On Adsorption at the Oil/Water Interface and the Calculation of Electrical Potentials in the Aqueous Surface Phase II. The Effects of Ionic Size

D. A. Haydon and F. H. Taylor

Email alerting service	Receive free email alerts when new articles cite this article - sign up in the box at the top right-hand corner of the article or click **here**

[255]

ON ADSORPTION AT THE OIL/WATER INTERFACE AND THE CALCULATION OF ELECTRICAL POTENTIALS IN THE AQUEOUS SURFACE PHASE

II. THE EFFECTS OF IONIC SIZE

By D. A. HAYDON

University of Cambridge, Department of Colloid Science, Free School Lane, Cambridge

AND F. H. TAYLOR*

Former Beit Memorial Fellow for Medical Research, Chemistry Department, Imperial College, London, S.W. 7.

CONTENTS

An equation is derived similar to the Gouy equation for a flat diffuse double layer but which takes into acount the finite sizes of the adsorbed and counter ions. The corresponding equation giving the variation of potential with the distance from the plane of charge is derived for systems where the potential exceeds *ca.* 50 mV. A relation between specific surface charge and surface pressure (equation of state) is deduced on this basis for completely ionized adsorbed films.

These equations are tested for films of sodium alkyl sulphates and dodecyltrimethylammonium bromide adsorbed at the petroleum-ether/water interface, allowance being made for the presence of counter-ions above the plane of the film ions.

The modified equations predict the electrical potentials in the region of the interface much more completely than the simple Gouy equation.

An estimate of the number of counter ions present in the region above the head groups is given and the possible effects of their presence there on surface viscosity and electrophoretic phenomena briefly considered.

Other possible corrections to simple diffuse double-layer theory are discussed; it is concluded (in agreement with other recent authors) that electrical polarization and dielectric saturation effects tend to cancel out over the experimental range of electric field strengths.

Fluctuation phenomena ('self atmosphere' effects) may become important at high values of κx and in this region may cancel out the ionic size effect, so that the potential-distance relation derived

---

* Present Address: Science Department, British Council, 65 Davies Street, London, W. 1.

31

from the standard Gouy–Chapman treatment should be obeyed in the outer regions of the diffuse double layer.

Deviations occur from the modified Gouy equation for the shorter chain surface active agents in absence of any added electrolyte. The causes suggested are:

(1) the inadequacy of the simple geometrical model used for determining the film ion size correction;

(2) the inapplicability of the expression used to calculate bulk phase activity coefficients for detergents at high concentrations.

INTRODUCTION

In the determination of the contribution of electrical interactions to the adsorption of long-chain ions at liquid/liquid and air/liquid interfaces, the Gouy equation (for 1:1 electrolytes)

$$\sinh \frac{\epsilon \psi_0}{2kT} = \frac{10^{16}\epsilon}{A\sqrt{c}} \sqrt{\frac{1000\pi}{2DkTN}} \tag{1}$$

is often employed, where

ψ_0 = electrical potential in plane of film ions;

A = area/molecule in the interface;

c = molar electrolyte concentration in the bulk phase;

ϵ = electronic charge.

In the derivation of this equation three main assumptions are made as to the conditions at the interface. These are:

(i) that the surface is an evenly charged impenetrable plane, which can be treated as a uniformly 'smeared out' set of charges;

(ii) that the film and counter ions are point charges;

(iii) that the high field strengths and ionic concentrations near the interface do not give rise to dielectric saturation or polarization effects.

Although Davies (1951) found that the Gouy equation for the electrical potential at a surface applied to insoluble ionized monolayers on substrates of ionic strengths of up to 2N, later investigators have questioned its applicability over such a wide range and have found it inadequate to explain experimental results. Thus it often fails to predict correctly the contribution of the electrical term to the pressure, as is shown by tests of the equation of state.

Haydon & Taylor (1960) derive an equation for the potential ψ_0 in which the first of the assumptions listed above is not made. Instead, a model is taken in which the plane of the film ions is assumed to be penetrable and to be situated a finite distance, d, from the interface. Since, in this system, the counter ions can penetrate above the plane of the film ions, the equilibrium potential in that plane is lower than that calculated from the simple Gouy equation. The three relations derived are

$$\frac{10^{16}\epsilon}{A\sqrt{c}} \sqrt{\left(\frac{1000\pi}{2DkTN}\right)} = \left\{1 + \sqrt{\left(1 - \frac{A'_0}{A}\right)}\right\} \sinh \frac{\epsilon \psi_0}{2kT} - \sqrt{\left(1 - \frac{A'_0}{A}\right)} \sinh \frac{\epsilon \psi_d}{2kT}, \tag{2}$$

$$\kappa d \sqrt{\left(1 - \frac{A'_0}{A}\right)} = \ln \left\{\frac{\tanh\left(\epsilon \psi_0/4kT\right)}{\tanh\left(\epsilon \psi_d/4kT\right)}\right\}, \tag{3}$$

and

$$\frac{\epsilon \psi_0}{kT} = \left[\frac{\Delta G_{o/w}}{NkT}\right]\frac{d}{l}, \tag{4}$$

where $\quad A_0' =$ the effective cross-sectional area of a hydrocarbon chain;

$\psi_0 =$ potentional in the plane of the film ions;

$\psi_d =$ potential at the interface;

$d =$ distance of plane of film ions from interface;

$1/\kappa =$ 'thickness of double layer'.

Calculations based on these equations give better agreement with the measured surface potentials and equations of state than those made based on the simple Gouy equation. In general the above equations are obeyed:

(i) when no electrolyte is added to the system for long-chain ions containing 12 or more carbon atoms (for shorter chain detergents, deviations occur where the bulk detergent concentration exceeds 0·006 M);

(ii) in presence of excess added electrolyte at low detergent ion concentrations (values of $A > 70$); considerable deviations occur below this value, particularly with the shorter chain detergents.

The nature of the deviations suggests that they arise from a neglect of the second of the assumptions mentioned above. In this paper the theory is developed by allowing for the finite sizes of the ions present.

THEORETICAL

Structure of the double layer

In any attempt to allow for the finite sizes of the film and counter ions in these systems, the problem resolves into two parts (cf. Aickin & Palmer 1944). Taking a point on the normal to the plane drawn through the centres of the film ions and a distance x from that plane, we must consider the potential drop and distribution of ions in two regions:

(*a*) Where $\tau < x < \infty$, τ being the average distance of closest approach of the centres of the counter ions to the centres of the film ions. In this region we need only consider the size of the counter ions. We give the potential in the plane of average closest approach the symbol ψ_τ.

(*b*) The region where $0 < x < \tau$. The potential drops in this region from that in the plane of the film ions, ψ_0, to ψ_τ. Thus, the plane of the film ions can be penetrated by counter ions but the average concentration of such ions in this region is restricted by the geometry of the system (the distance between the film ions, their size, and that of the counter ions).

The final solution must obey the requirement that the total diffuse charge (σ) in the system is given by

$$\sigma = -\int_0^\tau \rho \, \mathrm{d}x - \int_\tau^\infty \rho \, \mathrm{d}x. \tag{5}$$

We shall consider each of these regions in turn.

Electrical potentials in the 'diffuse' phase

(i) When allowance is made for the space occupied by the ions present in a system, the Boltzmann equation may be written in a form proposed by Bikerman (1942) and derived statistically by Schlögl (1954)

$$n_i = n_{i_0} \, \mathrm{e}^{-z_i \epsilon \psi / kT} \frac{1 - \Sigma \phi_i n_i}{1 - \Sigma \phi_i n_{i_0}}, \tag{6}$$

where z_i = valency of species i,

n_{i_0} = bulk phase concentration of i,

n_i = adsorbed concentration of i,

and where ϕ_i, ϕ_j, etc., are general 'space factors', which in all but very concentrated solutions may be taken as the volumes of the ions concerned. This equation and similar modifications which allow for the mutual penetrability of the ionic hydration sheaths have been discussed recently by Falkenhagen & Kelbg (1959). For any two ions i and j, it is also true that

$$\frac{n_i}{n_j} = \frac{n_{i_0}}{n_{j_0}} e^{-z_i \epsilon \psi / kT} / e^{-z_j \epsilon \psi / kT}. \tag{7}$$

Therefore elimination of all surface concentrations except that of species i yields

$$n_i = \frac{n_{i_0} e^{-z_i \epsilon \psi / kT}}{1 + \Sigma \phi_i n_{i_0} e^{-z_i \epsilon \psi / kT}} \frac{1}{1 - \Sigma \phi_i n_{i_0}} \tag{8}$$

The specific surface charge ρ is given by

$$\rho = \Sigma z_i \epsilon n_i, \tag{9}$$

so that the Poisson–Boltzmann equation takes the form

$$\frac{d^2 \psi}{dx^2} = -\frac{4\pi\epsilon}{D} \left\{ \frac{\Sigma z_i n_{i_0} e^{-z_i \epsilon \psi / kT}}{1 + \dfrac{1}{1 - \Sigma \phi_i n_{i_0}} \Sigma \phi_i n_{i_0} e^{-z_i \epsilon \psi / kT}} \right\} \frac{1}{1 - \Sigma \phi_i n_{i_0}}. \tag{10}$$

At this point, we restrict the discussion to a symmetrical binary electrolyte, where $z_i = -z_j$; $n_{i_0} = n_{j_0}$. (The derivation can also be carried out for 1:2 and 1:3 electrolytes.)

