

On Adsorption at the Oil/Water Interface and the Calculation of Electrical Potentials in the Aqueous Surface Phase I. Neutral Molecules and a Simplified Treatment for Ions

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

I. NEUTRAL MOLECULES AND A SIMPLIFIED TREATMENT FOR IONS

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Films of neutral substances adsorbed at the oil/water interface obey the equation of state and the adsorption isotherm which are derived assuming complete mobility of the molecules in the interface. The equations are obeyed down to areas of $\sim 30\text{\AA}^2$ per molecule; deviations which occur below this value result from interactions between the adsorbed molecules.

Adsorbed films of completely ionized sodium alkyl sulphates and quaternary ammonium compounds also obey these equations when allowance is made for the electrical contribution to the adsorption energy and for electrical interaction between the ions in the aqueous bulk phase.

The activity coefficients cannot be neglected in these systems at concentrations exceeding 0.001M. In the range 0.001 to 0.09M the 'complete' Debye-Hückel equation is used to calculate these coefficients; at the higher concentrations (for sodium decyl and octyl sulphates) the activity coefficients thus calculated are suspect.

The electrical energy is given exactly by a modified Gouy equation, when allowance is made for the film ions being situated a finite equilibrium distance from the interface and for the fact that counter-ions will be present above the head groups. This modified equation yields linear plots for the isotherm and leads to consistent values for the free energy of adsorption of the molecules.

It also

(a) demonstrates that the electrical potential at the phase boundary (ψ_d) differs from that in the plane for the film ions (ψ_0) and that the true ψ_0 is lower than that calculated from the simple Gouy equation; from the measured surface potentials (ΔV) interpreted by the equation of Schulman & Hughes (1932), it is shown that the calculated ψ_d is experimentally confirmed;

(b) predicts much more accurately than the simple equation the relation between the observed surface pressure (Π) and area per molecule (equation of state).

Deviations from the equations occur for short-chain compounds (C_8 and C_{10}) in water at high concentrations, and for all surface-active agents in high electrolyte concentrations ($> M/100$), especially where $A < 70 \text{ \AA}^2$. It is concluded that these deviations result mainly from a neglect of ionic size in the theoretical treatment.

There is no evidence in any of the systems for any specific interaction between counter ions and adsorbed film ions.

The experimental results are inconsistent with the view that appreciable energy changes associated with dehydration of the surface-active ions occur as they approach the oil/water interface.

INTRODUCTION

Studies of the adsorption of surface-active materials at the oil/water interface provide a convenient method for testing electrical double-layer theory and for determining the state of water and ions in the neighbourhood of an interface. The oil/water interface possesses the advantage over that between air and water that non-electrical interactions between adsorbed molecules (due to dipole and van der Waals's forces) are negligible over almost the entire experimental range.

In the theoretical treatment of adsorption, many authors use equations which imply a Langmuirian form for the adsorption isotherm. This assumes that the adsorbed molecules are immobile and adsorb on 'sites' in the surface and has the form

$$\frac{A_0}{A - A_0} = a e^{-\Delta G/kT}, \quad (1)$$

where A = area/molecule in the interface ($\text{\AA}^2/\text{molecule}$),

A_0 = limiting area/molecule in the interface ($\text{\AA}^2/\text{molecule}$),

ΔG = free energy of adsorption of the molecule,

a = bulk activity of the molecule in the aqueous phase.

It is more likely, however, that adsorbed molecules at an oil/water interface will be completely mobile, in which instance the equation becomes (de Boer 1953; Olivier & Ross 1957)

$$\frac{A_0}{A - A_0} e^{A_0/(A - A_0)} = a e^{-\Delta G/kT}. \quad (2)$$

It is only at high area (low concentrations) that equations (1) and (2) converge; at areas less than 100 \AA^2 per molecule they diverge considerably.

The total free energy of adsorption, ΔG , represents the work done by the molecule upon adsorption. This may be divided into work done against electrical forces ($\epsilon\psi_0$ univalent ion, where ψ_0 is the potential in the plane of the film ions) and a non-electrical component which, at the oil/water interface, is found to be independent of A when $A > 30 \text{ \AA}^2$ (see below), indicating that the only interaction between adsorbed molecules is due to electrical forces. This non-electrical component includes the work of transfer of the hydrocarbon chains from the aqueous bulk phase to the interface and that for the transfer of the polar groups.

We may therefore write

$$\Delta G = \Delta G_{o/w} + \epsilon\psi_0. \quad (3)$$

Both these components of ΔG vary to some extent with electrolyte concentration. It is possible also that a term for hydration changes at the interface should be included.

By combining either (1) or (2) with the Gibbs equation, other equations may be derived and used to test the assumptions of the theories. For strongly adsorbed neutral molecules and for ionized substances in swamping electrolyte the Gibbs equation takes the form (Davies 1952)

$$\frac{d\Pi}{d \ln a} = \frac{kT}{A}. \quad (4)$$

Non-ionized solutes

For neutral molecules $\psi_0 = 0$ and combination of (1) with the complete Gibbs equation (as opposed to the approximate form (4) for strongly adsorbed substances) yields, for *non-mobile* films,

$$\frac{A_0}{kT} (1 + a e^{-\Delta G_0/w/kT}) \frac{d\Pi}{da} = e^{-\Delta G_0/w/kT} - 1 \quad (5)$$

or, at low concentrations (Phillips & Rideal 1955 *a*)

$$1 + \frac{A_0}{kT} \left(\frac{d\Pi}{da} \right)_{a \rightarrow 0} = e^{-\Delta G_0/w/kT}. \quad (6)$$

Integration of (6) yields a relation between Π and a of the form of the Szyszkowski equation

$$\Pi = \frac{kT}{A_0} (1 - e^{-\Delta G_0/w/kT}) \ln (1 + a e^{-\Delta G_0/w/kT}). \quad (7)$$

Finally, if a instead of A is eliminated, the Volmer-Frumkin equation of state is obtained ($e^{\Delta G_0/w/kT} \ll 1$):

$$\Pi = \frac{kT}{A_0} \ln \frac{A}{A - A_0}. \quad (8)$$

For *mobile films*, on the other hand, the relationships derivable from (2) and (4) include the equation of state originally derived by Langmuir (1917)

$$\Pi = \frac{kT}{A - A_0}. \quad (9)$$

Ionized solutes in presence of swamping electrolyte

If it is assumed that, for ionized uni-univalent solutes, the Gouy equation holds in the form

$$\frac{10^{16} \epsilon}{A \sqrt{c'}} \sqrt{\frac{1000\pi}{2DkTN}} = \sinh \frac{\epsilon \psi_0}{2kT} \quad (10)$$

(where c' is the total electrolyte concentration in moles/l.), one may derive for presence of swamping electrolyte, the equations for *non-mobile* films equivalent to (7) and (8), for charged molecules. These are

$$\Pi = \frac{kT}{A_0} \ln (1 + a e^{-\Delta G_0/w/kT}) + \frac{kT \sqrt{c'}}{10^{16} \epsilon \sqrt{\left(\frac{8DkTN}{1000\pi}\right)}} \left\{ \cosh \frac{\epsilon \psi_0}{2kT} - 1 \right\} \quad (11)$$

and

$$\Pi = \frac{kT}{A_0} \ln \frac{A}{A - A_0} + \frac{kT \sqrt{c'}}{10^{16} \epsilon \sqrt{\left(\frac{8DkTN}{1000\pi}\right)}} \left\{ \cosh \frac{\epsilon \psi_0}{2kT} - 1 \right\}. \quad (12)$$

Davies (1958 *a, b*) has examined various approximations of the above equations and claims that they fit experimental data for adsorbed detergents at the oil/water interface.

Mobile films of ionized materials in presence of excess electrolyte should, if equation (10) holds, obey the equation of state of Davies (1951), here derived from equations (2), (4) and (10), namely

$$\Pi = \frac{kT}{A-A_0} + \frac{kT\sqrt{c'}}{10^{16}\epsilon\sqrt{\left(\frac{8DkTN}{1000\pi}\right)\left\{\cosh\frac{\epsilon\psi_0}{2kT}-1\right\}}}. \quad (13)$$

Tests of equations of state are usually employed in investigating the properties of adsorbed molecules. This is not a sensitive method for determining the importance of the mobility term in equation (2) or the range of validity of the Gouy equation, although papers by Davies (1956) and Haydon & Phillips (1958) have revealed that equation (13) is often seriously inadequate for predicting surface pressures.

Davies's (1958 *a, b*) generalized treatment of adsorption is unsatisfactory because it deals only with a limited range of potentials and detergent concentrations, and because equations derived for mobile films are combined with those based on the assumptions of Stern for immobile molecules.

THEORETICAL SECTION

Calculation of activity coefficients

Knowledge of the activity coefficients of the detergents is necessary for the calculation of A from the Gibbs equation, for determination of the free energy of adsorption of the compound (equations (2) and (6)) and, in certain instances, for the calculation of the theoretical equation of state.

For long-chain surface-active agents in water, the activity begins to differ significantly from the concentration when the latter exceeds 10^{-3} M. The 'complete' Debye-Hückel equation has been employed in this paper. We have, for uni-univalent electrolytes,

$$\log_{10} f_{\pm} = -\frac{\bar{A}\sqrt{(c_1+c)}}{1+a_i B\sqrt{(c_i+c)}}, \quad (14)$$

where c = detergent concentration;

c_1 = concentration of added electrolyte;

\bar{A}, B = constants;

a_i = ionic radius.

The 'ionic radius', which is a mean for the surface active and counter-ions, is arbitrarily taken as 5 \AA in all cases (cf. 4 to 4.5 for Na^+ , 3 \AA for Cl^- (Kielland 1937) and perhaps a higher value for alkyl sulphate and quaternary ammonium ions).

