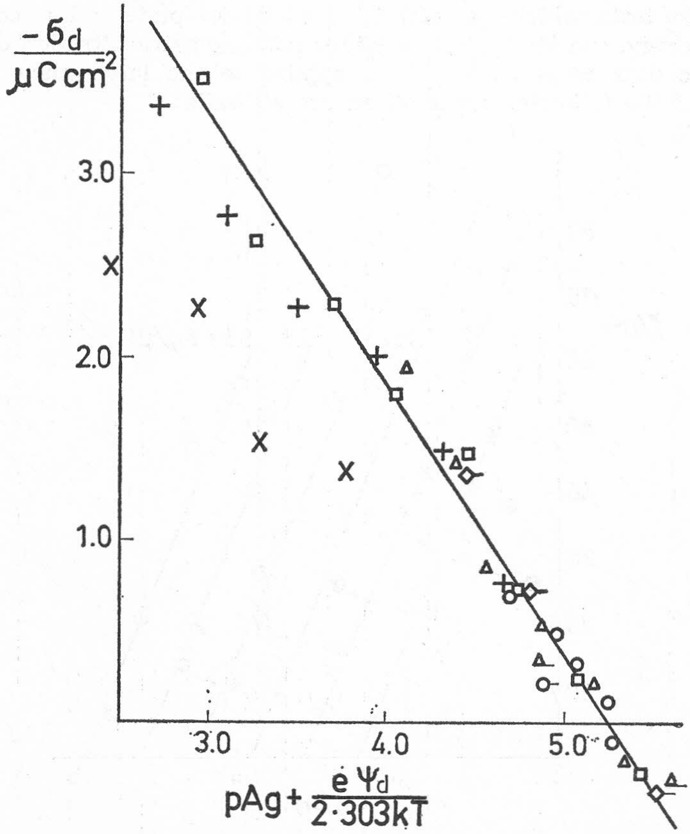

Figure 5. »Congruence plot« for AgI sol., $-\sigma_d$ vs $[pAg + e\,\psi_d/2.303\,kT]$ at various ionic strengths, ○ = 10^{-3}, △ = 10^{-3}, □ 5×10^{-3}, + = 10^{-1}, X = 1.5×10^{-1} diamond— = 10^{-1}, mpl respectively ○—, △—, diamond— denote titration data[10].

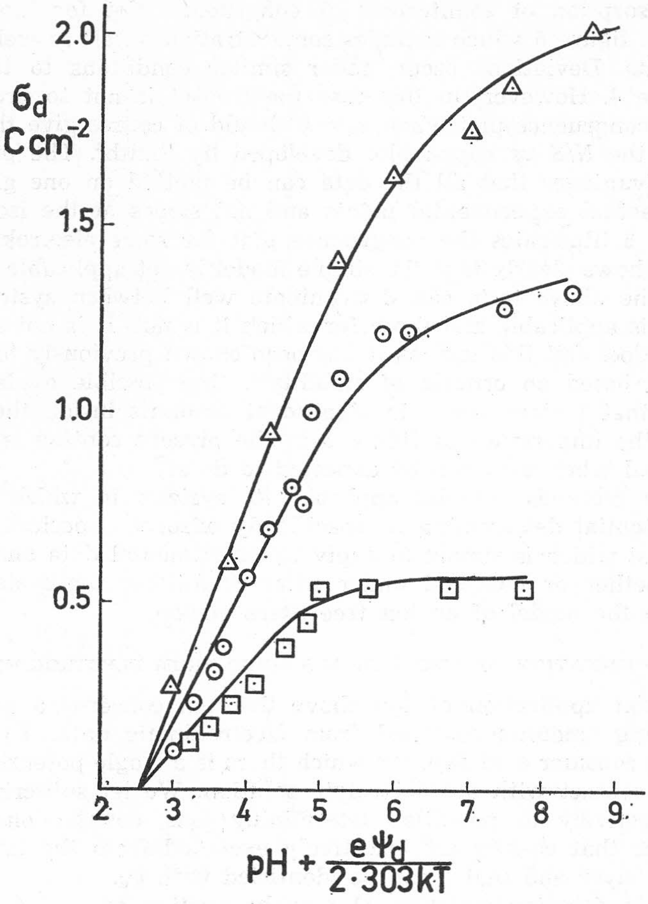

Figure 6. »Congruence plot« for silica, $-\sigma_d$ vs [pH + $e\,\psi_d/2.303\,kT$] at various strengths, □ = 10^{-4}, ○ = 10^{-3}, △ = 10^{-2} mlp respectively.

