

THE RELATION OF THE ELECTROKINETIC POTENTIAL TO ADSORPTION AT THE OIL/WATER INTERFACE

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ζ -Potentials of dispersions of *n*-decane in solutions of sodium dodecyl sulphate with and without excess neutral electrolyte have been determined. The electrokinetic data are compared with adsorption data for the same system in order to examine the relationship between the ζ -potential and the theoretical double-layer potentials. The applicability of the Gouy model to this system is examined and rejected. The implications of the assumption that the ζ -potential may be equated to the diffuse layer potential of the Stern theory are discussed. The specific adsorption potentials so calculated are compared with those obtained from other systems. Those calculated for octadecyl sulphate monolayers and for dodecyl sulphate micelles agree well with the present results.

Many workers have used the electrokinetic potential ζ to obtain information concerning adsorption processes at a variety of solid/liquid and liquid/liquid interfaces. A fundamental difficulty is that the relation between the ζ -potential (i.e. the potential at the hypothetical "slipping plane" in electrokinetics) and the theoretical double-layer potentials is by no means obvious and some assumption concerning this relation is implicit in all calculations of surface-charge densities from the ζ -potential. It has become usual to assume that the slipping plane corresponds to the plane of separation of the adsorbed (Stern) layer and the diffuse (Gouy) layer and accordingly ζ is equated to the Gouy potential ψ_δ . Whilst phenomena such as the sensitivity of ζ to indifferent electrolytes and the possibility of reversing the sign of ζ by multivalent non-potential-determining counterions are in qualitative agreement with this assumption, there has been no direct test of the latter. As pointed out by Phillips,¹ the liquid/liquid interface affords a better opportunity for such a test than does the solid/liquid interface since in the former case the total surface charge density σ may more easily be determined independently (e.g. by using the Gibbs adsorption isotherm in conjunction with interfacial tension measurements) and compared with the "electrokinetic charge density". Moreover, the liquid/liquid interface has the advantage that it may take the form of a plane interface for contact potential (ΔV) measurements as well as that surrounding dispersed droplets suitable for electrophoretic investigation.

In the present paper are reported the results of electrophoretic examinations of dispersions of *n*-decane in solutions of sodium dodecyl sulphate (S.D.S.) with and without excess neutral electrolyte (NaCl). This system was chosen since, in addition to the published work^{2,3} on interfacial and surface potentials (ΔV) for soluble and insoluble alkyl sulphates at the oil/water (O/W) and air/water (A/W) interfaces, Cockbain⁴ has determined directly the adsorption isotherms for this same system. By a comparison of all these results it is our purpose to examine the implications of the assumption that ζ may be equated to the diffuse-layer potential.

EXPERIMENTAL

The *n*-decane was the purest available B.D.H. reagent which was further purified by passage down an alumina column before redistillation. A.R. NaCl was roasted at 700°C

for 2 h and then twice recrystallized. The S.D.S. was an extremely pure sample, the characteristics of which have been given elsewhere.²¹ Water obtained by distillation from alkaline permanganate was redistilled from a quartz apparatus.

ζ -Potentials were determined by the micro-electrophoresis method described previously;⁵ all measurements being carried out at $20 \pm 0.1^\circ\text{C}$. Dispersions were obtained by adding 10^{-3} ml oil to 20 ml aqueous solution and agitating mechanically under fixed conditions. The latter were chosen so that the majority of the oil droplets were in the region of $20\text{--}40\ \mu$ as required to fulfil the conditions that the droplet is large compared with the double layer thickness ($\kappa a \gg 1$), and thereby allowing the calculation of ζ from the electrophoretic mobility.^{6,7} The optics of the system were chosen so that smaller droplets were not visible in the microscope. Normally, a period of 60 min was allowed between dispersion and examination; however, at the lowest detergent concentrations, a shorter interval had to be used due to the instability of the dispersions.

RESULTS

The possibility that a liquid droplet correction according to the theories of Jordan and Taylor⁸ or of Booth⁹ should be applied to the mobility data in calculating ζ -potentials

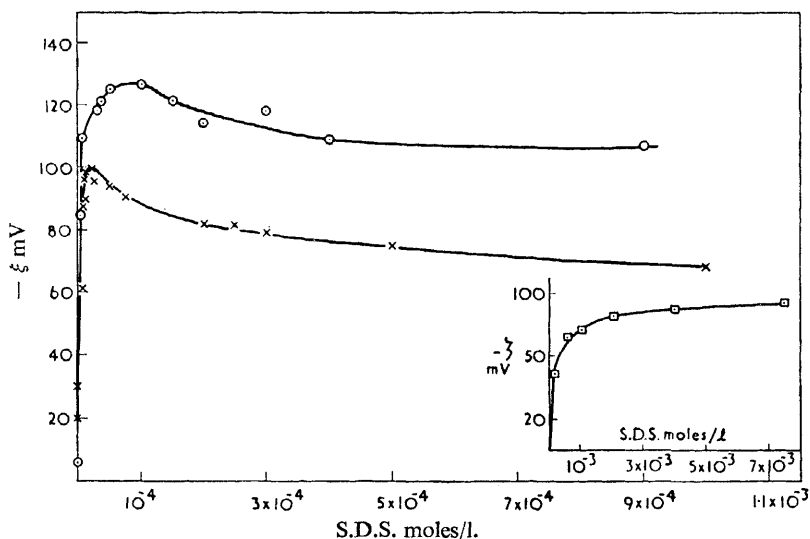


FIG. 1.— ζ -Potential against S.D.S. concentration relations for *n*-decane dispersions. \square zero NaCl; \circ 10^{-2} M NaCl; \times 10^{-1} M NaCl.

was considered but rejected in the light of recent experimental work^{10,11} This conclusion was confirmed for the present system by studying electrophoretic mobilities of *n*-octadecane dispersions at a series of temperatures above and below its m.p. The use of either liquid droplet correction implied a discontinuity in adsorption at the m.p., whereas no such discontinuity appears if the results are calculated without applying a correction. The latter is in accordance with direct analytical measurements of adsorption as a function of temperature.