Combination of (14) after differentiation, with the Gibbs equation yields

$$A = kT \left[1 - \frac{2.303\bar{A}c_i^{-\frac{1}{2}}c}{2(1+a_i B\sqrt{c_i})^2} \right] \frac{d \ln c}{dII} \quad (15)$$

for swamping electrolyte, when $c_i \gg c$; and with the Gibbs equation (18), for no added electrolyte ($c_i = 0$)

$$A = 2kT \left[1 - \frac{2.303\bar{A}\sqrt{c}}{2(1+a_i B\sqrt{c})^2} \right] \frac{d \ln c}{dII}. \quad (16)$$

Various approximations can be made to equation (16). If $d \log f_{\pm} / d \log c \ll 1$ then the equation employed by Kling & Lange (1957) can be derived. At very low detergent concentrations the form equivalent to the Debye-Hückel limiting law is

$$A \rightarrow 2kT \left[1 - \frac{2.303\bar{A}\sqrt{c}}{2} \right] \frac{d \ln c}{dII}. \quad (17)$$

In presence of excess electrolyte, the activity coefficient, given by (14) is constant; it disappears upon differentiation and does not appear in the equation of state which, therefore, is still given by equation (13).

The equation of state for ionized solutes in absence of added electrolyte

Much controversy has arisen over the form of the equation of state to be used for adsorbed films in the absence of added electrolyte. For fully ionized solutes, where the bulk concentration is very much greater than the hydroxyl or hydrogen ion concentrations, the Gibbs equation becomes (Pethica 1954; Cockbain 1954; Haydon & Phillips 1958)

$$\frac{d\Pi}{d \ln a} = \frac{2kT}{A}. \quad (18)$$

Equation (2) may be differentiated and rearranged to give

$$\frac{-A_0 dA}{(A-A_0)^2} - \frac{dA}{A-A_0} = \frac{da}{a} - \frac{1}{kT} d(\Delta G). \quad (19)$$

In this instance the detergent concentration, c , constitutes the total electrolyte; differentiation of (3), assuming the Gouy equation (10) to hold, gives

$$d(\Delta G) = -\frac{kT \times 10^{16}}{A\sqrt{c}} \sqrt{\left(\frac{1000\pi}{2DkTN}\right) \left(\frac{2dA}{A} + \frac{dc}{c}\right)} \frac{1}{\cosh \sinh^{-1} \frac{10^{16}\epsilon}{A\sqrt{c}} \sqrt{\frac{1000\pi}{2DkTN}}}. \quad (20)$$

$d(\Delta G)$ can now be eliminated from equations (19) and (20). The activity, a , and concentration, c , can be substituted for from the Gibbs equation (18) to yield a differential equation in Π and A which, on integration, gives the equation of state. This integration cannot be carried out completely unless two assumptions are made. These are

(i) that

$$\sinh \frac{\epsilon\psi_0}{2kT} = \frac{1}{2} e^{\epsilon\psi_0/2kT} \left(= \cosh \frac{\epsilon\psi_0}{2kT} \right).$$

This approximation applies where $\psi_0 > 100$ mV and holds over the whole of the normal experimental range in water.

(ii) That the activity and concentration of the detergent in the bulk phase are equal; for the shorter chain detergents this is not always a justifiable assumption.

With these assumptions, combination of (19) and (20) yields

$$-\frac{A_0 dA}{(A-A_0)^2} - \frac{dA}{A-A_0} = 2kT \left(\frac{dc}{c} + \frac{dA}{A} \right). \quad (21)$$

Integration after combination with the Gibbs equation leads to the equation of state

$$\Pi = \frac{kT}{A-A_0} + \frac{2kT}{A}. \quad (22)$$

Although this result can be obtained by the approximation for large potentials of the equation of state (13) proposed by Davies (1951), neither his complete equation nor that derived for absence of added electrolyte by Haydon (1958*a*) or by Phillips & Rideal (1955*b*) is correct. In adding the electrical free energy of the double layer to the kinetic term, these authors overlook that, when no added electrolyte is present c' ($= c$) is a variable. Also, their equations cannot be converted into an acceptable isotherm.

If the activity coefficient is not neglected, the equation of state becomes

$$\Pi = \frac{kT}{A - A_0} + \frac{2kT}{A} + kT \int \frac{1}{A} d \ln f_{\pm} + \text{constant.} \quad (23)$$

The last term cannot easily be integrated but an expression for $\log_{10} f_{\pm}$ is given by (14) with $c_i = 0$, permitting the result to be obtained graphically.

Calculation of potentials in the double layer

The following assumptions are implicit in the use of the Gouy equation (10) to calculate potentials:

- (i) that the surface charge is uniform ('smeared out');
- (ii) that the film of adsorbed ions is planar and impenetrable to the counter-ions, i.e. the whole space charge is on one side only of the charged surface;
- (iii) that all ions are point charges;
- (iv) that the dielectric constant in the vicinity of the charged film is the same as that in the bulk phase.

In this paper it is proposed to modify the second of these assumptions only. Several authors (Aickin & Palmer 1944; Davies & Rideal 1954; Phillips & Rideal 1955*a*; Payens 1955) suggest that the plane of the head groups in a monolayer may be penetrable by the counter-ions and cite experimental evidence to support this idea. Certainly, the plane of the head groups is unlikely to coincide with the phase boundary. We are dealing with a reversible system and can calculate approximately the number of $-\text{CH}_2-$ groups of a detergent immersed in the aqueous phase by dividing the electrical component of the adsorption energy of a molecule by the work of desorption of one $-\text{CH}_2-$ group from the oil/water interface to the aqueous phase. The results suggest that, at equilibrium, in systems containing no added electrolyte, an adsorbed long-chain sulphate ion has, on the average, just over half its chain immersed in the aqueous phase. For any particular sulphate this holds roughly over the whole experimental range since, in these systems, ψ_0 does not vary greatly as A and c alter.

Addition of swamping electrolyte lowers ψ_0 and, so, fewer carbon atoms are, in this instance, in the aqueous phase; the actual number varies with A (cf. table 3).

There is, then, a region above the head groups which can accommodate counter-ions forming the diffuse layer, and the electrical potential will fall off on each side of the plane of the head groups as depicted in figure 1. Allowance for this fall-off in the theory will yield smaller values of ψ_0 than predicted by the Gouy equation (10). For comparison with the experimental surface potentials (ΔV), calculations should involve the potential at the interface ψ_d , which varies with the distance of the head groups from the surface (d).

In the following treatment, allowance is made for limitation of space available for the counter-ions above the plane of the head groups by the presence of the hydrocarbon chains. This limitation is independent of distance from the phase boundary and is a function only of A . The basis for the derivation of the Gouy-type equation is then the modified Boltzmann equation

$$n_i = n_0 e^{-z_i e \psi / kT} (1 - A'_0/A), \quad (24)$$

where A is the area/molecule and A'_0 is the cross-sectional area of the hydrocarbon chain (taken as 20 Å).

From equation (24) we derive the expressions for uni-univalent electrolytes,

$$\frac{d\psi}{dx} = -\sqrt{\left\{\frac{32\pi n_0 kT}{D} \left(1 - \frac{A'_0}{A}\right)\right\}} \sinh \frac{\epsilon\psi}{2kT} \quad (25)$$

and

$$\kappa d \sqrt{\left(1 - \frac{A'_0}{A}\right)} = \ln \left\{ \frac{\tanh \epsilon\psi_0/4kT}{\tanh \epsilon\psi_d/4kT} \right\}, \quad (26)$$

where κ has its usual significance.

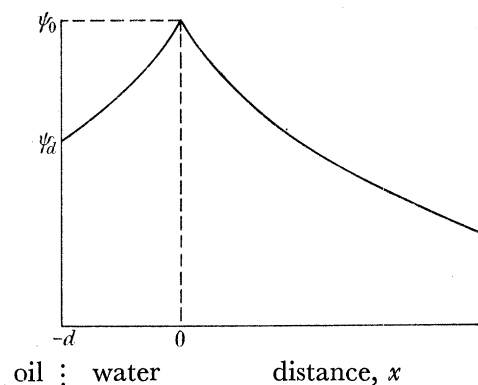


FIGURE 1. A qualitative picture of the distribution of electrical potential in the region of an ionized monolayer situated a distance d from the planar phase boundary. The dashed vertical line indicates the plane of the ionized detergent head groups.

The total diffuse charge (σ) is given by

$$\sigma = \sigma_1 + \sigma_2 = -\int_0^\infty \rho dx - \int_0^d \rho dx, \quad (27)$$

where σ_1 and σ_2 are the diffuse charges on the water and oil sides of the head groups. Using the Poisson equation, we may write this as

$$\sigma = \frac{D}{4\pi} \left[\int_0^\infty \frac{d^2\psi}{dx^2} dx + \int_0^d \frac{d^2\psi}{dx^2} dx \right] \quad (28)$$

$$= \frac{D}{4\pi} \left[-\frac{d\psi}{dx} \Big|_0 + \frac{d\psi}{dx} \Big|_d - \frac{d\psi}{dx} \Big|_0 \right]. \quad (29)$$

We substitute for the first term in the bracket (concerned with the 'aqueous' side of the film ions) from the simple Gouy theory and for the second and third, from (25) namely

$$\sigma = \frac{10^{16}\epsilon}{A} = \sqrt{\left(\frac{2n_0 DkT}{\pi}\right)} \left\{ 1 + \sqrt{\left(1 - \frac{A'_0}{A}\right)} \right\} \sinh \frac{\epsilon\psi_0}{2kT} - \sqrt{\left(\frac{2n_0 DkT}{\pi}\right)} \left(1 - \frac{A'_0}{A}\right) \sinh \frac{\epsilon\psi_d}{2kT}. \quad (30)$$

n_0 may be replaced by $cN \times 10^{-3}$, where c is in moles/l. As $A \rightarrow \infty$ we have

$$= 2 \sqrt{\left(\frac{2n_0 DkT}{\pi}\right)} \sinh \frac{\epsilon\psi_0}{2kT} - \sqrt{\left(\frac{2n_0 DkT}{\pi}\right)} \sinh \frac{\epsilon\psi_d}{2kT}; \quad (31)$$

also, as $d \rightarrow 0$ and $\psi_d \rightarrow \psi_0$ equation (30) reduces to the simple Gouy equation (10).