Figure 2 shows previously reported electrokinetic data for a Nylon Sol[6] plotted as — σ_d vs [(pH + $e\,\psi_d/2.303\,kT$] for several different ionic strengths. Since this surface acquires its charge through the ionisation of dissociable groups it is not obvious from an immediate inspection of the experimental data that the above model should or could be adequate. Figure 3 shows the Nernst Plot for the same system. Both graphs provide strong evidence that the simple model does indeed provide an adequate description of the system. Since the data was analysed successfully using this model before the above methods were devoloped it is not surprising that they work in this case. However, it is worth pointing out that had the two tests been applied to the data as originally obtained it would have become apparent far more quickly that the simple model applies.

Nernst plots for Silver Iodide obtained from electrokinetic data[9] are shown in figure 4. Deviations occur at ionic strengths greater than 10^{-1} mpl and for primary charges $> 1\ \mu$ C/cm². The deviations are consistent with the specific adsorption of counterions. A congruence plot for the same system is shown in figure 5 which includes some titration data[10] as well as electrokinetic results. Deviations occur under similar conditions to those apparent from figure 4. However, in this case their onset is not so pronounced. The slope of a congruence plot when $\sigma_d = 0$ should of course give the same information as the N/S vs kappa plot developed by Smith[3]. The present method has the advantages that all the data can be plotted on one graph and that one plots actual experimental points and not slopes at the isoelectric point.

Figure 6 illustrates the congruence plot for some electrokinetic data on silica[11]. It shows clearly that the simple model is not applicable to this system and that the above tests can discriminate well between systems for which the model is applicable and those for which it is not. It is not surprising that that silica does fail this test, as it has been shown previously to fail an alternative test based on criteria of stability[12]. One possible explanation of the failure is that co-ions occur in significant amounts inside the shear plane. However, the importance of figure 6 in the present context is that it shows the tests fail when they can be expected to do so.

Similar methods are also applicable to systems in which there may be several potential determining or specifically adsorbed species[8]. They provide a useful test which is simple to apply to experimental data and which shows clearly whether or not, and under what conditions, the systems concerned conform to the model of an ion free Stern region.

5. DETERMINATION OF AMOUNTS ADSORBED FROM ELECTROKINETIC DATA

The next application of the above theorem concerns a general method for obtaining amounts adsorbed from electrokinetic data. To illustrate the method we consider a surface for which there is a single potential determining species in contact with an electrolyte solution. We let subscripts 1, 2 and 3 refer respectively to potential determining ions, counter-ions and co-ions. We suppose that co-ions are effectively excluded from the inner regions of the double layer and that ζ can be identicied with ψ_d.

For this situation equation 11 may be written as —

$$\mathrm{d}\,L = \Gamma_1\,\mathrm{d}\,\mu_1 + \Gamma_2\,d\,\mu_2 \tag{19}$$

However since

$$\sigma_d = -\nu_1\,e\,\Gamma_1 - \nu_2\,e\,\Gamma_2 \tag{20}$$

we may re-write equation 19 as

$$\mathrm{d}\,L = \Gamma_1\,\mathrm{d}\,\Theta_1 - \frac{\sigma_d}{\nu_2\,e}\,\mathrm{d}\,\mu_2 \tag{21}$$

where

$$\Theta_1 = (\mu_1 - \frac{\nu_1}{\nu_2}\mu_2) \tag{22}$$

and is constant when the product $n_1\,(n_2)^{-\nu_1/\nu_2}$ is constant.
Let L_o denote the value of L for which $\sigma_d = 0$.

Evidently
$$\mathrm{d}\,L_o = \Gamma_{1o}\,\mathrm{d}\,\Theta_1 \tag{23}$$

So that
$$\mathrm{d}\,(L - L_o) = (\Gamma_1 - \Gamma_{1o})\,\mathrm{d}\,\Theta_1 - \frac{\sigma_d}{\nu_2\,e}\,\mathrm{d}\,\mu_2 \tag{24}$$

However, since changes in Θ_1, μ_2 and σ_d are all either obtainable from electrokinetic measurements or known, it follows that we may determine $L - L_o$ by evaluating the integral

$$L - L_o = -\int_{\sigma_d=0}^{\sigma_d} \frac{\sigma_d}{\nu_2 e} \, d\mu_2 \tag{25}$$

at constant Θ_1.