Integration of equation (10) yields

$$\left(\frac{d\psi}{dx}\right)^2 = -\frac{4\pi kT}{Db} \left\{ \frac{1-b}{\phi_i} \ln\left[e^{-z\epsilon\psi/kT} + \frac{1-b}{2\phi_i k_1} \right] - \frac{1+b}{\phi_i} \ln\left[e^{-z\epsilon\psi/kT} + \frac{1+b}{2\phi_i k_1} \right] \right.$$
$$\left. + \frac{1-b}{\phi_j} \ln\left[e^{z\epsilon\psi/kT} + \frac{1-b}{2\phi_j k_1} \right] - \frac{1+b}{\phi_j} \ln\left[e^{z\epsilon\psi/kT} + \frac{1+b}{2\phi_j k_1} \right] \right\}. \tag{11}$$

Where $\qquad b^2 = 1 - 4k_1^2 \phi_i \phi_j \quad$ and $\quad k_1 = \dfrac{n_0}{1 - \Sigma \phi_i n_0}$.

If $4\phi_i \phi_j n_0^2 \ll 1$ this equation reduces to

$$\left(\frac{d\psi}{dx}\right)^2 = \frac{8\pi kT}{D} \left\{ \frac{1}{\phi_i} \ln\left[e^{-z\epsilon\psi/kT} \phi_i k_1 + 1 \right] + \frac{1}{\phi_j} \ln\left[e^{z\epsilon\psi/kT} \phi_j k_1 + 1 \right] \right\}. \tag{12}$$

In practice, if reasonable values are assigned to ϕ_i, ϕ_j and n_0, the $4\phi_i \phi_j n_0^2$ is always very much less than unity. Thus, for a detergent dissolved in a swamping concentration, for example 0·5 M-NaCl, and taking values for the ionic radii (a_i) of Na$^+$ and Cl$^-$ of 1·1 and 1·81 Å, respectively (the radii of the unhydrated ions),

$$4\phi_i \phi_j n_0^2 = 4 \times \left(\frac{4\pi}{3}\right)^3 \times 1\cdot 33 \times 5\cdot 93 \times \left[\frac{0\cdot 5 \times 6\cdot 06 \times 10^{23}}{10^{24} \times 10^3} \right]^2 = 5\cdot 2 \times 10^{-5}.$$

For dodecyltrimethylammonium bromide, in absence of added electrolyte, n_0 is much smaller. Assuming the radius of the bromide ions to be 1·9 Å and that of the long-chain ion

$3\,\text{Å}$ and taking n_0 as the highest value used in the present investigation ($=0\cdot015\,\text{M}$ just below the cmc.), we have

$$4\phi_i\phi_j n_0^2 = 8\cdot4\times10^{-7}.$$

Equation (12) may therefore be assumed to hold under all experimental conditions. Inserting the boundary conditions

$$\mathrm{d}\psi/\mathrm{d}x = 0, \quad \psi = 0, \quad x = \infty,$$

we obtain

$$\left(\frac{\mathrm{d}\psi}{\mathrm{d}x}\right)^2 = \frac{8\pi kT}{D}\left\{\frac{1}{\phi_i}\ln\left[\phi_i k_1(\mathrm{e}^{-ze\psi/kT}-1)+1\right]+\frac{1}{\phi_j}\ln\left[\phi_j k_1(\mathrm{e}^{ze\psi/kT}-1)+1\right]\right\}. \tag{13}$$
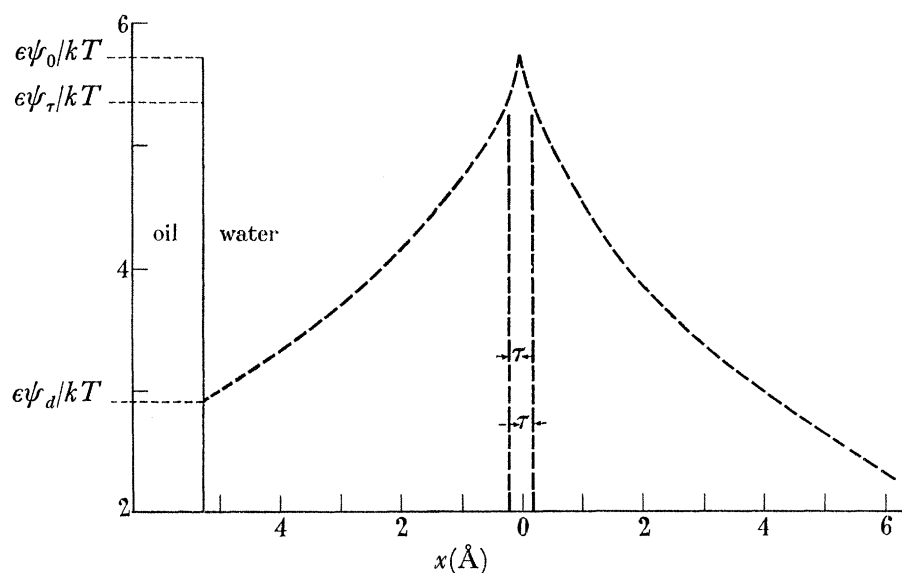

FIGURE 1. Distribution of electrical potential in the region of an adsorbed monolayer calculated according to equation (21). In this particular system, the electrolyte concentration is $0\cdot07\text{M}$, $A = 48\cdot2\,\text{Å}^2$, $d = 5\cdot28\,\text{Å}$, $\psi_0 = 144\,\text{mV}$ and $\tau = 0\cdot19\,\text{Å}$.

An equation analogous to the Gouy equation is obtained by combining (13) with the relation

$$\sigma = -\int_\tau^\infty \rho\,\mathrm{d}x = -\frac{D}{4\pi}\left(\frac{\mathrm{d}\psi}{\mathrm{d}x}\right)_{x=\tau}. \tag{14}$$

This assumed that all the diffuse charge lies outside a plane $\tau\,\text{cm}$ from the plane of the head groups. We obtain

$$\sigma = \frac{10^{16}e}{A} = \sqrt{\frac{DkT}{2\pi}}\left\{\frac{1}{\phi_i}\ln\left[\phi_i k_i(\mathrm{e}^{-ze\psi/kT}-1)+1\right]+\frac{1}{\phi_j}\ln\left[\phi_j k_1(\mathrm{e}^{ze\psi/kT}-1)+1\right]\right\}^{\frac{1}{2}}. \tag{15}$$

A similar result was obtained by Ohlenbusch (1956) for the condition $\phi_i = \phi_j$. When ϕ_i and ϕ_j are vanishingly small, equation (15) reduces to the simple Gouy equation (1). For a given surface charge density, the value of ψ calculated from (15) increases rapidly with increasing ionic size. In figure 2, values of the calculated potential are plotted against the ionic radius for a system in which $A = 60$ and the bulk electrolyte concentration is $0\cdot1\,\text{M}$. In this system, and in all others considered in this paper, little difference results to the potential if the approximation $k_1 = n_0$ (neglect of the ionic size correction in the bulk phase)

is made, except at high values ($> 4\cdot5$) of the ionic radius and at high ionic strengths ($> 1\cdot0\,\mathrm{N}$).

Where the calculated potential exceeds 50 mV, little difference to the result is obtained if the effect of the counter ions of similar charge to that of the film ions is neglected in equation (15). It is only by making this approximation that the theoretical equation of state and certain other equations considered later in this paper can be obtained. (ii) For
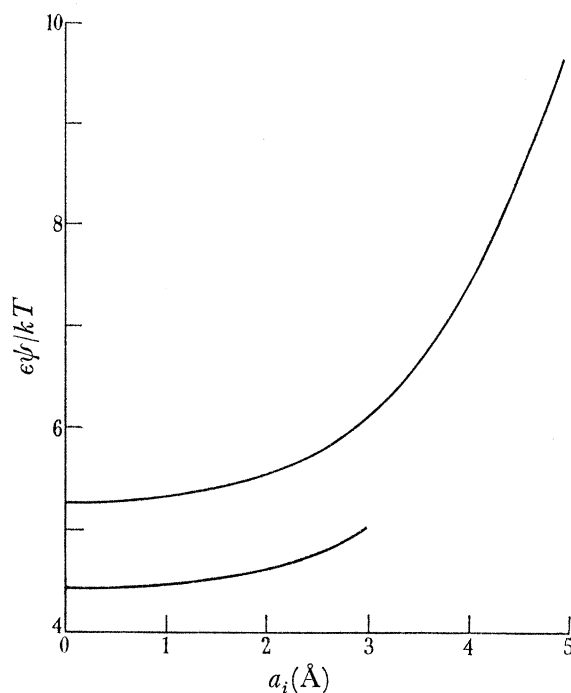