ψ_d will vary with distance (d) of the plane of the film ions from the interface; equation (26) relates ψ_0 , ψ_d and d . ψ_0 and d are also related directly,

$$\epsilon\psi_0 = -\Delta G_{-\text{CH}_2-\bar{l}}, \quad (32)$$

where $\Delta G_{-\text{CH}_2-}$ is the free energy of adsorption of one $-\text{CH}_2-$ group and l the effective carbon-carbon bond length (in crystalline hydrocarbon, 1.26 \AA). Using equations (30), (26) and (32) we can calculate ψ_d , ψ_0 and d from σ ($= 10^{16} \epsilon/A$) and $\Delta G_{-\text{CH}_2-}$.

The measured surface potential, ΔV may be related to ψ_d . Since ψ_d is the diffuse layer potential at the phase boundary, the relation used by Davies (1951, 1952) should be rewritten

$$\Delta V = \frac{4\pi\mu_D}{A} + \psi_d. \quad (33)$$

μ_D is a surface dipole moment found, in certain circumstances, to be a constant and independent of A . It is a resultant dipole of all molecules near the interface which, for adsorbed quaternary ammonium ions with no inherent dipole, probably originates entirely from the orientation of water molecules near the phase boundary. If so, the change produced upon adsorption of the long-chain ion (and hence μ_D), depends on the original conditions at the interface and so is, in particular, influenced by the electrolyte concentration.

The potential drop above the head groups and the equation of state

(i) *Presence of excess electrolyte*

Equation (13) can be derived by substituting for $1/A$ from the simple Gouy equation (10) in the following general equation obtained by combining the Gibbs equation with the adsorption isotherm (2):

$$\frac{\Pi}{n} = \frac{kT}{A-A_0} + \int \frac{1}{A} d(\epsilon\psi) + \text{constant}, \quad (34)$$

where $n = 1$ in presence of excess electrolyte and 2 with no added electrolyte.

The same procedure may be used when it is assumed that penetration of ions above the head groups can occur. In this instance $1/A$ is substituted for from equation (30). The result cannot be completely integrated but is conveniently written as

$$\begin{aligned} \Pi = \frac{kT}{A-A_0} + \frac{kT\sqrt{c'}}{10^{16}\epsilon} \sqrt{\left(\frac{2DkTN}{1000\pi}\right)} & \left\{ 4 \cosh \frac{\epsilon\psi_0}{2kT} - \frac{1}{2} \int \frac{A_0'}{A} \sinh \frac{\epsilon\psi_0}{2kT} d\left(\frac{\epsilon\psi_0}{kT}\right) \right. \\ & \left. - \int \sqrt{\left(1 - \frac{A_0'}{A}\right)} \sinh \frac{\epsilon\psi_d}{2kT} d\left(\frac{\epsilon\psi_0}{kT}\right) - 4 \right\}. \end{aligned} \quad (35)$$

The unsolved integrals can be determined graphically.

(ii) *Absence of added electrolyte*

In this instance, we put $n = 2$ in equation (34) and substitute for $1/A$ from (30). Only by employing the approximation to (30) applicable when $\psi_0 > 100 \text{ mV}$ can a simple equation of state be derived; substitution and further use of the Gibbs equation (18) yields

$$\begin{aligned} \Pi = \frac{kT}{A-A_0} + \frac{2kT}{A} + \frac{2kT}{A} \ln \left\{ 1 + \frac{1}{2} \frac{A\sqrt{c}}{10^{16}\epsilon} \sqrt{\frac{2DkTN}{1000\pi}} \sqrt{\left(1 - \frac{A_0'}{A}\right)} e^{\epsilon\psi_d/2kT} \right\} \\ - \frac{2kT}{A_0} \left\{ \sqrt{\left(1 - \frac{A_0'}{A}\right)} - 1 + \frac{1}{2} \frac{A_0'}{A} \right\} \\ + 2kT \int \frac{1}{A^2} \ln \left\{ 1 + \frac{1}{2} \frac{A\sqrt{c}}{10^{16}\epsilon} \sqrt{\frac{2DkTN}{1000\pi}} \sqrt{\left(1 - \frac{A_0'}{A}\right)} e^{\epsilon\psi_d/2kT} \right\} dA + kT \int \frac{1}{A} d \ln f_{\pm} + C'. \end{aligned} \quad (36)$$

The two integrals may be determined graphically. C' is zero. This, then, is the equation of state for no added electrolyte with allowance for potential decay above the film-ions and for the activity coefficient being less than unity.

Some penetration of counter-ions above the head groups will occur under all experimental conditions. In proposing that the diffuse layer is not entirely confined to one side only of the charged film we do not postulate any new types of interaction. Our model, therefore, differs from that assumed by Few & Pethica (1954) to explain the anomalously low potentials which they found for adsorbed films of sodium dodecyl sulphate at the air/water interface. Ion pair formation could account for the effects observed by these authors, but experimental evidence in such simple uni-univalent systems provided by Kling & Lange (1957), Phillips & Rideal (1955 *a, b*), Payens (1955) and the present work, strongly suggests otherwise. Our surface potentials and those of Few & Pethica are both measured under conditions where, as shown below, penetration of ions above the film most probably occurs.

Our picture of the interface resembles that which Phillips & Rideal suggest for insoluble films. However, our interpretation differs from that of these authors, since they explain anomalously high surface pressures by assuming that penetration of counter-ions above the film causes an increase in the number of 'kinetic units' in the interface and hence an increase in surface pressure. The extent of such penetration is calculated for a Stern-type theory. We do not believe that the presence of ions above the plane of the film ions will, in this kinetic sense, cause any change in surface pressure in these systems at equilibrium.

EXPERIMENTAL

The principal systems employed in the experimental work were, for neutral absorbing molecules, short-chain alcohols, and for ionized molecules, long-chain sodium alkyl sulphates and dodecyl trimethylammonium bromide in water and excess sodium chloride. The oil was petroleum ether. Use was made of the data of Harkins & McLaughlin (1925) for butyric acid, and of Kling & Lange for long-chain sodium sulphates in water at 50 °C.

The petroleum ether (boiling point > 120 °C) was of Analar grade redistilled under vacuum. Analar sodium chloride was generally used, although a sample of this, purified further by precipitation from solution by hydrogen chloride, rinsed with water and roasted at 300 °C gave identical results. The water was kindly supplied by Drs J. A. Kitchener and J. H. Schenkel. It was distilled in Pyrex under nitrogen and condensed in silica, and had a specific conductance of $0.55 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$. Unless otherwise stated, all results are for 20 °C.

(i) *Neutral molecules*

The drop-volume technique (Harkins & Brown 1919; Cockbain & McMullen 1951) was used to measure interfacial tensions. It was ensured that the systems were at equilibrium by shaking known amounts of the solute with water and petroleum ether vigorously for 5 to 10 min, and leaving the two phases in contact overnight. After further shaking, the two phases were separated and the concentration of solute in the aqueous phase determined, by one of three methods:

- (a) by calculation from published values of the partition coefficient;
- (b) by titration methods, for substances which were either acids, or could be quantitatively hydrolyzed to give acids;
- (c) by separation of the phases, and measurement of the interfacial tension of one phase (i) against a pure sample of the other (ii). This was followed by comparison with tensions

for known amounts of solute in the phase (i). These tensions were all measured for drops of the same age (30 s) during which time no appreciable change in the interfacial tension occurred. This is presumably because the diffusion rate across the interface is comparatively slow, as observed by Haydon (1958*b*). The method was checked in some cases against method (a), when close agreement was found. The densities of the two phases were never significantly different from those of the pure phases.

The actual method used for the various systems is indicated in table 5.

The alcohols used were Kahlbaum pure samples; the benzoic acid was spectroscopically pure; 1-menthol was kindly supplied by Dr D. F. Cheesman; the phenol, skatol, pyridine, and β -ionone were as pure as could be obtained commercially.

(ii) *Ionized molecules*

Interfacial tensions were measured by the drop-volume method, as described for neutral molecules. In calculating the surface pressures of the adsorbed films the values found for γ_0 , the interfacial tensions between petroleum ether and the various pure sodium chloride solutions were for 0.05 M, 50.73 dyn/cm; 0.07 M, 50.78 dyn/cm; 0.10 M, 50.9 dyn/cm; 0.25 M, 51.2 dyn/cm and 0.5 M, 51.6 dyn/cm. Sodium *n*-dodecyl sulphate was kindly supplied by Professor K. J. Mysels, and *n*-dodecyl trimethylammonium bromide, by I.C.I. Ltd. The latter was extracted with ether and twice recrystallized from acetone. The critical micelle concentrations (c.m.c.) were, for sodium *n*-dodecyl sulphate in water 0.00795 M, and for *n*-dodecyl trimethylammonium bromide in water 0.0159 M. None of the detergents showed any detectable ageing or any minima in interfacial tensions near the c.m.c.