Since equation 24 shows that

$$\nu_1 e \frac{(\Gamma_1 - \Gamma_{1o})}{\sigma_d} = \left(\frac{d\mu_2}{d\Theta_1}\right)_{(L - L_o)} \tag{26}$$

and the RHS of this expression is measurable, it follows that we may obtain the LHS of equation 26 which in turn leads to $(\Gamma_1 - \Gamma_{10})$ and $\Gamma_2 - - \Gamma_{20})$. When the concentration of potential determining ions at the isoelectric point is independent of ionic strength it is probably reasonable to suppose that Γ_{10} and Γ_{20} are both zero, in which case we obtain the actual values of Γ_1 and Γ_2.

Alternatively we may proceed via the expression —

$$\Gamma_1 - \Gamma_{1o} = \frac{1}{\nu_2 e} \int_{\sigma_d=0}^{\sigma_d} \left(\frac{d\mu_2}{d\Theta_1}\right)_{\sigma_d} d\sigma_d \tag{27}$$

where again the integration is performed at constant Θ_1.

This method can readily be extended to more complex systems and will be equally valid provided it is reasonable to suppose that at least one ionic species in solution is not found in significant amounts on the solid side of the shear plane. It does not depend on any model for the inner regions of the double layer. By using it, it may be possible to estimate amounts adsorbed in some systems for which potentiometric experiments are not feasible. When both kinds of measurement are feasible it may be possible by comparing values of $(\Gamma_1 - \Gamma_{10})$ to establish the conditions under which electrokinetic studies provide a realistic estimate of ψ_d and in some cases to estimate the specific adsorption of co-ions.

6. A GENERAL METHOD FOR ESTIMATING THE ELECTROCHEMICAL CONTRIBUTION TO THE INTERACTION BETWEEN CHARGED PLATES WITH OVERLAPPING DOUBLE LAYERS

This application of the theorem is described fully in refs[12,13] and it is proposed here to give only a brief outline of the method. Consider two charged surfaces I and II whose outer Stern planes are separated by distance x. When x is altered at equilibrium both σ_d and ψ_d for each of the two surfaces will in general change. Consequently, to calculate interactions on the assumption that either of these quantities is constant is in general incorrect. A more correct calculation is possible if we have a graph of σ_d vs ψ_d at the outer Stern plane for each surface which includes the values of these quantities that actually occur as the plate separation is altered in the system of interest.

To show how this can be done we note that a first integration of the Poisson-Boltzmann equation leads to the results —

$$\left.\begin{aligned} \sigma_d^{I} &= g\,(\psi_d^{I},\, n_i^{b},\, C)\,\frac{\varepsilon}{4\,\pi} \\ \sigma_d^{II} &= g\,(\psi_d^{II},\, n_i^{b},\, C)\,\frac{\varepsilon}{4\,\pi} \end{aligned}\right\} \qquad (28,\,a,\,b)$$

where

$$g\,(\psi,\, n_i^{b},\, C) = \left[\frac{8\,\pi\,kT}{\varepsilon}\sum_{i}\,(n_i^{b}\exp\,(-\,\nu_i\,e\,\psi/kT) + C)\right]^{1/2} \qquad (29)$$

Values of σ_d^{I}, σ_d^{II}, ψ_d^{I} and ψ_d^{II} which actually occur as the plate separation is varied must satisfy equations 28 a b with the same C and must be such that —

a) when $\sigma_d^{I}/\sigma_d^{II}$ and ψ_d^{II}/ψ_d^{II} are both + ve, $C < -1$

b) when $\sigma_d^{I}/\sigma_d^{II}$ and ψ_d^{I}/ψ_d^{II} are both — ve, $C > -1$

Appropriate values can be obtained from the charge potential curves by plotting e. g. C vs ψ_d for each curve, choosing points with the same C, estimating the appropriate σ_d s and checking that one or the other of the above conditions is satisfied.

The force X per unit area between the plates (+ ve when attractive) is given by the expression first derived by Langmuir[14] namely —

$$X = kT\sum_{i} n_i^{b}\,[C + 1] \qquad (30)$$

Also when $C < -1$ the appropriate separation x is given by —

$$x = \int_{\psi_m}^{\psi_d^{I}} g\,(\psi,\, n_i^{b},\, C)^{-1}\,d\,\psi + \int_{\psi_m}^{\psi_d^{II}} g\,(\psi,\, n_i^{b},\, C)^{-1}\,d\,\psi \qquad (31)$$