FIGURE 2. The variation of the value of the electrical potential ψ_τ calculated from equation (15) with the ionic radius of the counter ion (the radius of the ion of similar charge to the film ion is kept constant at $1\cdot2$ Å). The effects of neglecting the ionic volume term in the bulk are only noticeable at high values of a_i:

$$a_i = 4\cdot0, \quad e\psi_\tau/kT \text{ with the use of } k_1 = 7\cdot389; \text{ with the use of } n_0 = 7\cdot405$$
$$5\cdot0, \quad e\psi_\tau/kT \quad ,, \qquad ,, \quad k_1 = 9\cdot899; \quad ,, \qquad ,, \quad n_0 = 9\cdot931$$
$$5\cdot81, \quad e\psi_\tau/kT \quad ,, \qquad ,, \quad k_1 = 13\cdot126; \quad ,, \qquad ,, \quad n_0 = 13\cdot175.$$

In this system, $n_0 = 0\cdot1\,\mathrm{M}$, $A = 60$ Å^2, $T = 20$ °C. When allowance is made for penetration of ions above the film-ion plane, the lower curve is obtained.

systems where the plane of the film ions is situated a finite distance (d) from the phase boundary, equation (15) must be modified (see part I, Haydon & Taylor 1960). The total space charge/cm^2 is given by equation (5) where τ is the effective distance of closest approach of the centres of the counter ions to the plane of the film ions. Equation (5) may be rewritten, in this instance,

$$\sigma = -\frac{D}{4\pi}\left\{\int_\tau^\infty \frac{\mathrm{d}^2\psi}{\mathrm{d}x^2}\,\mathrm{d}x + \int_\tau^d \frac{\mathrm{d}^2\psi}{\mathrm{d}x^2}\,\mathrm{d}x\right\}$$

$$= -\frac{D}{4\pi}\left\{-\left(\frac{\mathrm{d}\psi}{\mathrm{d}x}\right)_\tau + \left(\frac{\mathrm{d}\psi}{\mathrm{d}x}\right)_d - \left(\frac{\mathrm{d}\psi}{\mathrm{d}x}\right)_\tau\right\}.$$

Following the procedure employed in part I and making allowance for the restriction in the space available above the head groups caused by the presence of the aliphatic chains, we obtain

$$\frac{10^{16}\epsilon}{A} = -\sqrt{\frac{DkT}{2\pi}}\left[\left\{1+\sqrt{\left(1-\frac{A_0'}{A}\right)}\right\}\left\{\frac{1}{\phi_i}\ln\left(\phi_i k_1(e^{-ze\psi_\tau/kT}-1)+1\right)\right.\right.$$
$$\left.+\frac{1}{\phi_j}\ln\left(\phi_j k_1(e^{ze\psi_\tau/kT}-1)+\right)\right\}^{\frac{1}{2}} - \sqrt{\left(1-\frac{A_0'}{A}\right)}\left\{\frac{1}{\phi_i}\ln\left(\phi_i k_1(e^{-ze\psi_d/kT}-1)+1\right)\right.$$
$$\left.\left.+\frac{1}{\phi_j}\ln\left(\phi_j k_1(e^{ze\psi_d/kT}-1)+\right)\right\}^{\frac{1}{2}}\right]. \quad (16)$$

The potential ψ_τ obtained when penetration of the counter ions above the head groups occurs is, of course, smaller than that found when there is no such penetration. Where $a_i = 0$, this difference in $\epsilon\psi/kT$ is ~ 0.85 for all values of A and all bulk electrolyte concentrations (see table 3 in part I). However, as a_i increases, this difference increases also. For the system in figure 2 when $a_i = 1.2$, $\Delta\epsilon\psi/kT = 0.875$ and for $a_i = 1.81$, $\Delta\epsilon\psi/kT = 0.915$; it also increases slightly as A decreases.

The potential at the phase boundary, ψ_d and the measured surface potential are related directly (by equation (33) in part I).

Electrical potentials in the region of the head groups

The potential drop in this region will be particularly important in determining the value of ψ_0 when either the film ions or the counter ions are large and when the area per adsorbed molecule is less than a certain critical value at which the counter ions can just fit between the film ions.

An exact statistical relationship between τ and A is difficult to derive and the present authors have been forced to employ a simple geometrical model for the system. The average arrangement of the ions below the 'critical' A value will correspond to hexagonal packing of the molecules and so we can write

$$\tau = \sqrt{\{(a_i+a_F)^2-2\sqrt{3}A/9\}}, \quad (17)$$

where a_F and a_i are the radii of the film ions and the counter ions, respectively. The dynamic conditions at the interface mean that, even in the critical range referred to above, this model is approximate; in particular it will lead to too high a value for τ. Above the 'critical' value, on the other hand, the above model yields $\tau = 0$.

We may treat the 'impenetrable' region lying between $x = \tau$ and $x = 0$ as a condenser in which

$$\psi_0 = \psi_\tau+4\pi\sigma\tau/D. \quad (18)$$

Distribution of potential normal to the interface

It is of interest to determine the effect of the allowance for the finite sizes of the counter ions on the decay of electrical potential with distance from the interface. A knowledge of this relationship is necessary for the calculation of ψ_d, the potential at the interface. For this purpose, in this paper, we shall only develop the equation which applies for small distances from the plane of charge (i.e. $x < 1/\kappa$). The starting point is then the approximation for high potentials of equation (13), i.e.

$$\left(\frac{d\psi}{dx}\right)^2 = \frac{8\pi kT}{D\phi_i}\ln\{\phi_i k_1(e^{-ze\psi/kT}-1)+1\}. \quad (19)$$

If we put $\ln\{\phi_i k_1 (e^{-ze\psi/\kappa T}-1)+1\} = y$ the result of integrating this equation is (see appendix B)

$$\sqrt{\left(\frac{8\pi kT}{D\phi_i}\right)}x = -\frac{2kT}{z\epsilon}\frac{1}{y}\left\{-1+\tfrac{1}{2}y^2+\tfrac{1}{36}y^4+\ldots+\frac{1}{3}\left(\frac{\phi_i k_1}{y^2}\right)-\frac{1}{5}\left(\frac{\phi_i k_1}{y^2}\right)^2+\ldots\right\}+\text{constant.} \quad (20)$$

Our boundary conditions are

$$x = \tau, \quad \psi = \psi_\tau \quad (y = y_\tau),$$

so that the final space relationship becomes

$$-\sqrt{\left(\frac{2\pi\epsilon^2 z^2}{D\phi_i kT}\right)}(x-\tau) = \left\{\frac{f(y^2)}{y}-\frac{f(y_\tau^2)}{y_\tau}\right\}, \quad (21)$$

where

$$\left\{-1+\tfrac{1}{2}y^2+\tfrac{1}{36}y^4+\ldots+\frac{1}{3}\left(\frac{\phi_i k_1}{y^2}\right)-\frac{1}{5}\left(\frac{\phi_i k_1}{y^2}\right)^2+\ldots\right\} = f(y^2).$$

In calculating ψ_d, we apply the condition $x = d$ when $\psi = \psi_d$. In this instance, if allowance is made for the space occupied by the carbon chains above the head groups of the detergents, the left-hand side of (21) must be multiplied by $\sqrt{(1-A_0'/A)}$.

The quantity $f(y^2)$ is always very close to (but slightly less than) unity, and, for adsorbed detergents in absence of added electrolyte, is accurately given by $(-1+\tfrac{1}{2}y^2)$.

Derivation of the equation of state

The most convenient procedure for deriving the relation between surface pressure and A has already been described (part I).

(i) In the presence of excess added electrolyte, we start with the expression

$$\Pi = \frac{kT}{A-A_0}+\int_0^{\psi_0}\frac{1}{A}\,d(\epsilon\psi_0). \quad (22)$$

Where the film-ion size correction is negligible, we can substitute for ψ_τ from equation (15) and this is most conveniently done by using the form of this equation that is valid where $\epsilon\psi_\tau/kT > 3$, namely

$$\frac{\alpha}{A^2} = \ln(k_1\phi_i e^{-ze\psi/kT}+1), \quad (23)$$

where

$$\alpha = \frac{2\pi\phi_i\epsilon^2 10^{32}}{DkT}.$$

This approximation holds over the experimental range considered in this paper. The equation of state then becomes

$$\Pi = \frac{kT}{A-A_0}+\frac{kT}{A}\ln(e^{\alpha/A^2}-1)+kT\int\frac{1}{A^2}\ln(e^{\alpha/A^2}-1)\,dA+\text{constant.} \quad (24)$$

This last integral can be evaluated only after expansion of the logarithmic term as a series (see appendix B). The final equation of state is

$$\Pi = \frac{kT}{A-A_0}+\frac{kT}{A}\ln\frac{e^2A^2}{\alpha}(e^{\alpha/A^2}-1)-\frac{\alpha kT}{6A^3}-\frac{\alpha^2 kT}{120A^5}. \quad (25)$$

As $\phi_i \to 0$ then $\alpha \to 0$ and we obtain the equation of state

$$\Pi = \frac{kT}{A-A_0} + \frac{2kT}{A}, \tag{26}$$

which is the approximation to the Gouy equation of state valid at high potentials.