Contact (ΔV) potentials were determined with a vibrating condenser apparatus of the type described by Davies (1951) and modified by members of the British Rubber Producers' Research Association.

EXPERIMENTAL RESULTS AND TESTS OF THE THEORY

Neutral films

In figures 2, 3 and 4 the equation of state (9) and the adsorption isotherm (2) for mobile adsorbed films are tested for three short-chain alcohols and *n*-butyric acid. The plot of $1/\Pi$ against A for these substances yields a straight line over almost the entire experimental range of slope 0.00246 ($= 1/kT$) and gives values of A_0 for the alcohols of 18.5 Å² and for the acid 21.5 Å². These values of A_0 are used in testing the isotherm, where

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

is plotted against the molar bulk concentration. Again, the relation is linear. The dashed line in figure 4 shows the curve obtained if the non-mobile isotherm (1) is tested. At high areas, where $e^{A_0/(A - A_0)} \rightarrow 1$, the two curves coincide, but at low areas ($A < 80$ Å²) the line for the non-mobile isotherm falls well below the other.

The linearity of the isotherm down to areas of 30 Å² confirms that dipole or van der Waals's interaction between the adsorbed molecules does not occur in this range, in marked contrast to the behaviour of similar films at the air/water interface, where Guastalla (1942, 1946) has shown that such interaction commences at high values of A .

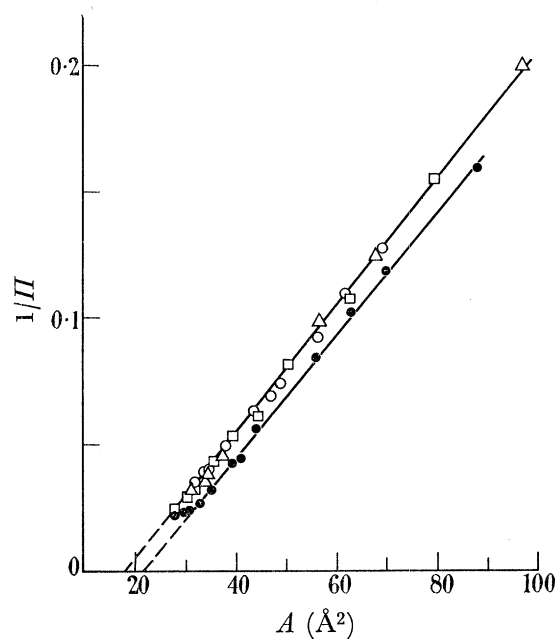


FIGURE 2. The equation of state (9) for four un-ionized substances at 20°C.
 ●, *n*-butyric acid; ○, *n*-butyl alcohol; □, *n*-propyl alcohol; △, ethyl alcohol.

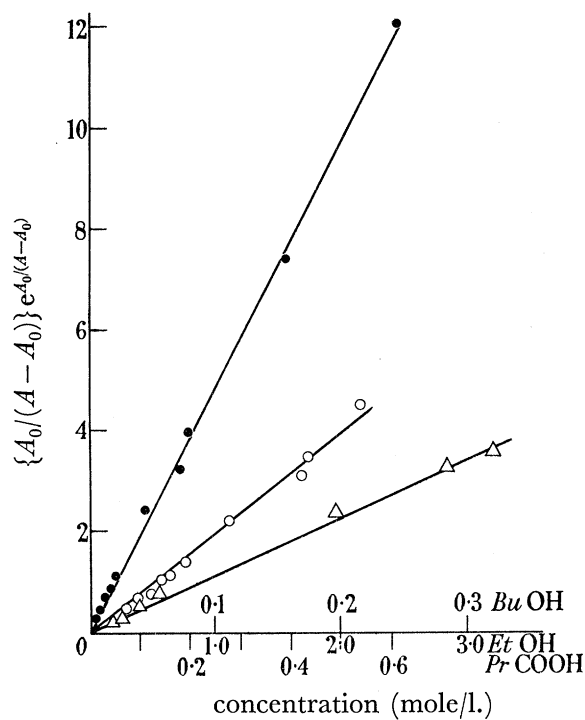


FIGURE 3. The adsorption isotherm for mobile films (2) at 20°C. ●, *n*-butyric acid; ○, *n*-butyl alcohol; △, ethyl alcohol.

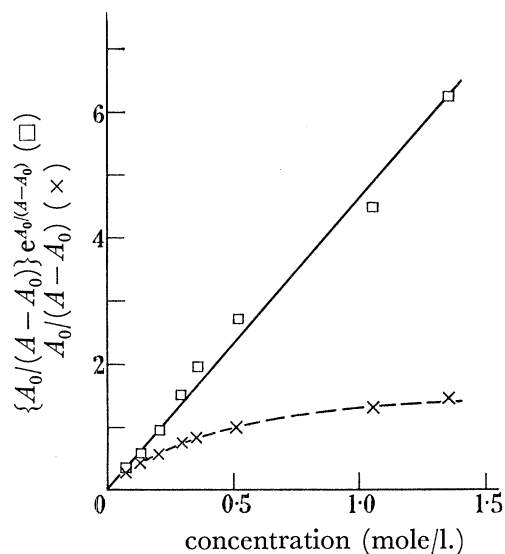


FIGURE 4. Isotherms obtained by assuming the adsorbed molecules to be mobile (equation (2), □) and non-mobile (equation (1), ×). The results are for the adsorption of *n*-propyl alcohol.

All the neutral molecules employed obey the 'mobile' adsorption isotherm and the associated equation of state (9), although most of the substances were not examined over such wide concentration ranges as those mentioned above. In table 5 are listed free energies of adsorption for these substances calculated from the slopes of the isotherms.

TABLE 1. SURFACE POTENTIALS, AND EQUILIBRIUM DISTANCES OF THE IONIC GROUPS FROM THE INTERFACE (d), FOR $n\text{-C}_n\text{H}_{2n+1}\text{SO}_4\text{Na}$ IN WATER AT 50°C

A (\AA^2)	d^* (\AA)	ψ_d (mV)	ψ_0 (mV)	ψ_0^\dagger (mV)	A (\AA^2)	d^* (\AA)	ψ_d (mV)	ψ_0 (mV)	ψ_0^\dagger (mV)
$n = 18$					$n = 12$				
49.3	11.47	215	313	339	49.4	7.62	128	208	234
54.7	11.52	220	314	340	51.9	7.67	131	209	235
62.4	11.61	226	316	343	54.5	7.75	133	211	237
75.5	11.59	231	315	342	59.9	7.79	137	212	238
90.9	11.57	239	315	342	65.4	7.83	141	212	240
108	11.51	244	314	340	80.4	7.89	149	215	232
125	11.37	239	318	343	102.6	7.71	152	210	234
136	11.75	258	320	347	115	7.83	159	214	239
169	11.57	265	321	348	143	7.83	165	214	238
					212	8.08	180	220	241
$n = 16$					$n = 10$				
47.4	10.09	182	275	299	57.6	6.04	98	165	190
50.9	10.12	186	276	303	61.8	6.12	102	167	192
56.1	10.21	191	280	305	65.2	6.30	107	172	196
63.3	10.25	196	280	306	71.0	6.53	115	179	203
76.7	10.26	203	280	306	76.9	6.64	120	182	206
106	10.35	215	282	309	86.5	6.75	126	185	210
201	10.36	235	282	307	120	6.74	134	184	208
235	10.48	244	286	307	265	6.44	142	176	194
					364	6.57	154	179	194
					533	6.60	161	181	193
$n = 14$					$n = 8$				
49.4	9.05	160	246	271	52.9	4.90	72.8	134	157.5
52.4	9.12	164	249	275	56.1	5.10	78.0	139	162.5
59.4	9.13	168	251	274	59.1	5.13	80.0	140	164
68.9	9.23	175	249	277	65.7	5.33	87.0	145	169
96.6	9.13	184	248	275	71.3	5.45	92.0	149	172
127	9.09	191	246	277	84.2	5.53	98.0	151	174
176	9.00	198	246	269	97.3	5.53	102	151	174
217	9.04	205	248	269	115	5.67	109	155	176
295	9.07	212	260	267	133	5.70	113	155	177.5
					152	5.77	118	157	179
					216	5.63	122	154	172
					295	5.56	126	152	168
					590	5.08	124	138	150

* In the calculations of d it has been assumed that the vertical distance between two adjacent carbon atoms is 1.26\AA .

† Calculated from the simple Gouy equation (10).

(i) *The value of A_0*

Ionized films

It is not possible to find for charged films an accurate value for A_0 by extrapolation of a plot of $1/II$ against A as the graph becomes non-linear at low areas and its behaviour as $A \rightarrow A_0$ is uncertain. In 1951, Davies took 30\AA^2 for the octadecyl trimethylammonium ion and in 1956, 33\AA^2 for the alkyl sulphate ion. Phillips & Rideal (1955*a*), on the other hand, assumed 20\AA^2 for both sulphate and quaternary ions. The latter authors show that equimolar films of octadecyl trimethylammonium chloride and sodium docosylsulphate obey the equation of state (9) and in other respects behave as neutral films. The plot of $1/II$ against

A is thus perfectly linear and extrapolation to $1/H = 0$ yields an A_0 of 25 \AA^2 . Comparison of the theoretical radii of the two ionic groups points to a slightly larger average for A_0 . We have therefore taken values of A_0 for the alkyl sulphate and quaternary ammonium ions of 25 and 30 \AA^2 , respectively.