Where ψ_m is the value of ψ for which

$$g\,(\psi,\, n_i^{b},\, C) = 0 \qquad (32$$

The free energy of interaction per unit area may then be obtained from

$$\Delta\,G_E = \int_{\infty}^{L\,c\,x} X\,d\,x \qquad (33)$$

which can be done by numerical integration. Alternatively, $\Delta\,G_E$ may be obtained from the expression[13]

$$\Delta\,G_E = [X\,x]_x - \frac{\varepsilon}{4\,\pi}\Big[\int_{\psi_m}^{\psi_d^{I}} g\,(\psi,\, n_i^{b},\, C)\,d\,\psi + \int_{\psi_m}^{\psi_d^{II}} g\,(\psi,\, n_i^{b},\, C)\,d\,\psi\Big] + \frac{\varepsilon}{4\,\pi}\Big[\int_{0}^{\psi_d^{I}(\infty)} g\,(\psi,\, n_i^{b},\, -1)\,d\,\psi + \int_{0}^{\psi_d^{II}(\infty)} g\,(\psi,\, n_i^{b},\, -1)\,d\,\psi\Big] + \int_{\psi_d^{I}(\infty)}^{\psi_d^{I}} \sigma_d^{I}\,d\,\psi_d^{I} + \int_{\psi_d^{II}(\infty)}^{\psi_d^{II}} \sigma_d^{II}\,d\,\psi_d^{II} \qquad (34)$$

where ψ_d (∞) refers to the value of ψ_d for which $X = \infty$.

The final two terms of equation 34 are determined by the charge vs potential curves for the two surfaces concerned and may be obtained from these curves by numerical integration. For symmetrical electrolytes the remaining integrals can be expressed analytically in terms of elliptic functions and in general may be obtained without undue difficulty by numerical integration.

The appropriate sign of g in the above integrals is that of the charge in the plate whose ψ_d appears as a limit of integration.

Clearly then, we can obtain ΔG_E from graphs of ψ_d vs σ_d which include the values that actually occur as the plate separation is varied. The remaining problem is to obtain such graphs. In the case that at least one ionic species in the bulk solution can be assumed absent from the inner regions of the double for each plate the graphs concerned may be obtained from experimental studies of the two surfaces in isolation. The argument goes as follows.

When the plate separation is varied at constant μ_i^b and adsorption equilibrium is maintained, both σ_d and ψ_d can be expected to change for each plate. From the definition of the μ_i it follows that these quantities also change by amounts which are given by

$$\Delta \mu_i = -\nu_i e (\psi_d - \psi_d(\infty)) \tag{35}$$

Consider now an isolated plate in equilibrium with a solution in which the interactions we are concerned with take place and suppose we change the n_i^b. In this case the changes in the μ_i are given by —

$$\Delta \mu_i = kT \Delta \ln n_i^b - \nu_i (\psi_d^*(\infty) - \psi_d(\infty)) \tag{36}$$

Where $\psi_d^*(\infty)$ is the value of $\psi_d(\infty)$ in the altered solution. Evidently if we change the n_i^b in such a way that $(\Delta \ln n_i^b)/\nu_i$ is the same for all species found on both sides of the outer Stern plane, we can so arrange matters that the $\Delta \mu_i$ for these species in equations 35 and 36 are all the same. In this case —

$$\psi_d = \psi_d^*(\infty) - kT (\Delta \ln n_i^b)/\nu_i e \tag{37}$$

However, since the σ_d which corresponds to the ψ_d in equation 35 is according to our theorem completely determined by fixing the μ_i of all species found on both sides of the outer Stern plane, it follows that it is equal to the σ_d which corresponds to $\psi_d^*(\infty)$ in equation 36. Thus σ_d is given by —

$$\sigma_d = \frac{\varepsilon}{\psi \pi} g(\psi_d^*(\infty), n_i^b, -1) \tag{38}$$

Now since $\psi_d^*(\infty)$ refers to an isolated surface it can be found from electrokinetic studies of such a surface. The corresponding σ_d is given by equation 38 and the corresponding ψ_d is given by equation 37. Values of σ_d and ψ_d found in this way are points on the curve which contain the actual values of these quantities which occur when the plate concerned interacts with another plate in the solution of interest. Hence by measuring $\psi_d^*(\infty)$ for solutions which differ from that of interest in that $\Delta \ln n_i^b/\nu_i$ is the same for all i found on both sides of the outer Stern plane, we may obtain the information needed to calculate ΔG_E.

For a negatively charged AgI surface in the presence of KNO_3, the appropriate variations in concentration are those for which the product $[K^+][I^-]$ is the same as in the solution of interest. We must however assume that $\Gamma(NO_3^-)$ (Γ as defined by equation (12)) is effectively zero. The reason for this is that not all the n_i^b can be varied in the appropriate manner (without violating the electrical neutrality condition for the bulk solution) when all ionic species in the bulk solution have non negligible Γ_i.