Below the critical value of A, where the film ion correction is important, a term

$$\frac{4\pi\epsilon}{D} 10^{13} kT \int_0^{1/A} \frac{1}{A} d\left(\frac{\tau}{A}\right)$$

must be added, and this term is best determined graphically.

(ii) For adsorption in absence of added excess electrolyte, the approximation represented by (23) can always be employed. Since $\Sigma\phi_j n_0$ in such systems is always very small, k_1 can assume the value n_0 (this is equivalent to assuming that the ions occupy a negligible volume in the bulk phase). Following the procedure of part I (bearing in mind that n_0 is a variable) one obtains an expression of the form of equation (25) with the addition of one term involving the bulk phase activity coefficient

$$kT \int \frac{1}{A} d\ln f.$$

This term also is best determined graphically.

(iii) The corresponding equations of state for systems where ionic 'penetration' effects are important cannot be derived, as the equation resulting from the combination of (16) and (22) is not amenable to simple integration even when the approximation for high potentials is made. In this instance also, the results must be obtained by graphical integration.

APPLICATION TO EXPERIMENTAL SYSTEMS

Tests of the equations

The equations relating the potentials in the diffuse phase in the region of a charged plane are of general application (within the limits of the mathematical approximations); however, the equations of state have been developed for reversibly adsorbed, charged mobile films of long-chain electrolytes and it is intended to test the equations using results of measurements on such systems adsorbed at the oil/water interface. The experimental results of Kling & Lange (1957) for some sodium alkyl sulphates dissolved in water at 50 °C and of Haydon & Taylor (1960) for sodium dodecyl sulphate and dodecyl trimethyl ammonium bromide in presence of swamping electrolyte are used.

It is necessary to assume values for the radii of the film and counter ions involved. In view of the difficulty of assigning a fixed and constant radius to hydrated ions, we have chosen values corresponding roughly to the crystal lattice radii of the counter ions so that we actually calculate the *minimum* effect that the introduction of finite ion size will have on the electrical potentials.

Calculation of electrical potentials

For systems, such as those now under consideration, where penetration of counter ions above the plane of the charged head groups can occur, the necessary equations for determination of the electrical potentials are

$$\frac{\epsilon\psi_0}{kT} = \left\{\frac{\Delta G_{o/w}}{NkT}\right\} \frac{d}{l} = \frac{\epsilon\psi_\tau}{kT} + \frac{4\pi 10^{13}\epsilon\tau}{AD}; \tag{27}$$

equation (16), here approximated for $\epsilon\psi/kT > 2.5$, $z = -1$,

$$\frac{10^{16}\epsilon}{A}\sqrt{\bigg/\bigg(\frac{8\pi^2 N}{3000DkT}\bigg)}a_i^{\frac{3}{2}} = \bigg\{1 + \sqrt{\bigg/\bigg(1-\frac{A_0'}{A}\bigg)}\bigg\}[\ln\{\phi_i k_1(e^{\epsilon\psi_\tau/kT}-1)+1\}]^{\frac{1}{2}}$$
$$-\bigg[\bigg(1-\frac{A_0'}{A}\bigg)\ln\{\phi_i k_1(e^{\epsilon\psi_d/kT}-1)+1\}\bigg]^{\frac{1}{2}} \quad (28)$$

with a_i = radius of counter ion in centimetres, and equation (21).

The constants needed in these various calculations are listed in table 1 and the potentials and values of d for the alkyl sulphates and the quaternary compound in table 2.

The adsorption isotherm

Adsorbed mobile films of long-chain ions should obey the isotherm (part I)

$$\frac{A_0}{A-A_0}e^{A_0/(A-A_0)}e^{\epsilon\psi_0/kT} = a\,e^{-\Delta G_{o/w}/NkT}, \quad (29)$$

where a is the bulk phase activity. $\Delta G_{o/w}$ is the non-electrical component of the free energy of adsorption. This quantity is constant where the bulk phase detergent concentration is low or in presence of swamping electrolyte, so that a plot of a against

$$\frac{A}{A-A_0}e^{A_0/(A-A_0)}e^{\epsilon\psi_0/kT}$$

should yield a straight line.

When ψ_0 is substituted from the simple Gouy equation (with or without allowance for penetration) a linear plot is obtained at low detergent concentrations (so that $\Delta G_{o/w}$ may be estimated) but deviations occur at high concentrations.

In figure 3, two of the isotherms are plotted for sodium alkyl sulphates in swamping salt concentrations and in figure 4 for dodecyltrimethylammonium bromide under similar conditions; ψ_0 has been calculated from equations (28), (21) and (27). Isotherms for sodium octyl sulphate and the quaternary ammonium compound in water are plotted in figure 5.

In the region where the film-ion size becomes important, the top point has been fitted to the straight line of slope $e^{-\Delta G_{o/w}/NkT}$ and from this a value for τ and hence the film-ion radius, a_F has been calculated. This value of a_F is used in determining τ for any other points involved; the values of a_F obtained are compared in table 3.

The isotherm plots are satisfactorily linear for both the sodium dodecyl sulphate and dodecyl trimethylammonium bromide in presence of excess added electrolyte.

TABLE 1. CONSTANTS USED IN CALCULATING POTENTIALS AND PRESSURES AT THE PETROLEUM-ETHER/WATER INTERFACE

solute	counter-ion radius a_i(Å)	$\left[\dfrac{\Delta G_{o/w}^{CH_2}}{NkT}\right]\dfrac{1}{l}$	$\dfrac{4\pi\epsilon 10_0^3}{D}$ (τ in Å)	$10^{16}\epsilon\sqrt{\dfrac{8\pi^2 Na_i^3}{3000DkT}}$	$\sqrt{\dfrac{2\pi\epsilon^2}{D\phi_i kT}}$ (d and τ in Å)	α
Na alkyl sulphates in water, 50 °C	1·2	0·9825	92·92	18·33	2·483	336·4
Na alkyl sulphates in NaCl, 20 °C	1·2	1·083	89·4	17·97	2·534	322·9
dodecyltrimethylammonium bromide in NaCl, 20 °C	1·81	1·083	89·4	33·285	1·340	1109·0
dodecyltrimethylammonium bromide in water, 20 °C	1·95	1·083	89·4	37·235	1·196	1385·5

TABLE 2. SURFACE POTENTIALS AND EQUILIBRIUM DISTANCES OF THE IONIC GROUPS FROM THE INTERFACE (d) FOR SURFACE ACTIVE COMPOUNDS IN WATER AND SODIUM CHLORIDE SOLUTIONS AT 20 °C

n-C$_{12}$H$_{25}$SO$_4$Na

A (Å^2)	d† (Å)	ψ_d (mV)	ψ_τ (mV)	ψ_0 (mV)	$\psi_0{}^*$ (mV)
0.05 M					
43.0	5.70	81.0	147.5	155	145
47.0	5.24	80.0	143		140
50.1	5.05	79.0	138		137
54.7	4.95	78.0	135		133
65.0	4.64	76.0	127		125
76.0	4.35	74.0	119		118
90.5	4.08	73.0	111.5		112
0.01 M					
45.0	5.28	67.0	128	144	126
48.0	4.58	67.5	125		122
49.7	4.52	67.0	123.5		120
51.7	4.44	66.5	121		119
53.5	4.37	66.0	119		117
64.5	4.04	64.0	110		110
72.9	3.85	63.0	105		104
80.1	3.68	61.0	100		98
90.1	3.47	59.5	95		92
0.25 M					
41.2	4.39	53.0	111	120	109
43.5	3.96	53.5	108		106
46.0	3.86	53.0	105.5		99
54.1	3.56	51.0	97.0		95
61.0	3.36	49.0	91.8		90
67.0	3.12	49.0	87.7		86
77.5	3.00	46.0	82.0		82
0.50 M					
41.0	3.98	41.0	95.0	108.5	91.5
43.0	3.40	43.0	93.0		90
45.5	3.29	42.5	89.7		87
49.6	3.10	40.0	84.5		83
59.0	2.81	40.0	77.0		77
69.3	2.57	38.0	70.3		72

n-C$_8$H$_{17}$SO$_4$Na‡

A (Å^2)	d† (Å)	ψ_d (mV)	ψ_τ (mV)	ψ_0 (mV)	$\psi_0{}^*$ (mV)
water					
52.9	4.97	70.0	135.5		134
59.1	5.21	78.0	142		140
71.3	5.49	90.0	150		149
97.3	5.60	100	152		151
133	5.72	111	156		155
216	5.68	122	155		154