(ii) *Tests of the theory*

The neutral films obey the 'mobile' isotherm over the whole experimental range, and one expects similar behaviour from ionized films when allowance is made for the ionic double layer. The appropriate isotherm is obtained by combining equations (2) and (3),

$$\frac{A_0}{A - A_0} e^{A_0/(A - A_0)} e^{\epsilon\psi_0/kT} = a e^{-\Delta G/kT}, \quad (37)$$

where ψ_0 is calculated from equations (26), (30) and (32).

TABLE 2. SODIUM DODECYL SULPHATE IN SODIUM CHLORIDE AT 20°C

concn. (10^{-3} mole/l.)	H (dyn/cm)	A (\AA^2)	concn. (10^{-3} mole/l.)	H (dyn/cm)	A (\AA^2)
0.05M-NaCl			0.10M-NaCl		
1.95	44.43	43.0	1.00	43.03	45.0
1.00	38.38	47.0	0.631	39.04	48.0
0.501	32.53	50.1	0.398	35.11	49.7
0.251	26.78	54.7	0.251	31.62	51.7
0.126	21.08	65.0	0.158	27.91	53.5
0.0631	17.78	76.0	0.100	24.64	58.0
0.0398	14.58	90.5	0.0631	21.62	64.5
			0.0398	17.83	72.9
			0.0251	16.31	80.1
			0.0158	14.15	91.0
0.25M-NaCl			0.50M-NaCl		
0.500	46.21	41.2	0.250	46.12	41.0
0.250	39.83	43.5	0.125	39.40	43.0
0.125	33.19	46.0	0.0625	33.17	45.5
0.0625	27.41	54.1	0.03125	27.14	49.6
0.03125	22.50	61.0	0.0156	21.90	59.0
0.01562	18.11	67.0	0.0078	17.11	69.3
0.01000	15.52	77.5			

DODECYL TRIMETHYLAMMONIUM BROMIDE IN SODIUM CHLORIDE AT 20°C

concn. (10^{-3} mole/l.)	H (dyn/cm)	A (\AA^2)	ΔV (mV)	concn. (10^{-3} mole/l.)	H (dyn/cm)	A (\AA^2)	ΔV (mV)
0.07M-NaCl				0.10M-NaCl			
7.14	41.68	48.2	318	5.25	40.60	49.3	306
3.57	36.03	51.3	307	2.63	34.91	52.0	297
1.785	31.18	55.3	296	1.32	29.93	56.5	281
0.892	26.28	61.0	283	0.661	25.37	60.5	262
0.446	21.93	68.0	260	0.3305	20.90	67.0	240
0.223	18.08	77.5	236	0.166	16.92	76.0	215
0.111	15.18	91.0	215	0.0832	13.30	91.0	200
0.056	12.40	102	200	0.0417	10.52	109	170
0.25M-NaCl				0.50M-NaCl			
2.55	39.91	51.5	280	2.04	42.81	49.8	268
1.275	34.73	54.0	270	1.02	37.40	51.8	256
0.637	29.70	58.5	250	0.510	31.99	54.5	236
0.318	25.32	64.0	227	0.255	27.03	58.0	221
0.159	21.09	69.7	210	0.1275	22.30	62.5	201
0.0796	17.69	76.0	195	0.0637	17.90	70.8	191
0.0390	14.00	86.0	181	0.0318	14.02	82.8	170
				0.0199	11.85	93.0	156

TABLE 3. SURFACE POTENTIALS, AND EQUILIBRIUM DISTANCES OF THE IONIC GROUPS FROM THE INTERFACE (d), FOR n -C₁₂ DETERGENTS IN WATER AND SODIUM CHLORIDE SOLUTIONS AT 20°C

A (Å ²)	d^* (Å)	ψ_d (mV)	ψ_0 (mV)	ψ_0^\dagger (mV)	A (Å ²)	d^* (Å)	ψ_d (mV)	ψ_0 (mV)	ψ_0^\dagger (mV)
n -C ₁₂ H ₂₅ SO ₄ Na					n -C ₁₂ H ₂₅ NMe ₃ Br				
0.05M					Water				
43.0	5.35	81.5	145	166	60.5	6.15	107	167	189
47.0	5.20	80	140	161	64.5	6.46	115	175	198
50.1	5.06	79	137	158	70.5	6.71	123	182	204
54.7	4.87	78	133	154	80.0	6.87	131	186	209
65.0	4.62	76	125	145	96.0	7.00	138	189	211
76.0	4.36	74	118	138	113	7.14	146	193	214
90.5	4.16	72	112	129	131	7.32	153	198	219
0.10M					0.07M				
45.0	4.65	68	126	147	48.2	4.85	74.5	131	151
48.0	4.52	67.5	122	144	51.3	4.73	73	128	149
49.7	4.45	67	120	141	55.3	4.60	72	125	145
51.7	4.40	66.5	119	140	61.0	4.43	70.5	120	140
53.5	4.35	66	117	138	68.0	4.20	67.5	114	135
64.5	4.06	64	110	129	77.5	4.01	68	109	132
72.9	3.85	63	104	122	91.0	3.80	66.5	102	120
80.1	3.62	61	98	118	102	3.58	65	97	115
90.1	3.37	59.5	92	112					
0.25M					0.10M				
41.2	4.01	54	109	128	49.3	4.66	67	126	142
43.5	3.90	53.5	106	126	52.0	4.39	66.5	119	139
46.0	3.65	53	99	123	56.5	4.20	65.5	114	135
54.1	3.50	51	95	115	60.5	4.10	64.5	111	131
61.0	3.30	50	90	109	67.0	3.94	63	107	127
67.0	3.17	49	86	103	76.0	3.65	62	100	120
77.5	3.02	48	82	98	91.0	3.48	61.5	94	111
					109	3.20	57.5	86	103
0.50M					0.25M				
41.0	3.38	42	91.5	112	51.5	3.58	51.5	97	117
43.0	3.32	43	90	109	54.0	3.50	51	95	115
45.5	3.20	42.5	87	106	58.5	3.45	50	91	111
49.6	3.06	40	83	102	64.0	3.20	48	87	107
59.0	2.84	40	77	94	69.7	3.10	48	84	102
69.3	2.61	39	72	86	76.0	2.97	48	80.5	98
					86.0	2.80	48	76	92
					0.50M				
					49.8	3.06	42	83	102
					51.8	3.00	41.5	81.5	100
					54.5	2.97	40.5	80.5	98.5
					58.0	2.81	39.5	76	94.5
					62.5	2.70	39	73	91
					70.8	2.55	37	68	85
					82.8	2.35	37	64	77.5
					93.0	2.15	35.5	58	72.5

* In the calculations of d it has been assumed that the vertical distance between two adjacent carbon atoms is 1.26 Å.

† Calculated from the simple Gouy equation (10).

Potentials and equilibrium distances of the ionic head groups from the interface (d), calculated from the results of Kling & Lange (1957) for adsorption of sodium alkyl sulphates in absence of added electrolyte, are shown in table 1; those of dodecyl trimethylammonium bromide in water (data of Haydon & Phillips 1958) are given in table 3.

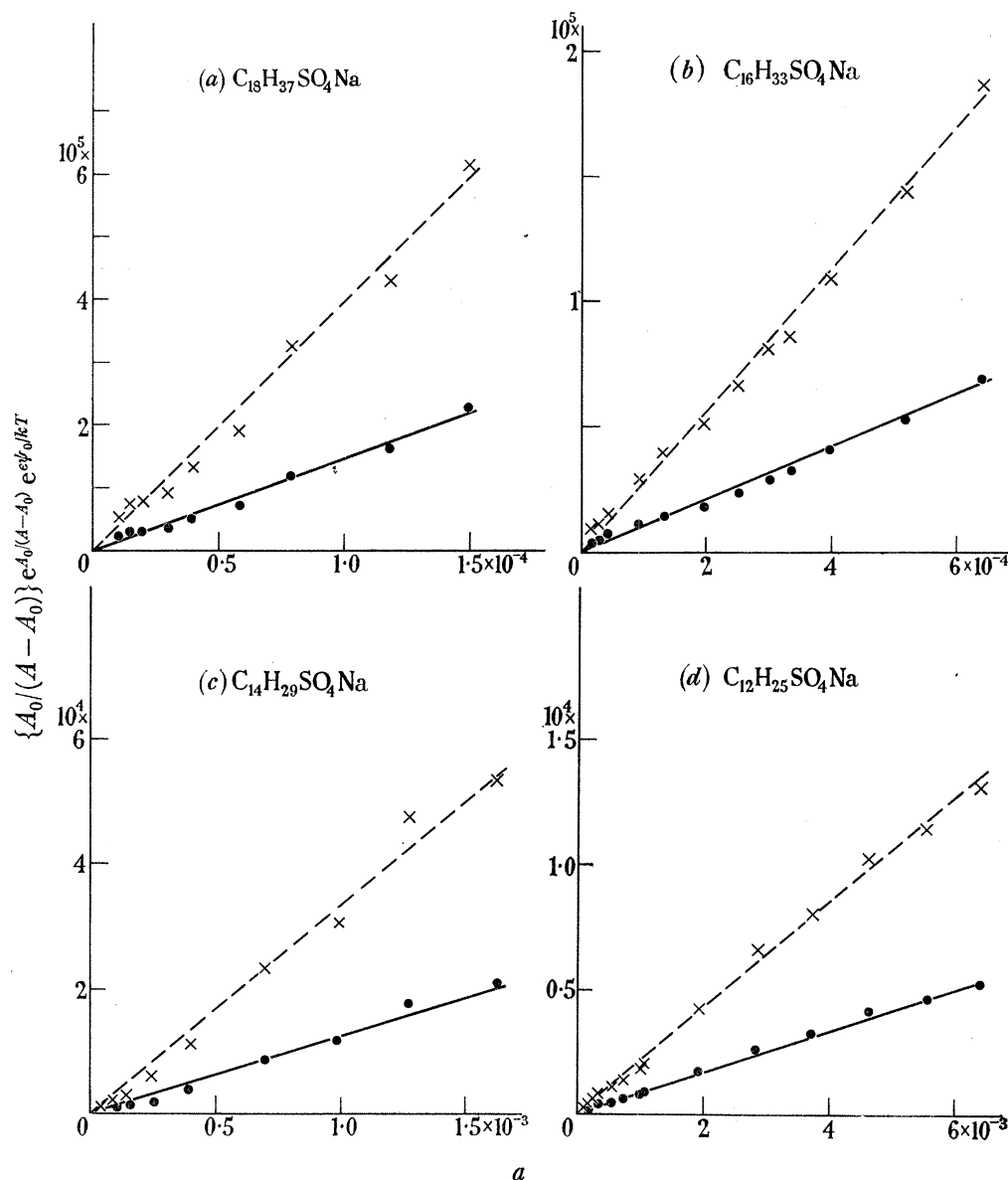


FIGURE 5. Adsorption isotherms (equation (37)) for sodium n -alkyl sulphates in water at 50°C. \times , ψ_0 calculated from the simple Gouy equation (10); \bullet , ψ_0 calculated from equations (26), (30) and (32).