The more important features of this treatment of interacting double layers may be summarised as follows:

i) The experimental information required to apply it can be obtained from electrokinetic or potentiometric titration studies of the isolated surfaces concerned.

ii) The calculations required to apply it are no more difficult and hardly more extensive than the corresponding calculations for the unrealistic boundary conditions of constant σ_d or constant ψ_d.

iii) It takes full account of specific adsorption and the formation of Stern layers in a way which does not depend on any model for the inner regions of the double layer.

iv) It is applicable to complex systems in which there may be several potential determining and specifically adsorbed species.

v) It can be extended to deal with some non-equilibrium situations if so desired, (e. g. constant primary surface charge but adsorption equilibrium of the supporting electrolyte ions).

vi) Theoretical estimates of σ_d and ψ_d as well as experimental estimates can readily be used.

In these respects the treatment goes much further than previous treatments such as those based on the Grahame model of the double layer[4,15] and those based on the notion of charge regulation[16,17].

7. ELECTROKINETIC STUDIES OF SURFACTANT ADSORPTION

In this section we are concerned with systems which contain, in addition to a potential determining species a strongly adsorbing ionic surfactant. To deal with this situation equations relating the Γ_1 and the n_i^b are required which are more explicit than can be obtained solely from the theorem outlined above. In the paper in which the data to be discussed below was first presented[18] the equations used to interpret the data were based on the Grahame model of the double layer. Although this interpretation was remarkably successful it can be argued, as was suggested in section II above, that the equations lack a sound theoretical basis. In this section of the paper we outline the alternative derivation of the appropriate equations described more fully in ref. (19). This alternative treatment, which is based on the virial expression of the surface pressure, π, in terms of the amounts adsorbed, Γ_i, is a little more general and arguably more soundly based than the original.

To illustrate the general ideas involved we consider first the adsorption of an ionic surfactant from a solution of supporting electrolyte onto an uncharged solid surface. We suppose that neither ion of the supporting electrolyte is specifically adsorbed under the conditions of interest. Let Γ_1 be the amount of adsorbed surfactant. At constant concentration of supporting electrolyte the Gibbs adsorption isotherm takes the form —

$$d\pi = \Gamma_1 kT \, d\ln n_1^b \tag{39}$$

When Γ_1 is small we suppose that π can be expressed as a virial expansion in integral powers of Γ_1, the first two terms of which are given by —

$$\pi = kT\,\Gamma_1 + B_1\,\Gamma_1^2 + \dots \tag{40}$$

Where the term $B_1\,\Gamma_1^2$ allows for interactions between adsorbed surfactant ions. Since these interactions can be expected to be largely electrostatic, and as such will be influenced by the concentration of supporting electrolyte, we expect B_1 to depend on $\varkappa$. Equations 39 and 40 lead to the expression —

$$kT\,\mathrm{d}\ln n_1^{\mathrm{b}} = kT\,\mathrm{d}\ln \Gamma_1 + 2\,B_1\,\mathrm{d}\,\Gamma_1 \tag{41}$$

from which we obtain

$$kT\left(\frac{\mathrm{d}^2 \ln n_1^{\mathrm{b}}}{\mathrm{d}\,\Gamma_1\,\mathrm{d}\,\varkappa}\right)_{\Gamma_1} = 2\,\frac{\mathrm{d}\,B_1}{\mathrm{d}\,\varkappa} \tag{42}$$

However, since at constant T, p and Γ_1 when Γ_1 is small we have according to our theorem —

$$kT\ln n_1^{\mathrm{b}} - \nu_1\,e\,\psi_{\mathrm{d}} = kT\ln n_1^{\mathrm{b}} - \frac{4\,\pi\,\nu_1^2\,e^2\,\Gamma_1}{\varkappa\,\varepsilon} = \text{const} \tag{43}$$

We find that

$$kT\left(\frac{\mathrm{d}^2 \ln n_1^{\mathrm{b}}}{\mathrm{d}\,\Gamma_1\,\mathrm{d}\,\varkappa}\right)_{\Gamma_1} = -\,\frac{4\,\pi\,\nu_1^2\,e^2}{\varepsilon}\;\frac{\mathrm{d}\,(1/\varkappa)}{\mathrm{d}\,\varkappa} \tag{44}$$

Which when compared with equation 42 shows that —

$$B_1 = \frac{2\,\pi\,\nu_1^2\,e^2}{\varkappa\,\varepsilon} + B_1^{\circ}\,(T, p) \tag{45}$$

Where $B_1^{\circ}\,(T, p)$ is the constant of integration.