n-C$_{12}$H$_{25}$NMe$_3$Br

A (Å^2)	d† (Å)	ψ_d (mV)	ψ_τ (mV)	ψ_0 (mV)	$\psi_0{}^*$ (mV)
water					
58.0	7.76	96.87	161.5	211.8	181
60.5	7.53	106.1	170.7	205.6	167
64.5	6.54	115.2	178.4		175
70.5	6.78	123.6	185.1		182
80.0	7.01	132.5	191.2		185
96.0	7.05	138.7	192.6		189
113	7.19	146.3	196.2		193
131	7.35	155.1	200.7		198
0.07 M					
48.2	5.28	73.1	135.2	144.1	131
51.3	4.83	73.30	131.8		128
55.3	4.68	72.34	127.8		125
61.0	4.50	71.0	122.8		120
68.0	4.30	69.9	117.4		114
77.5	4.07	68.4	111.1		109
91.0	3.80	66.4	103.8		102
102	3.60	64.9	98.4		97
0.10 M					
49.3	5.12	66.0	125.3	139.7	126
52.0	4.49	66.8	122.5		119
56.5	4.33	65.6	118.2		114
60.5	4.20	63.5	114.7		111
67.0	4.02	63.7	109.6		107
76.0	3.80	62.3	103.6		100
91.0	3.50	60.0	95.5		94
109	3.21	57.6	87.6		86
0.25 M					
51.5	4.27	49.7	100.7	116.4	97
54.0	3.61	50.9	98.6		95
58.5	3.47	50.1	94.7		91
64.0	3.31	49.1	90.3		87
69.7	3.16	48.1	86.3		84
76.0	3.01	46.9	82.2		80.5
86.0	2.82	45.6	76.9		76
0.50 M					
49.8	3.97	38.1	86.1	108.4	83
51.8	3.11	40.5	84.8		81.5
54.5	3.01	39.8	82.1		80.5
58.0	2.88	39.1	78.6		76
62.5	2.77	38.1	75.5		73
70.8	2.55	36.6	69.7		68
82.8	2.31	35.1	63.1		64
93.0	2.14	33.7	58.2		58

* Calculated without assuming ionic size (cf. part I).
† In calculating d the vertical distance between adjacent carbon atoms, l has been taken as 1.26 Å.
‡ 50 °C.

32-2

At high areas (low c) the potentials calculated do not differ significantly from those predicted by the equivalent Gouy equation; at low areas, however, ψ_0 is higher than that found from the simpler equation.
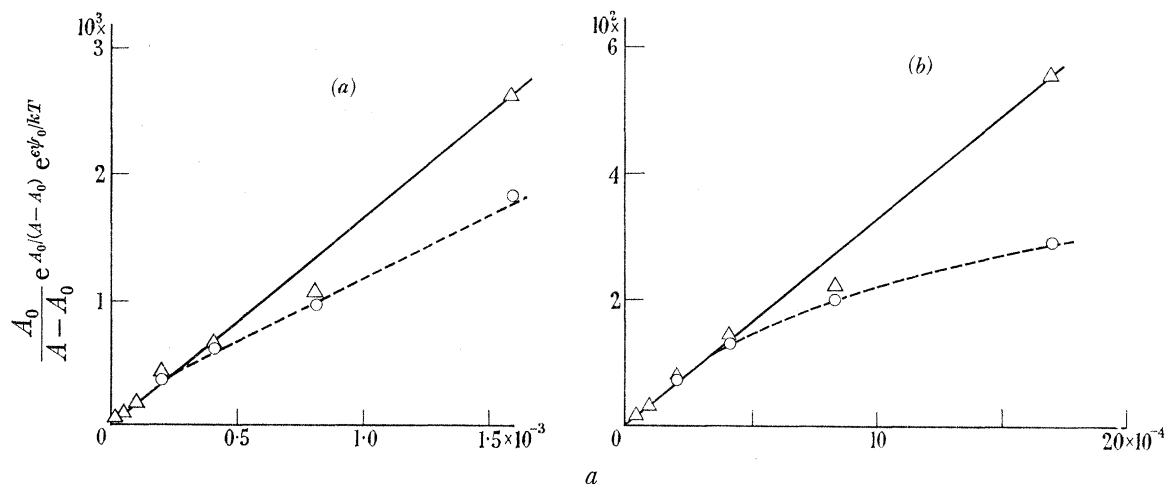

FIGURE 3. Adsorption isotherms (equation (29)) for sodium n-dodecyl sulphate in presence of excess sodium chloride at 20 °C. (a) 0·05M-NaCl; (b) 0·5M-NaCl. △, ψ_0 calculated from equations (27), (21) and (28); ○, ψ_0 calculated without allowing for ionic size.
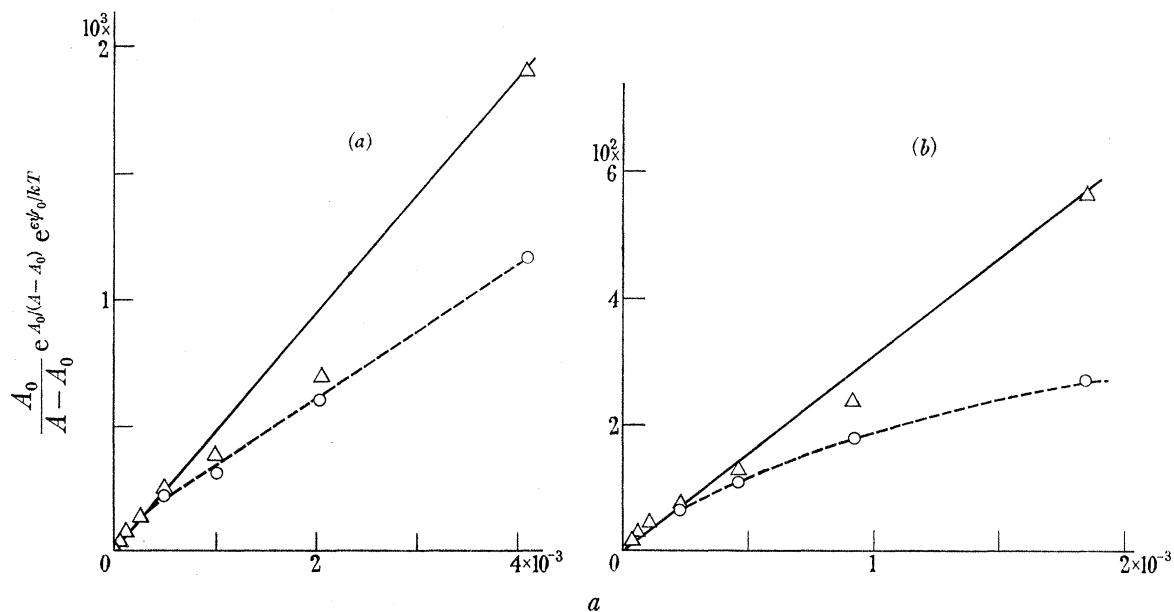
FIGURE 4. Adsorption isotherms for n-dodecyltrimethylammonium bromide in presence of excess sodium chloride at 20 °C. (a) 0·10M-NaCl; (b) 0·25M-NaCl. △, ψ_0 calculated from (27), (21) and (28); ○, ψ_0 calculated without allowing for ionic size.

When no electrolyte is added to the system, the results are more complex. Where the bulk phase detergent concentration is less than 0·008M (which condition holds over the entire experimental range for C_{12}, C_{14}, C_{16} and C_{18} sulphates and for values of $A > 90$ Å^2 for the remaining compounds), the isotherms are satisfactorily linear when the Gouy equation (in its simple form or modified for penetration) is used to calculate the potentials and these are not significantly altered when allowance is made for the finite sizes of the ions. Mathe-

matically, this implies that $\phi_i k_1 \ll 1$ so that equation (15) reduces to a form of the Gouy equation. Moreover, in these particular concentration ranges, A is never small enough for there to be a finite film-ion size correction.

At the higher concentrations, which occur for sodium decyl and octyl sulphates and dodecyltrimethylammonium bromide, the introduction of finite ion sizes certainly increases the value of ψ_0 but not sufficiently to ensure linearity over the whole experimental range.
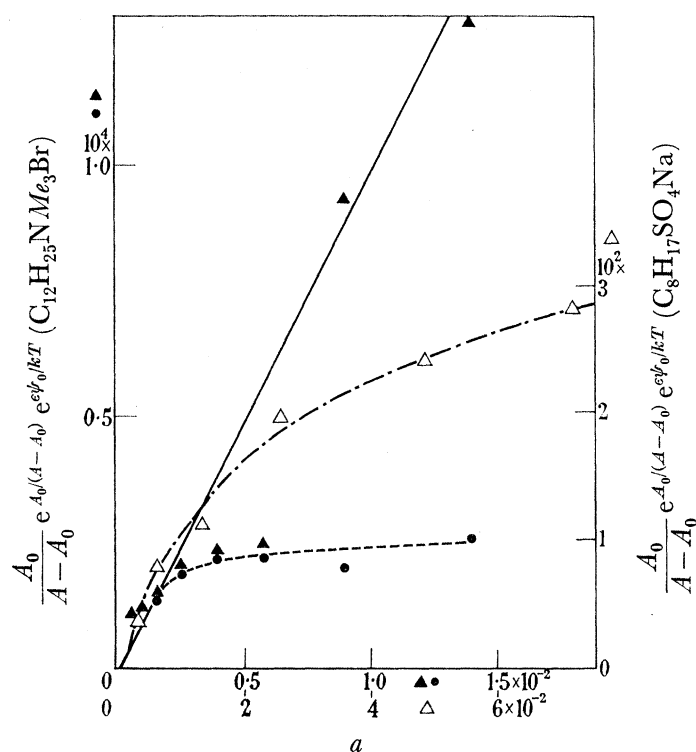
FIGURE 5. Adsorption isotherms for dodecyltrimethylammonium bromide in water at 20 °C: ▲, ψ_0 calculated from (27), (21) and (28); ●, ψ_0 calculated without allowing for ionic size. Adsorption isotherm for sodium octyl sulphate in water at 50 °C: △, ψ_0 calculated from (27), (21) and (28).