Experimentally determined pressures and areas calculated using the appropriate form for the Gibbs equation for sodium dodecyl sulphate and dodecyl trimethylammonium bromide, in presence of excess sodium chloride, are listed in table 2 and the potentials and equilibrium distances in table 3.

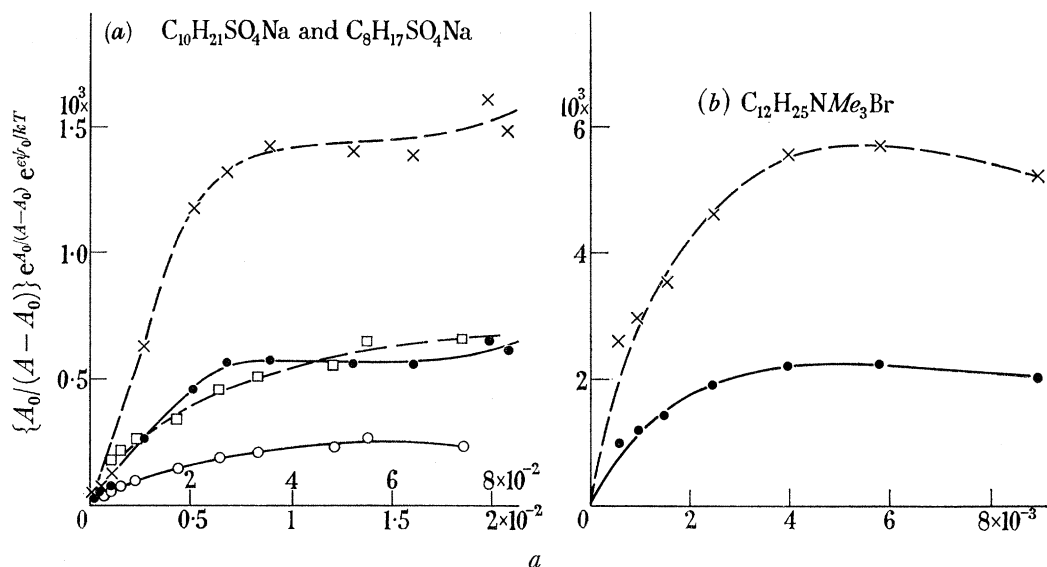


FIGURE 6. Adsorption isotherms (equation (37)) for sodium *n*-alkyl sulphates in water at $50^\circ C$. \times , \bullet , $C_{10}H_{21}SO_4Na$, lower scale, \square , \circ , $C_8H_{17}SO_4Na$, upper scale, and dodecyl trimethylammonium bromide in water at $20^\circ C$. \times , \square , ψ_0 calculated from the simple Gouy equation (10); \bullet , \circ , ψ_0 calculated from equations (26), (30) and (32).

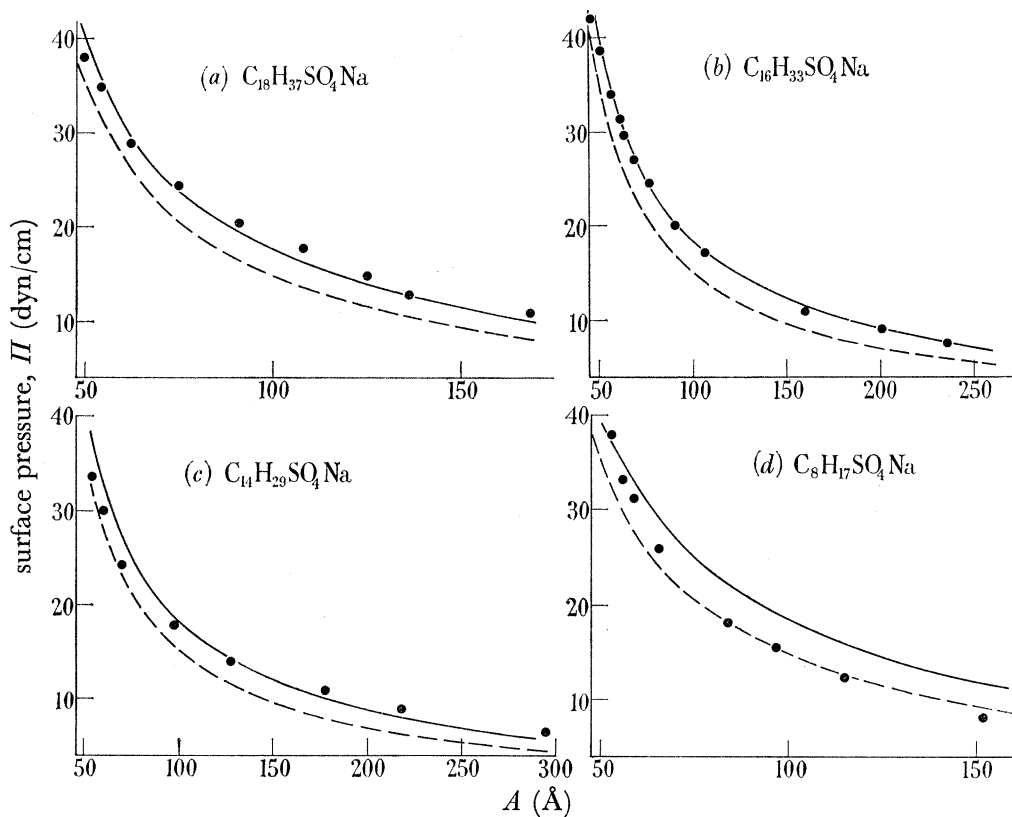


FIGURE 7. Measured and predicted surface pressures, (Π) for four sodium *n*-alkyl sulphates in water at $50^\circ C$. \bullet , experimental pressures; —, pressures calculated from equation (36); ---, pressures calculated from equation (22).

The main criteria in assessing the validity of the model and theoretical treatment adopted for these systems are:

- that a plot of the left-hand side of equation (37) against the bulk activity or concentration should be linear;
- that the relevant equation of state should predict accurately the measured surface pressures;
- that the theoretically determined ψ_d should be consistent with the measured contact potentials;

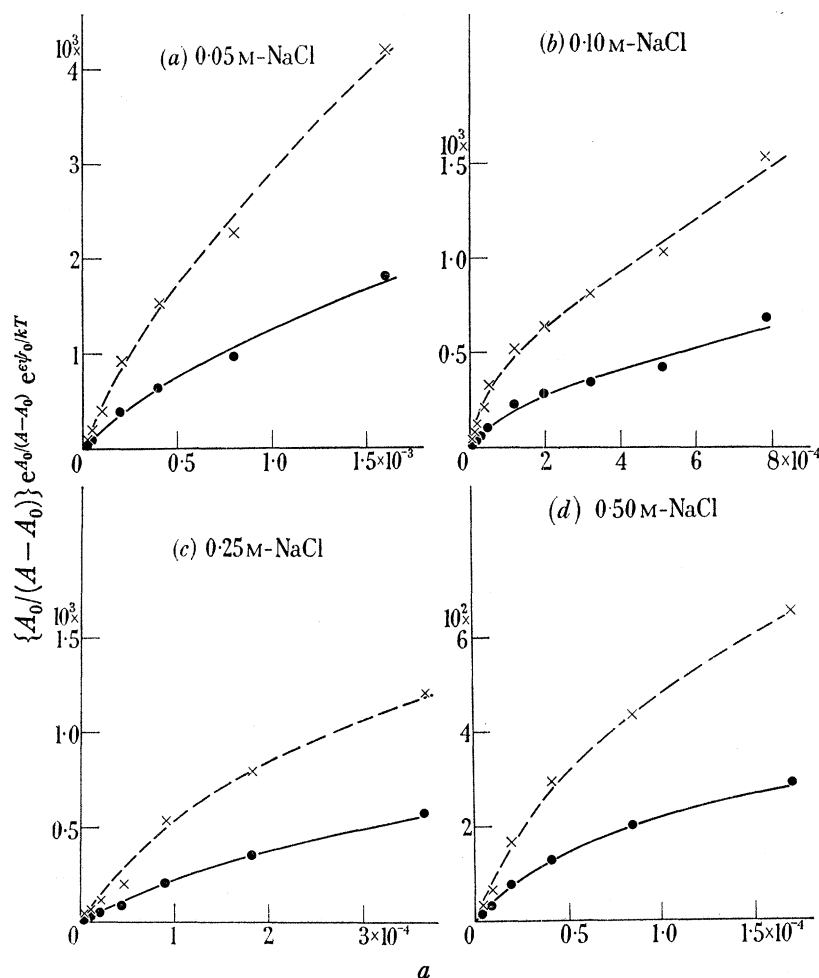


FIGURE 8. Adsorption isotherms (equation (37)) for sodium *n*-dodecyl sulphate in presence of excess sodium chloride at 20°C. \times , ψ_0 calculated from the simple Gouy equation (10); \bullet , ψ_0 calculated from equations (26), (30) and (32).