Integrating equation 41 at constant T, p and $\varkappa$ we find that

$$kT\ln n_1^{\mathrm{b}} = kT\ln \Gamma_1 + 2\,B_1\,\Gamma_1 + g\,(T, p, \varkappa) \tag{46}$$

where $g\,(T, p, \varkappa)$ is the constant of integration. However, because $kT\ln n_1^{\mathrm{b}} - \nu_1\,e\,\psi_{\mathrm{d}}$ depends only on Γ_1 it follows that g cannot depend on $\varkappa$ and that

$$kT\ln n_1^{\mathrm{b}} - \nu_1\,e\,\psi_{\mathrm{d}} = g\,(T, p) + kT\ln \Gamma_1 + 2\,B_1^{\circ}\,\Gamma_1 \tag{47}$$

A similar argument can be applied to a surface such as AgI in equilibrium with I^- ions. In this case we find that —

$$kT\ln n_1^{\mathrm{b}} - \nu_1\,e\,\psi_{\mathrm{d}} = kT\ln n_1^{\circ} + 2\,B_1^{\circ}\,\Gamma_1 \tag{48}$$

where n_1° is the value of n_1^{b} at the zero point of charge.

Equation 48 is identical in form to the expression obtained from the Grahame model of the double layer when the inner regions are effectively devoid of supporting electrolyte ions. In this case we may identify B_1° with the integral capacitance through the expression

$$B_1^{\circ} = \frac{\nu_1^2\,e^2}{2\,K} \tag{49}$$

When we have both a potential determining species and a specifically adsorbed species such as a surfactant ion we suppose that in the presence of indifferent supporting electrolyte π, or an alternative appropriate quantity[19], can be written as

$$\pi = \pi_o + \pi_1 + \pi_2 + B_{12}\,\Gamma_1\,\Gamma_2 \tag{50}$$

where subscript 1 now refers to the potential determining species and subscript 2 refers to the surfactant ion. π_o is the surface pressure at the zero point of charge in the absence of surfactant. π_1 is the surface pressure for the Γ_1 of interest when $\Gamma_2 = 0$. π_2 is the surface pressure for the Γ_2 of interest when $\Gamma_1 = 0$. The term B_{12} accounts for interactions between adsorbed ions of 1 and 2. Since these interactions will be influenced by the concentration of supporting electrolyte we expect B_{12} to be a function of π as well as of T & p.

By arguments essentially the same as those outlined above we find that —

$$\left.\begin{aligned} kT \ln n_1^{\mathrm{b}} - \nu_1\, e\, \psi_{\mathrm{d}} &= f\,(T, p\, \Gamma_1) + B_{12}^{\circ}\, \Gamma_2 \\ kT \ln n_2^{\mathrm{b}} - \nu_2\, e\, \psi_{\mathrm{d}} &= g\,(T, p) + kT \ln \Gamma_2 + B_{21}^{\circ}\, \Gamma_1 \end{aligned}\right\} \tag{51, a, b}$$

where $B_{12}^{\circ} = B_{21}^{\circ}$ is a function of T and p only.

B_{12} describes the effect of surfactant adsorption on the value of n_1^{b} for which Γ_1 has a given value and B_{12}^{0} is zero if this effect vanishes as $\varkappa \to \infty$. We will suppose for simplicity that this is the case in the analysis of the experimental data. In this case it is clear that equations 51 a and b become —

$$\left.\begin{aligned} kT \ln n_1^{\mathrm{b}} - \nu_1\, e\, \psi_{\mathrm{d}} &= f\,(T, p, \Gamma_1) \\ kT \ln n_2^{\mathrm{b}} - \nu_2\, e\, \psi_{\mathrm{d}} &= g\,(T, p) + kT \ln \Gamma_2 \end{aligned}\right\} \tag{52 a, b}$$

which are in effect identical to the equations used in the original interpretation[18]. However, it is apparent from the above theorem that equation 52a necessarily holds if 52b holds. This is not immediately obvious from the Grahame model.