TABLE 3. IONIC RADII REQUIRED FOR PREDICTION OF THE FILM-ION

SIZE CORRECTION

Na alkyl sulphate in	film-ion radius a_F	d.t.a.b. in	film-ion radius a_F
0·5M-NaCl	2·79	0·5M-NaCl	2·596
0·25	2·79	0·25	2·658
0·10	2·97	0·10	2·558
0·05	2·866	0·07	2·501
0	—	0	(2·949)
average	2·854	average	2·60
crystal radius	2·65	crystal radius	2·89

The number of ions above the head groups

Comparisons of the values of ψ_r and ψ_d given in table 2 reveal that an important part of the potential drop in the double layer occurs between the plane of the head groups and the phase boundary. By combining equations (14) (integrated between $x = r$ and $x = d$) and

268   D. A. HAYDON AND F. H. TAYLOR ON THE

(16) an equation is obtained from which the number of ions actually present in this region can be calculated; the result is

$$n_p = \frac{1}{A} - \frac{1}{10^{16}\epsilon}\sqrt{\left(\frac{DkT}{2\pi}\right)\left\{\frac{1}{\phi_i}\ln(\phi_i k_1(e^{-ze\psi_T/kT}-1)+1)+\frac{1}{\phi_j}\ln(\phi_j k_1(e^{ze\psi_T/kT}-1)+1)\right\}^2}, \quad (30)$$

where n_p = number of ions/cm^2 of interface, present above the head groups.

Figure 6 shows that n_p increases sharply as A decreases; the fraction of the double layer present in this region also increases in this sense, varying from ~ 0.25 at high areas to ~ 0.4 at low values of A. The number decreases as the ionic strength increases (A being kept constant).
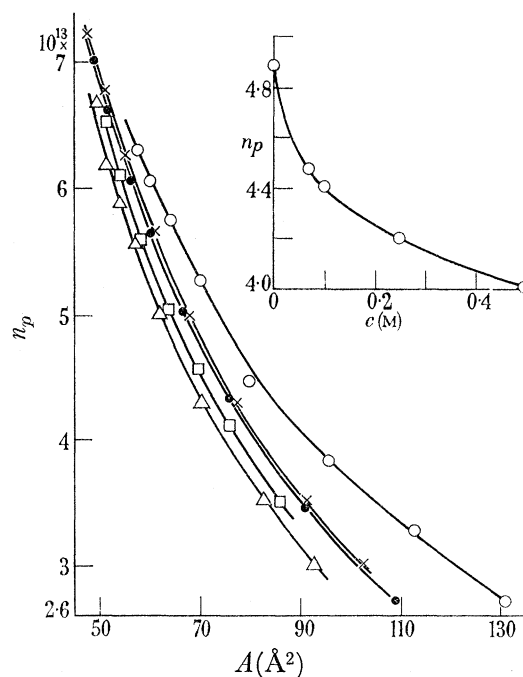
FIGURE 6. Variation of the number of counter-ions cm^2. surface which penetrate above the plane of the film ions (n_p), with the area/adsorbed film ion at the interface. The results are for n-dodecyl-trimethylammonium bromide at 20 °C in presence of: $\circ$, no added electrolyte; $\times$, 0.07 M-NaCl; $\bullet$, 0.1 M-NaCl; $\square$, 0.25 M-NaCl; $\triangle$, 0.5 M-NaCl. Inset: the variation of n_p with the bulk electrolyte concentration, c, for $A = 75$ Å^2.

We may conclude that, in the absence of any specific forces tending to bring the counter ions to the interface or to the plane of the head groups (and there is no evidence for the occurrence of either of these phenomena in the present systems), the value of n_p varies quite simply with the space available in the region above the head groups (i.e. with d). The value of n_p as predicted by equation (30) may be an overestimate in certain systems where the diameter of the counter ion is the same magnitude as d, particularly at low areas where the space above the head groups is restricted.

The differences between the concept of 'penetration' in the above sense and that, usually involving specific interaction and the assumptions of Stern, have already been discussed (part I). The introduction into the present systems of small amounts of counter ions which are likely to interact specifically with some component of the surface phase would provide a sensitive test of specific interaction.

It is interesting to consider what happens when the bulk phase and the surface move relative to one another. The problem is the location of the plane of shear, and the possibility that the ions above the head groups may be carried with the surface when it moves. The ions above the film ions form part of the diffuse phase and in absence of any interference structurally by the film ions, the plane of shear must be at the phase boundary. Here, the potential is ψ_d and it is this potential which should be compared with the zeta potential.
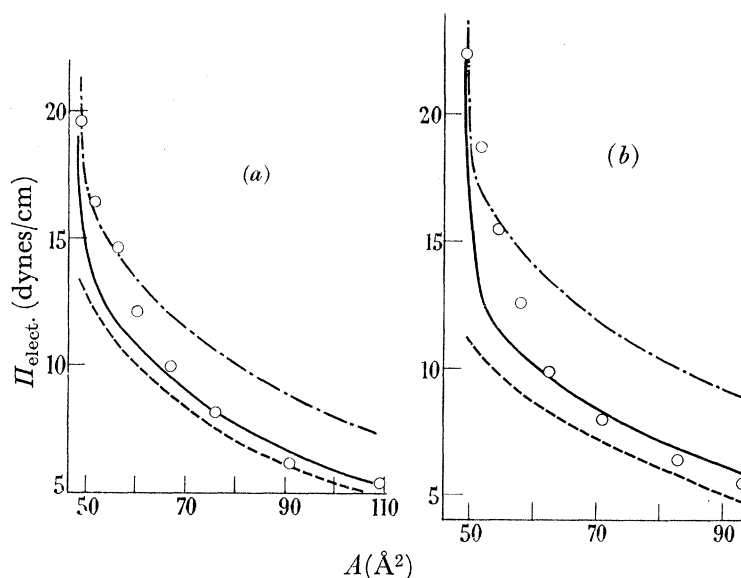
FIGURE 7. Measured and predicted values of the electrical contribution to the surface pressure for n-dodecyltrimethylammonium bromide in presence of excess sodium chloride at 20 °C. (a) 0·10M-NaCl; (b) 0·5M-NaCl. ○, Experimental values; ---, allowance for penetration but not for ionic size; —, allowance for ionic size and penetration; —·—·—, allowance for ionic size only (equation (25)).

If, on the other hand, the ionized film has an appreciable rigidity or viscosity, the plane of shear will be approximately at $x = \tau$ and ψ_τ (figure 1) must be compared with the zeta potential. The mechanical properties of the film are therefore likely to be important in electro-kinetics quite apart from their influence in preventing internal circulation of oil in droplets.

The presence of ions between the film-ion heads and the phase boundary is also likely to be relevant to explanations of high surface viscosities of films on electrolytes as observed by Davies & Rideal (1954).

Equation of state

Comparison of the measured and theoretical Π against A plots provides a simple and convenient but insensitive test of double-layer theory.

Where excess electrolyte is added to the system, the pressures predicted by the simple Gouy equation are too low; those calculated from the equation which allows for the presence of counter ions above the head groups are even lower (see figure 7). When account is taken of the finite sizes of the ions present, pressures are found which agree satisfactorily with the experimental values over the whole experimental range. In figure 7 data are presented for

dodecyltrimethyl bromide only. Results for sodium dodecylsulphate are similar but deviations from ideal behaviour are less marked.

From figure 7 it is seen that there is a tendency for the experimental points to drift, at the lower areas, from the theoretical curve predicted that allows for the presence of part of the diffuse layer above the plane of the head groups and ionic size to that for ionic size only (given by equation (25)). This suggests that we are over-allowing for the 'penetration' effect in this region where the space available to accommodate the ions is of the same order as their dimensions.