(d) that reasonable adsorption energies for the molecules should be obtained from the slopes of the isotherm.

Each of these tests of the theory is considered in turn.

(a) The isotherm plots shown in figure 5 for the C_{18} , C_{16} , C_{14} and C_{12} sulphates are perfectly linear. When the simple Gouy equation is used to calculate the potentials the dashed line is obtained.

The isotherms for the C_{10} and C_8 alkyl sulphates in water (figure 6) are linear at high dilutions but show serious deviations above 0.01 M. Use of the Debye-Hückel limiting law

to calculate activity coefficients instead of the 'complete' equation leads to much smaller deviations from linearity, suggesting that the assumption of 5 \AA as the mean ionic radius for these ions may be wrong.

Dodecyl trimethylammonium bromide (figure 6) shows similar but more marked deviations at high concentrations.

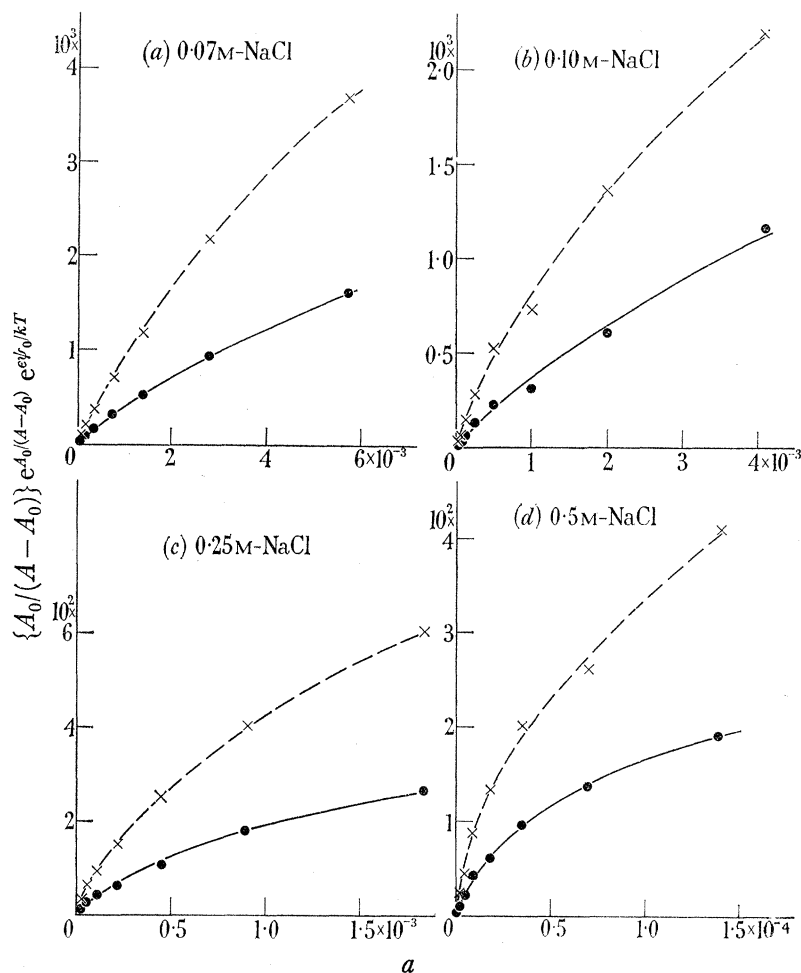


FIGURE 9. Adsorption isotherms for *n*-dodecyl trimethylammonium bromide in presence of excess sodium chloride at 20°C . \times , ψ_0 calculated from the simple Gouy equation (10); \bullet , ψ_0 calculated from equations (26), (30) and (32).

Figures 8 and 9 show the isotherms for sodium dodecyl sulphate and dodecyl trimethylammonium bromide in sodium chloride solutions. None of the graphs is linear over the whole experimental range and the non-linearity is most marked in the higher sodium-chloride concentrations. When plotted on a large scale, the graphs are found to be linear for dilute detergent concentrations.

These isotherm plots can never be made linear over the whole experimental range by adjustment of A_0 . Increases in A_0 yields S-shaped curves. As expected, use of the Stern-type 'immobile' isotherm results in much greater deviations from linearity which commence at higher areas/molecule and lower concentrations.

(b) Plots of surface pressure against area for four sodium alkyl sulphates in water shown in figure 7 demonstrate that the pressures are predicted accurately by equation (36).

Equation (22), derived from the simple Gouy equation, is represented by the dashed curves and predicts pressures which are far too low. The curve for the C_8 sulphate reveals departures from equation (36) as expected, since the isotherm and the equation of state are theoretically consistent. The $\Pi-A$ curves for C_{12} and C_{10} alkyl sulphates are omitted but, as with the isotherm, only the latter shows any departure from theoretical behaviour.

Equations of state for dodecyl trimethylammonium bromide in sodium-chloride solutions are plotted in figure 10. The dashed curve shows the theoretical behaviour. In excess electrolyte, unlike the water systems (figure 7) allowance for fall-off of potential makes little

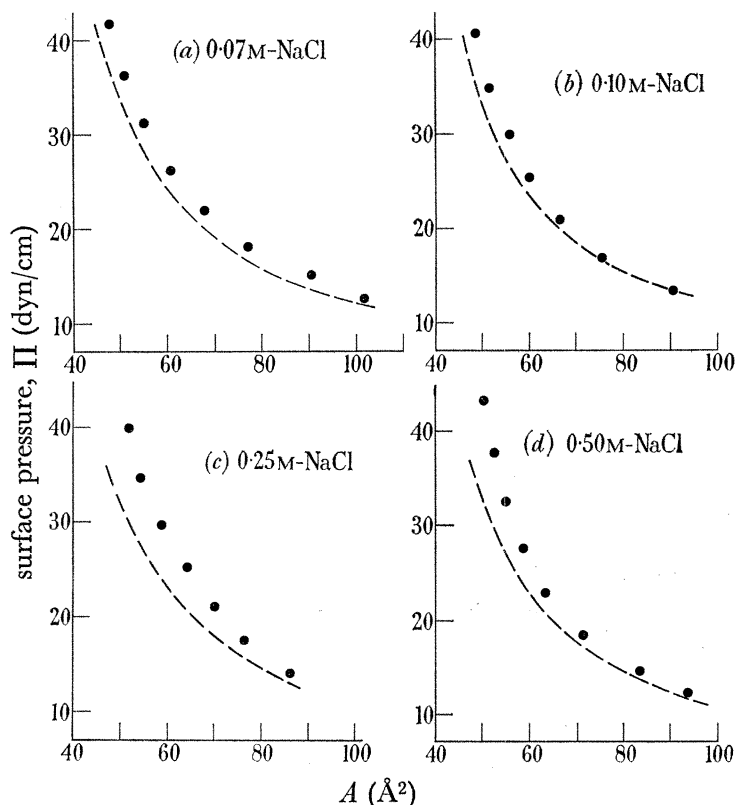


FIGURE 10. Measured and predicted surface pressures (Π) for *n*-dodecyl trimethylammonium bromide in presence of excess sodium chloride at 20°C. ●, experimental pressures; ---, pressures calculated from equation (35).

difference to the pressures predicted by the Davies equation (13). The experimental points are close to the predicted pressures at high areas and low detergent concentrations but, as expected from the isotherm plots, they diverge increasingly at low areas. Corresponding curves for sodium dodecyl sulphate are not given; the deviations are similar in character though much less pronounced.

(c) Measured surface potentials for dodecyl trimethylammonium bromide in sodium chloride are given in table 3; the corresponding measurements for the alkyl sulphates are not considered owing to inconsistencies between various sets of recently published data and because of the difficulty of interpreting μ_D for these ions.

If the measured ΔV_s are to be used to check the theoretically predicted ψ_d , investigations must be restricted to low concentrations where other types of deviation are negligible.

Table 3 shows that, at high areas, the predicted ψ_d is either constant or varies by no more than 5 mV. According to equation (33), if ψ_d and μ_D (as it should be for a quaternary ammonium ion) are constant, a plot of ΔV against $1/A$ should be linear with an intercept of ψ_d . This is tested in figure 11 and found to be correct. Close agreement between theoretical and experimental ψ_d s is shown in table 4. The theoretical prediction of the potential drop above the plane of the adsorbed ions is thus quantitatively consistent with our interpretation of ΔV potentials.

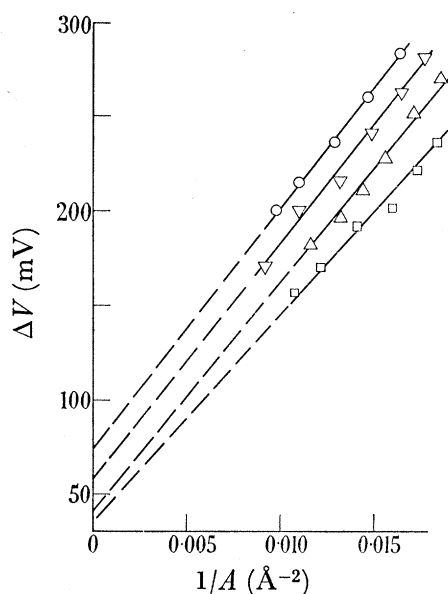


FIGURE 11. Surface potentials (ΔV) for low concentrations of *n*-dodecyl trimethylammonium bromide in excess sodium chloride at 20°C as a function of $1/A$. \circ , 0.07 M NaCl; ∇ , 0.10 M NaCl; \triangle , 0.25 M NaCl; \square , 0.50 M NaCl.