Equations 52a, b lead to the result

$$\frac{\mathrm{kT}}{\nu_2\, e}\left(\frac{\partial \ln n_2^{\mathrm{b}}}{\partial \psi_{\mathrm{d}}}\right)_{n_1^{\mathrm{b}}\,\mathrm{K}} = 1 + \left[\frac{\varkappa\, \varepsilon}{4\pi\, \nu_2^{2}\, e^{2}} + \frac{\nu_1^{2}}{\nu_2^{2}\, f\,(\Gamma_1)}\right]\frac{kT}{\Gamma_2} \tag{53}$$

For a given n_1^{b} it is apparent from equation 52 a that the value of Γ_1 for which $\sigma_{\mathrm{d}} = 0$ is the same, irrespective of the nature of the surfactant and the ionic strength. It follows that for a given n_1^{b} and ionic strength the LHS of equation 53 should be the same for all surfactants of a given charge type when $\sigma_{\mathrm{d}} = 0$.

That this is so in practice is apparent from Figure 7, which shows ζ vs u.c.s. (pS = — $\log_{10}$ (surfactant concentration)) for a variety of ionic surfactants adsorbed on nylon in a 10^{-3} M HCl solution which gives both constant pH and ionic strength. The different intercepts on the abscissa provide a measure of differences in $g\,(T, p)$ for the various surfactants and as such reflect differences in the free energy of adsorption. These differences are very much as one would expect and it is clear that the method provides a sensitive technique for determining small differences in adsorption free energies.

A further deduction from equations 52a, b is that when $\psi_{\mathrm{d}} = 0$

$$\frac{kT}{\nu_2\, e}\left(\frac{\partial \ln n_2^{\mathrm{b}}}{\partial \psi_{\mathrm{d}}}\right)_{n_1^{\mathrm{b}}\,\mathrm{K}} \approx 1 - \left[\frac{kT}{\nu_2\, e\, \psi_{\mathrm{d}}^{*}}\right] \tag{54}$$

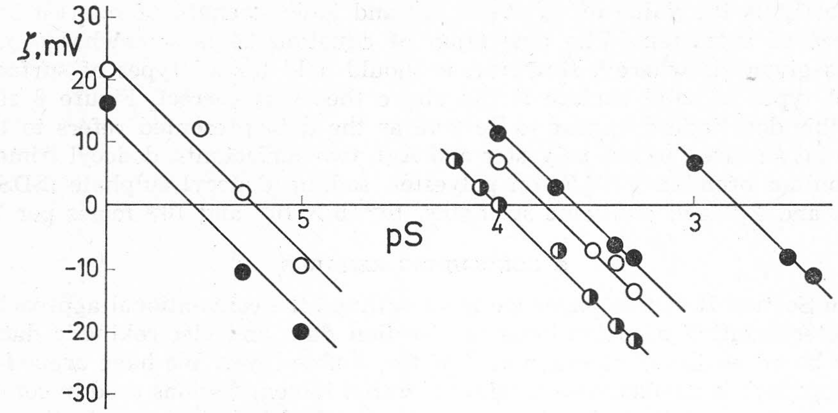

Figure 7. ζ vs pS for nylon sol at pH 2 in the presence of various surfactants, from L — R ● = sodium cetyl sulphonate.
○ = sodium terphenyl sulphonate, half filled circles = sodium dodecyl sulphate,
○ = sodium octyl benzene sulphonate, ● = sodium dodecyl sulphonate,
● = sodium decyl sulphonate.

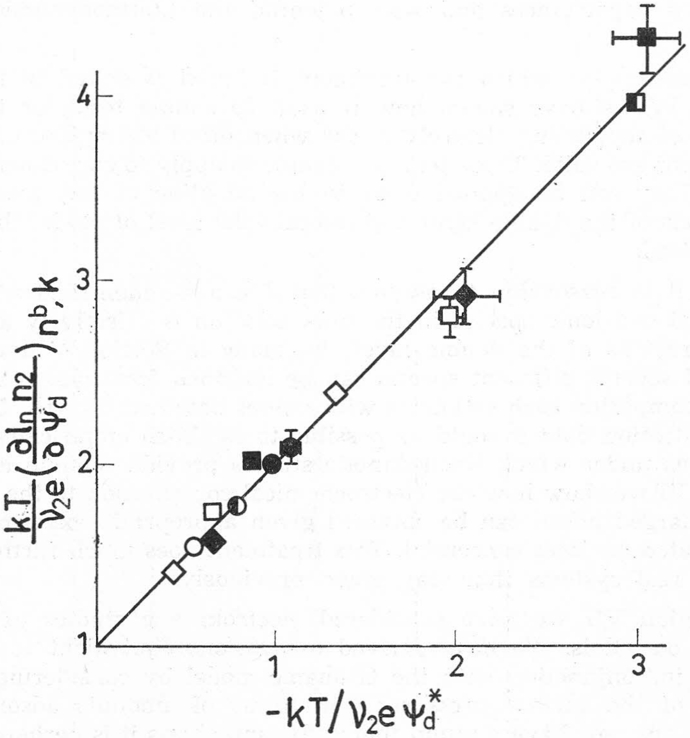

Figure 8. $\frac{kT}{\nu_2 e}\left(\frac{\partial \ln n_2^b}{\partial \psi_d}\right)_{n_1^b\,\varkappa}$ vs $-kT/\nu_2 e \psi_d^*$ for
☐ polyester/dodecyl trimethyl ammonium bromide,
»diamond« AgI/SDS, ○ nylon/SDS
Ionic strengths mpl 10^{-3} (open) 5×10^{-3} (half filled) 10^{-2} (filled)