In absence of added electrolyte, the C_{18}, C_{16}, C_{14} and C_{12} sodium alkyl sulphates obey the equation of state derived on the assumption that the ions are point charges but with an allowance for penetration; in these cases, the introduction of an ionic size term has little effect on the results, owing to the low ionic strength.
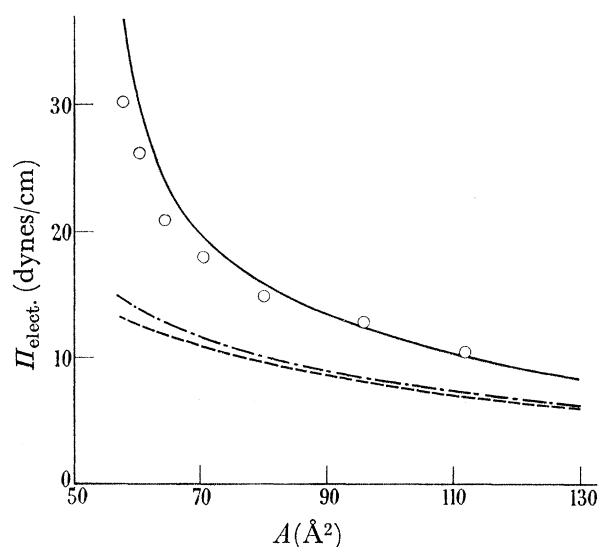

FIGURE 8. Measured and predicted electrical contributions to the pressure for n-dodecyltrimethyl-ammonium bromide in water at 20 °C. ○, Experimental values; ——, calculated curve allowing for ionic size and penetration; —·—·—, curve calculated for ionic size only (25); ---, curve given by simple Gouy equation (26).

The electrical contribution to the pressure calculated for dodecyltrimethylammonium bromide in water agrees far better with the experimental results than does that given by the simple Gouy theory (equation (26)) or that allowing for ionic size only. At low areas the theory slightly overestimates the pressure.

For sodium octyl sulphate, both the pressure calculated by numerical integration of (22) and that which allows for penetration only, overestimate the electrical contribution to the pressure by about 4 dynes over the whole experimental range.

DISCUSSION

The comparisons made above and in part I between observed and theoretical electrical potentials in the region of an adsorbed charged film suggest strongly that the simple Gouy equation often does not predict the double-layer potential accurately and that this failure is mainly due to:

(1) A neglect of the possibility of penetration of ions above the plane of the charged head groups. This arises because the head groups are usually situated a short distance from the phase boundary.

(2) The assumption that all the ions present are point charges.

When these two factors are taken into account, most of the discrepancies between theoretical and experimental results disappear.

The only serious divergence between experimental potentials and those calculated from our modified Gouy theory occurs in systems to which no electrolyte has been added where the bulk concentration of surface active agent exceeds $\sim 0\cdot01$ M. Two possible causes for this behaviour may be considered:

(1) That at high detergent concentration ϕ_i, the effective volume of the counter ion is not a constant.

(2) That the expression used to calculate the bulk phase activity coefficients is inapplicable at these concentrations of long-chain electrolytes.

Of these possibilities, the latter seems to be the most likely. Unfortunately, no reliable measurements of the activity coefficients in such systems have yet been made. Investigations into the behaviour of short-chain surface active agents adsorbed at the oil/water interface are now in progress.

The general validity and limitations of the proposed modifications to the Gouy equation can only be ascertained by investigating the adsorption of various types of surface-active agent in presence of counter ions of widely varying sizes (preferably under conditions where other corrections are unimportant); this should help in determining the magnitude of specific adsorption effects. The least satisfactory aspects of the present approach certainly lie in the expression used to calculate τ (equation (17)) which is based on a very simple geometrical model for the sytem, and in the uncertainty as to the correct value of ϕ to employ for any system. The values of the ionic volumes employed in this paper are almost certainly too low so that we are underestimating the effects of ionic size on the potentials. An examination of the isotherms in figures 4 and 5 certainly suggests that this is so. At the lower areas (but where the film-ions correction is not important) the potentials predicted from equation (16) are still too low. The discrepancies largely disappear if radii of $1\cdot4$ and $2\cdot4$ Å are employed for Na^+ and Cl^-, respectively.

Many authors have considered possible corrections to the theory of the flat diffuse double layer but, until recently, little suitable experimental data has been available for testing modified forms of the Gouy equation.

Besides the two corrections referred to above, the following effects have been held to be responsible for deviations from the Gouy equation.

(i) The effect of ionic strength and electric field strength on the dielectric constant near the interface (dielectric saturation).

(ii) Electric polarization of the solution near the interface.

(iii) Coulombic interactions between particles in the diffuse phase (image forces: 'self atmosphere' effect of ions).

(iv) Effects which may be safely disregarded in the present systems. These include electrostriction (shown essentially to be a second-order effect by Levine (1953)); non-Coulombic interactions with the interface and dehydration phenomena (which Grahame

(1951) has suggested to be unimportant unless the dielectric constant of non-aqueous phase is high; the latter effect in particular, has been shown in part I to be negligible in the present systems; finally, there are discreteness of charge effects which Grahame (1958) considers also to be relatively unimportant where an insulating surface is concerned.

Of recent attempts to introduce and to estimate the effects of these factors, the most comprehensive are those of Bolt (1955), whose results apply at high potentials only, and Sparnaay (1958) who neglects corrections (iii) and (iv) above.

Dielectric saturation (Grahame 1950; Booth 1951) leads to a lowering of the dielectric constant compared with the bulk phase value and hence to an increase in surface concentration. The experimental results described above suggest that this effect is unimportant in the present systems, since it is in precisely those systems which show the highest potentials (C_{12}–C_{18}) alkyl sulphates in water, that the simple Gouy equation is most closely obeyed. Dielectric saturation therefore either leads to a correction to the Gouy equation much smaller than that due to ionic size, or its effects are counterbalanced by others which tend to decrease the ionic concentration near the surface. In fact, each of these propositions seem to be true; calculations from the empirical equations of Malsch (1929) and Hasted, Ritson & Collie (1948) demonstrate that, in the experimental range considered here, the dielectric constant effect is smaller than that due to ionic size and results in a lowering of the potential of between 1 and 3 %.

The solution near a charged interface is polarized by the electric field (Prigogine, Mazur & Defay 1953) and the effect is to decrease the ionic concentration in this region. Bolt and Sparnaay, although they give slightly different treatments of the two effects, both conclude that dielectric saturation and polarization corrections are of the same order and tend to cancel out almost completely where the field strength is less than 5×10^6 V/cm, and this is always so in the present systems.

Thus, the only important remaining correction to the Gouy equation which might be considered is that due to Coulombic interactions between particles in the diffuse phase (iii). According to Williams (1953) this effect will tend to decrease the ionic concentration near the surface, the reduction in ψ slowly decreasing as κx increases. Bolt concludes that where this effect is at all important (at high values of κx or where the surface concentration of ions is less than ~ 1.5M), it will tend to cancel with the short-range repulsion effect (which we may equate roughly with our ionic size effect). The ionic size effect exceeds the Coulombic interaction in the range of distances and potentials for which equation (21) is valid. We agree with Bolt that at greater distances the two effects are of the same order of magnitude which means that equation (3) without the term $\sqrt{(1 - A_0'/A)}$ will predict with accuracy the decay of potential with distance.

Appendix A. Insoluble monolayers

The expressions for the equations of state given above and in part I should certainly apply to insoluble charged films. Where these are spread on salt solutions the equations need no modification. If the insoluble films are spread on water, however, the expressions derived for substrates consisting of excess concentrations of electrolyte will still apply since the effective bulk electrolyte is constant,

(1) when the potential is varied by compression of a spread film;

(2) since the very small bulk electrolyte concentration is swamped by the presence of hydroxyl and hydrogen ions.

The theory of penetration of counter ions proposed in part I will apply to insoluble monolayers (if no specific adsorption forces operate). The presence of counter ions above the film will not alter the kinetic contribution to the surface pressure.