TABLE 4. COMPARISON OF THE THEORETICAL ψ_d s WITH THOSE FOUND FROM ΔV MEASUREMENTS

NaCl concn. (M)	ψ_d (mV) approx. values calculated from (30), (26) and (32) for the four highest (ideal) areas, cf. table 6	ψ_d (mV) from ΔV s measured for higher (ideal) areas (figure 11)
0.07	67	73
0.10	61	59
0.25	48	51
0.50	37	36

Deviations from theoretical behaviour

Deviations are found only at high ionic strengths for both the short-chain detergents in water and the C_{12} compounds in presence of added sodium chloride. The behaviour in these cases suggests that either $\{A_0/(A - A_0)\} e^{A_0/(A - A_0)}$ or $e^{\epsilon\psi_0/kT}$ is too small. The isotherms for the neutral films are ideal, so there is no reason to suspect the first of these terms. The ideal behaviour of the higher chain length alkyl sulphates in water suggests that the values of A are being determined correctly. We conclude, therefore, that ψ_0 is often too small at high-

charge densities and salt concentrations. Ion pairing or specific interaction would lead to lower potentials and are concluded not to occur in these systems.

Some assumptions of the Gouy theory have not so far been considered. The dielectric constant has been taken as that of the bulk solution. If this is not so, it is difficult to explain why the systems which have the highest potentials and potential gradients in their double layers behave ideally. It has been assumed that all the ions are point charges. A simple treatment allowing for this shows that, at high-charge densities and electrolyte concentrations, the potentials should be higher than predicted by the Gouy theory. This would qualitatively explain all the discrepancies in the present treatment. The application of this conclusion will be considered in another publication.

Discussion of adsorption energies

In table 5 are listed the free energies of adsorption (from the bulk of an infinitely dilute aqueous solution to the petroleum ether/water interface) for various neutral molecules and detergent ions. The former have been calculated from the slopes of the isotherms and from equation (6), the two methods giving identical results. In figure 12 these energies are plotted for the aliphatic compounds against chain length. The graphs are linear and from the slopes one obtains the free energy of adsorption/ $-\text{CH}_2-$ group; at 20 °C this comes to -820 cal/mole and at 50 °C to -800 cal/mole, in good agreement with the values found by Crisp (1949) and, from desorption rate measurements, by Davies (1952). They can be compared with the values of -625 cal/mole at the air/water interface found by Langmuir (1917) and confirmed by the present authors using the more recent data of Spivakowa (1940).

$\Delta G_{-\text{CH}_2-}$ at the oil/water interface is much closer to the value for transference of one $-\text{CH}_2-$ group from water to the oil (bulk) phase than is the value for adsorption at the air/water interface to that for transference from water to the air (bulk) phase. The considerable discrepancy in the latter case suggests that the adsorbed molecules do not have their hydrocarbon chains completely in air, but rather that they are lying, possibly folded, in contact with water.

Subtraction of the contribution of the aliphatic chain to the adsorption energy of the molecule from the total value for the compound yields the adsorption energy of the polar group for monohydric and monocarboxylic substances (see table 5). For dihydric substances, however, the energies are not simply additive, but decrease as one increases the number of hydroxyl groups in the molecule, e.g. $-\Delta G(\text{propanol}) > -\Delta G(\text{glycerol})$.

These energies are, surprisingly, all negative in sign. The oil/water values are always numerically larger than those for the air/water interface, which implies a difference in structure or orientation of the molecules at the two interfaces.

For a given polar group, the adsorption energy decreases as one passes from aliphatic to cyclic or branched chain derivatives and thence to aromatic compounds. The adsorption energies for such compounds are of use in the investigation of biological phenomena which involve adsorption on to an oil or fatty membrane as a preliminary stage (Rideal & Taylor 1958; Davies & Taylor 1957).

Temperature changes have little effect on the adsorption energy of the hydrocarbon portion of the molecule; there is a slight numerical decrease in passing from 20 to 50 °C. A larger effect is observed on the value for the whole molecule; at 20 °C the adsorption

energy of the C_{12} sulphate in water is $-11\,000$ cal/mole (calculated from the results of Haydon & Phillips 1958) and at 50°C , $-11\,400$ cal/mole.

The adsorption energy for each of the ions listed in table 5 is *ca.* 650 cal/mole lower than that calculated from the simple Gouy equation; allowance for fall-off of potential therefore leads only to a difference in the calculated energy for the polar part of the molecule; the value per $-\text{CH}_2-$ group is unaffected.

TABLE 5. CHEMICAL-FREE ENERGIES OF ADSORPTION OF NEUTRAL AND IONIZED MOLECULES AT A PETROLEUM ETHER/WATER INTERFACE

		$n\text{-C}_n\text{H}_{2n+1}\text{SO}_4\text{Na}$ in water (50°C)	
		n	$-\Delta G$
non-ionized compounds	$-\Delta G$		
ethanol ^{a†}	2400	18	16200
<i>n</i> -propanol ^{a,c}	3250	16	14450
<i>n</i> -butanol ^{b,c}	4090	14	13200
<i>n</i> -hexanol ^{a,†}	5900	12	11400
<i>n</i> -octanol ^{a,†}	7150	10	9950
<i>n</i> -decanol ^c	9360	8	8600
<i>iso</i> -amyl alcohol [†]	5000		
<i>cyclo</i> -hexanol ^c	5290		
glycerol ^{b,c}	2600	$n\text{-C}_{12}\text{H}_{25}\text{SO}_4\text{Na}$ in sodium chloride solutions (20°C)	
phenol (pH 7.2) ^{a,c}	4100	NaCl concn. (M)	
1-menthol ^c	6080		$-\Delta G$
skatole ^c	6420	0.05	10700
butyric acid*	4090	0.10	10700
benzoic acid ^b	4800	0.25	10900
piperonal ^c	4630	0.50	11050
β -ionone ^c	7800		
pyridine ^a	4380		
		$n\text{-C}_{12}\text{H}_{25}\text{NMe}_3\text{Br}$ in water and sodium chloride solutions (20°C)	
polar groups	$-\Delta G_{o/w}$	NaCl concn. (M)	
$-\text{CH}_2-$	20°C		$-\Delta G$
$-\text{OH}$	20°C		10550
$-\text{COOH}$	20°C	0.07	10000
$-\text{SO}_4^-$	50°C	0.10	10000
$-\text{N}^+(\text{CH}_3)_3$	20°C	0.25	9750
$-\text{CH}_2-$	50°C	0.50	9950

All energies are expressed in cal/mole.

* Results of Harkins & McLaughlin (1925).

† Calculations based on the data of Spivakowa (1940) for the heptane/water interface gave results in close agreement with the above values.

Addition of excess electrolyte lowers the adsorption energy for the ionized compounds and, again, there is a difference of 650 cal/mole between values derived from the Gouy equation and from our modified equations. The salting-out effect of the electrolyte on the hydrophobic portion of the molecule is apparently outweighed by the 'salting-in' of the polar groups, although results at higher electrolyte concentrations indicate some reversal of this tendency.

Payens (1955) and Matijevic & Pethica (1958) suggest that the work done in partially dehydrating an ion as it approaches an interface contributes to the adsorption energy.

Payens derives the equation
$$[\Delta G_{o/w}]_{\text{dehyd.}} = 3\epsilon^2/4Dd,$$

where d is the distance of the ion (a point charge) from the interface, D is the bulk dielectric constant for water and ϵ is the electronic charge.

Our calculations (table 4) indicate that, when no electrolyte is added to the system, d for any one compound remains constant over the whole experimental range. Also, linear plots are obtained for the isotherms (figure 5). However, the equilibrium value of d decreases as the chain length decreases and so, according to Payens's theory the contribution of the dehydration terms should increase, yielding either a non-linear plot in figure 12 or a gradient differing from that for neutral compounds. In fact, no significant difference is found.

Where excess electrolyte is added, d varies continuously over the whole experimental range. If, therefore, a dehydration effect contributes appreciably to the adsorption energy, this should vary with d , leading to a non-linear isotherm near the origin. The curves are, in fact, linear in this region. The discrepancy in surface pK found by Payens and attributed to surface dehydration could be explained, at least qualitatively, by allowing for ionic size.

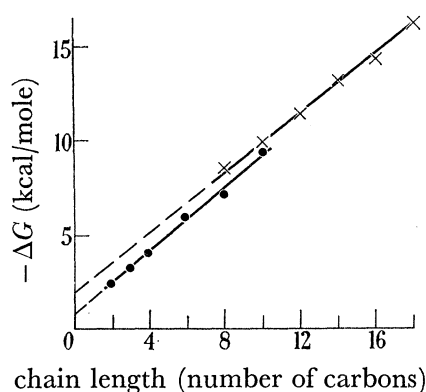


FIGURE 12. Chemical free energies of adsorption ($\Delta G_{ol/w}$) plotted against chain length for two series of homologous compounds. \times , sodium n -alkyl sulphates, 50°C; \bullet , n -alkyl alcohols, 20°C.

We therefore conclude that dehydration of the ions is not important in the adsorption of the compounds, indeed it is difficult to see how it could play any part in adsorption of quaternary ammonium ions, which are unlikely to be hydrated at all in aqueous solution.

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