where ψ_d^* is the value of ψ_d at the n_1^b and ionic strength of interest in the absence of surfactant. The derivation of equation 54 is somewhat complex and is given elsewhere[19]. However, it should hold for all types of surfactant on all types of solid surface if the above theory is correct. Figure 8 shows that this does indeed appear to be true as the data presented refers to three different surfaces, nylon, polyester and AgI, two surfactants, dodecyl trimethyl ammonium bromide (DTAB) on polyester, sodium dodecyl sulphate (SDS) on nylon and AgI and two ionic strengths, 10^{-3}, 5×10^{-3} and 10^{-2} moles per litre.

8. CONCLUDING REMARKS

In Section II of this paper we have outlined the conventional approach for the interpretation of potentiometric titration data and electrokinetic data on solids based on the Grahame model of the double layer. We have argued that this approach is cumbersome to apply and that the expressions used in conjunction with the model which relate amounts adsorbed to bulk concentrations lack a firm theoretical basis. The remainder of the paper has been concerned with the development and application of an alternative thermodynamic approach. Both approaches have in common the assumptions that there is an outer Stern plane beyond which the Poisson Boltzmann equation holds. However, whereas the Grahame model introduces other concepts from electrostatics such as inner region capacitances and wall potential the thermodynamic approach does not.

The theorem on which the treatment is based is stated in Section III. In Section IV we have shown how it leads to simple tests for the specific adsorption of supporting electrolyte ions when other assumptions inherent in the treatment are valid. These tests are simple to apply to experimental data as obtained. They can be applied prior to the adoption of any model for the inner regions of the double layer and indicate the level of model that is likely to be required.

When it is reasonable to assume that ζ can be identified with ψ_d and that at least one ionic species in the bulk solution is effectively absent from the inner regions of the double layer, we show in Section V how adsorbed amounts of several different species can be obtained from electrokinetic data alone. By comparing such estimates with values obtained directly from potentiometric titration data it could be possible to establish empirically the range of conditions under which electrokinetic studies provide reliable information. In Section VI we show how the electrochemical contribution to the interaction between charged plates can be obtained given appropriate experimental data on the isolated surfaces concerned. This treatment goes much further towards describing real systems than any given previously.

In Section VII we have considered electrokinetic studies of surfactant adsorption on solids. We have derived expressions equivalent to those used previously in conjunction with the Grahame model by considering the virial expansion of the surface pressure π in terms of amounts adsorbed. Since these equations now have a sound thermodynamic basis it is perhaps no longer surprising that they work as well as they do.

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SAŽETAK

Primjena jednoga korisnog teorema u teoriji dvosloja

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Predložen je nov termodinamički pristup teoriji stvaranja naboja na granici faza čvrsto/tekuće, koji odstupa od polaznih osnova Grahameova modela elektrokemijskog dvosloja. Taj se pristup također služi koncepcijom vanjske Sternove plohe, ali ne zahtijeva druge elektrostatske koncepcije, pa tako niti potencijal čvrste površine, ψ_0. Primjenom predloženog pristupa moguće je, služeći se samo elektrokinetičkim podacima, izračunati količinu više specifično adsorbiranih vrsta odjednom. Isto je tako moguće izračunati elektrokemijski doprinos ukupnoj energiji interakcije između identičnih ili različitih ploha. Za površine koje se nalaze u stanju bliskom izoelektričkoj točki, i kada su adsorbirane količine male, kemijski potencijal adsorbata moguće je izračunati iz površinskog tlaka, π.

Iako su konačni izrazi na osnovi ovog pristupa slični onima koji slijede iz Grahameova razmatranja, njihov je izvod manje opterećen pretpostavkama. Testirani u interpretaciji elektrokinetičkih veličina za adsorpciju površinski aktivnih tvari na koloidnim disperzijama nylona, srebrnog jodida i silike, pokazali su odlično slaganje s eksperimentom.

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