Appendix B. The variation of potential with distance from the interface

If we define y by the relation

$$y^2 = \ln\{\phi_i k_1 (e^{-ze\psi/kT} - 1) + 1\}, \tag{B1}$$

then the equation (19) may be rewritten as

$$-\frac{ze}{kT}\sqrt{\left(\frac{8\pi kT}{D\phi_i}\right)}\, dx = \frac{1}{y}\, d\ln(e^{y^2} - 1 + \phi_i k_1) \tag{B2}$$

y^2 lies, in practice, between 0 and 0·2. The exponential term may be expanded to yield a rapidly converging series

$$-\frac{ze}{kT}\sqrt{\left(\frac{8\pi kT}{D\phi_i}\right)}\, dx = \frac{2dy}{y^2} + \frac{1}{y}\, d\ln\left\{1 + \frac{\phi_i k_1}{y^2} + \sum_2^\infty \frac{y^{2n-2}}{n!}\right\}. \tag{B3}$$

The quantity

$$\left(\frac{\phi_i k_1}{y^2} + \sum_2^\infty \frac{y^{2n-2}}{n!}\right)$$

is always very much less than unity; the maximum value of $\phi_i k_1$ (for dodecyltrimethyl-ammonium bromide in 0·5 M-NaCl) is 0·00753 so that the expression attains a maximum value of $\sim 0\cdot14$. We may therefore expand the logarithmic function as

$$\frac{1}{y}\, d\ln\left\{1 + \frac{\phi_i k_1}{y^2} + \sum_2^\infty \frac{y^{2n-2}}{n!}\right\}$$

$$= \frac{1}{y}\, d\left\{\left[\sum_2^\infty \frac{y^{2n-2}}{n!} + \frac{\phi_i k_1}{y^2}\right] - \frac{1}{2}\left[\frac{\phi_i k_1}{y^2} + \sum_2^\infty \frac{y^{2n-2}}{n!}\right]^2 \cdots \frac{(-1)^{m+1}}{m}\left[\frac{\phi_i k_1}{y^2} + \sum_2^\infty \frac{y^{2n-2}}{n!}\right]^m\right\}$$

or, on differentiating,

$$dy\left\{\sum_2^\infty \frac{2n-2}{n!}y^{2n-4} - \frac{2\phi_i k_1}{y^4}\right\}\left\{1 - \left[\frac{\phi_i k_1}{y^2} + \sum_2^\infty \frac{y^{2n-2}}{n!}\right] + \left[\frac{\phi_i k_1}{y^2} + \sum_2^\infty \frac{y^{2n-2}}{n!}\right]^2 + (-1)^m\left[\frac{\phi_i k_1}{y^2} + \sum_2^\infty \frac{y^{2n-2}}{n!}\right]^m\right\}.$$

Equation (B3) may now be integrated to yield

$$-\frac{ze}{kT}\sqrt{\left(\frac{8\pi kT}{D\phi_i}\right)}x = \frac{2}{y}\left\{-1 + \frac{y^2}{2}\left[1 + \frac{(\phi_i k_1)}{6} + \frac{(\phi_i k_1)^2}{12} - \frac{(\phi_i k_1)^3}{1}\right]\right.$$

$$+ \frac{y^4}{2}\left[-\frac{1}{18} + \frac{(\phi_i k_1)^2}{45}\right] + \frac{y^6}{2}\left[\frac{91}{100}(\phi_i k_1)\right] \cdots + \frac{1}{2y^2}\left[\frac{2(\phi_i k_1)}{3} + \frac{(\phi_i k_1)^2}{3} - \frac{(\phi_i k_1)^3}{9}\right]$$

$$\left. + \frac{1}{2y^4}\left[-\frac{2}{5}(\phi_i k_1)^2 - \frac{2}{5}(\phi_i k_1)^3\right] + \sum_3^\infty\left[\left(\frac{\phi_i k_1}{y^2}\right)^n \frac{1}{2n+1}(-1)^{n+1}\right]\right\}.$$

In the expansion, terms higher than y^6 and $(\phi_i k_1)^3$ are neglected. Considering the relative magnitudes of the various terms, the expression as used becomes

$$-\frac{z\epsilon}{2kT}\sqrt{\left(\frac{8\pi kT}{D\phi_i}\right)}x = \frac{1}{y}\left\{-1+\frac{y^2}{2}+\frac{y^4}{36}+\sum_1^\infty\left(\frac{\phi_i k_1}{y^2}\right)^n\frac{(-1)^{n+1}}{2n+1}\right\}. \tag{B4}$$

The term in $(\phi_i k_1)/y^2$ is found to be negligible in cases where no electrolyte is added to the system. The usefulness of (B4) is limited not so much by the range over which the series expansions apply as by the range of validity of equation (19) (i.e. (B2)).

Although equation (13) cannot be integrated completely, approximations can be obtained for low values of the potentials and large distances which can be integrated. Little reliable experimental data is available in this region however.

Appendix C. The equation of state

The integral
$$\int\frac{1}{A^2}\ln\left(e^{\alpha/A^2}-1\right)\mathrm{d}A \tag{C1}$$

cannot be evaluated completely. We may split it into two parts to yield

$$\int\left\{\frac{\alpha}{2A^2}+\ln 2\right\}\frac{\mathrm{d}A}{A^2}-\int\ln\sinh\frac{\alpha}{2}\left(\frac{1}{A}\right)^2 d\left(\frac{1}{A}\right) \tag{C2}$$

α/A^2 varies from $0\cdot005$ to $0\cdot7$, so that the hyperbolic function, when expanded as a series, converges rapidly

$$\int\ln\left[\sinh\frac{\alpha}{2}\left(\frac{1}{A}\right)^2\right]d\left(\frac{1}{A}\right)=\int\ln\sum_1^\infty\left[\frac{\alpha}{2}\left(\frac{1}{A}\right)^2\right]^{2n-1}\frac{1}{2n-1}d\left(\frac{1}{A}\right)$$
$$=\int\ln\left[\frac{\alpha}{2}\left(\frac{1}{A}\right)^2\right]d\left(\frac{1}{A}\right)+\int\ln\left(1+\sum_2^\infty\left[\frac{\alpha}{2}\left(\frac{1}{A}\right)^2\right]^{2n-2}\frac{1}{(2n-1)!}\right)d\left(\frac{1}{A}\right).$$

The condition for expansion of the logarithm is that

$$\frac{A^2}{\alpha}\sinh\frac{\alpha}{2}\left(\frac{1}{A}\right)^2<1;$$

this quantity is always of the order of $0\cdot5$ so that it is only necessary to take the first few terms in the expansion. Integral (C2) therefore becomes

$$\int\left[\frac{\alpha}{2A^2}+\ln\left(\frac{\alpha}{A^2}\right)\right]\frac{\mathrm{d}A}{A^2}-\int\left[\frac{\alpha^2}{A^4}\frac{1}{2^2}\frac{1}{3!}+\frac{\alpha^4}{A^8}\frac{1}{2^4}\frac{1}{5!}\cdots\right]d\left(\frac{1}{A}\right)$$
$$+\int\frac{1}{2}\left[\frac{\alpha^2}{A^4}\frac{1}{2^2}\frac{1}{3!}+\frac{\alpha^4}{A^8}\frac{1}{2^4}\frac{1}{5!}\right]^2 d\left(\frac{1}{A}\right)-\int\frac{1}{3}\left[\frac{\alpha^2}{A^4}\frac{1}{2^2}\frac{1}{3!}+\frac{\alpha^4}{A^8}\frac{1}{2^4}\frac{1}{5!}\right]^3 d\left(\frac{1}{A}\right)\cdots.$$

Upon integration this becomes

$$-\frac{1}{A}\left[\ln\frac{\alpha}{A^2}-2\right]-\frac{\alpha}{6A^3}-\frac{\alpha}{A^5 2.3!5}-\left[\frac{1}{5!}-\frac{1}{2(3!)^2}\right]\frac{\alpha^4}{2^4 9}\left(\frac{1}{A}\right)^9.$$

All terms after the third are completely negligible.

The result may be added to the other terms of the integral; applying the boundary conditions $\Pi=0$ when $A\to\infty$ we obtain the equation of state.

REFERENCES

Aickin, R. G. & Palmer, R. C. 1944 *Trans. Faraday Soc.* **40**, 116.

Bikerman, J. J. 1942 *Phil. Mag.* **33**, 384.

Bolt, G. H. 1955 *J. Colloid Sci.* **10**, 206.

Booth, F. 1951 *J. Chem. Phys.* **19**, 391, 1327, 1615.

Brodowsky, H. & Strehlow H. 1959 *Z. Elektrochem.* **63**, 262.

Davies, J. T. 1951 *Proc. Roy. Soc.* A, **208**, 225.

Davies, J. T. & Rideal, E. K. 1954 *J. Colloid Sci. Suppl.* **1**, 1.

Falkenhagen, H. & Kelbg, G. 1959 *Modern aspects of electrochemistry*, **2**, chap. 1, p, 37. London: Butterworths.

Grahame, D. C. 1950 *J. Chem. Phys.* **18**, 903.

Grahame, D. C. 1951 *J. Electrochem. Soc.* **98**, 343.

Grahame, D. C. 1958 *Z. Elektrochem.* **62**, 264.

Hasted, J. B., Ritson, D. M. & Collie, C. H. 1948 *J. Chem. Phys.* **16**, 1.

Haydon, D. A. & Taylor, F. H. 1960 *Phil. Trans.* A, **252**, 225 (part I).

Kling, W. & Lange, H. 1957 *Proc. 2nd Int. Cong. Surf. Activity*, **1**, 295. London: Butterworths.

Levine, S. 1953 *Proc. Phys. Soc.* A, **66**, 365.

Malsch, J. 1929 *Phys. Z.* **30**, 837.

Ohlenbusch, H. D. 1956 *Z. Elektrochem.* **60**, 607.

Prigogine, I., Mazur, P. & Defay, R. 1953 *J. Chim. Phys.* **50**, 146.

Schlögl, R. 1954 *Z. Phys. Chem.* **202**, 379.

Sparnaay, M. J. 1958 *Rec. trav. Chim. Pays-Bas.* **77**, 872.

Williams, W. E. 1953 *Proc. Phys. Soc.* A, **66**, 372.