ζ -Potential curves of *n*-decane in solutions of S.D.S. with and without excess NaCl are plotted in fig. 1; the potentials are probably accurate to within ± 1 mV. Charge densities σ_2 calculated from the potentials by means of the diffuse layer equation²⁰

$$\sigma_2 = \frac{\sqrt{2\epsilon k T n}}{\pi} \sinh\left(\frac{e\zeta}{2kT}\right), \quad (1)$$

(where ϵ is the dielectric constant for water and n the number of ions per cm^3 in the bulk solution) for the water and 10^{-1} M NaCl cases are plotted in fig. 2 and 3 where they may be compared with the values of the total charge σ taken from Cockbain's results.⁴

FIG. 2.—Surface charge density against S.D.S. concentration relations with no added NaCl.

○ σ taken from Cockbain's results;⁴
 ×, σ'_2 calculated from ζ -potentials.

Inset: σ'_2/σ ratio as a function of the total charge.

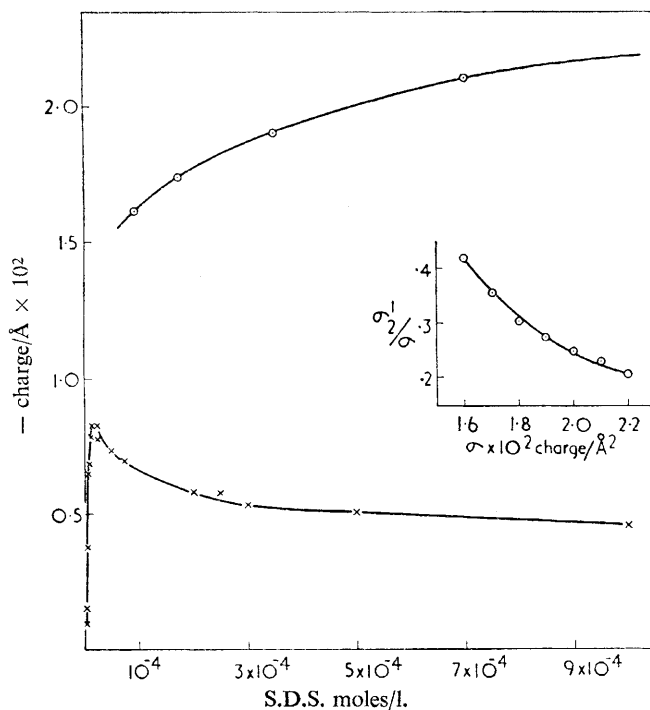
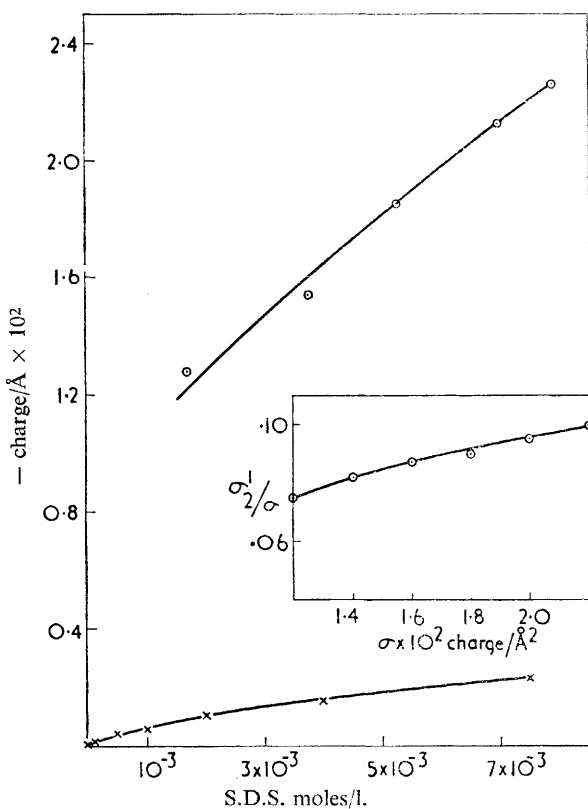


FIG. 3.—As for fig. 2; *n*-decane + S.D.S. concentration with 10^{-1} M NaCl.

DISCUSSION

APPLICATION OF THE GOUY THEORY

From the kinetics of desorption of monolayers of quaternary ammonium ions¹² and of lauric acid and laurate ions,¹³ Davies has argued that the Gouy theory may be applied to calculate the potential ψ_0 at the charged surface in such systems at electrolyte concentrations greater than 10^{-1} N and charge densities as high as $85 \text{ \AA}^2/\text{molecule}$. In the first attempt to interpret our data, we calculate ψ_0 from the adsorption data of Cockbain assuming a complete Gouy counterion distribution (eqn. (1)) and compare these with the corresponding ζ -potentials in fig. 4 and 5. Although the surface-charge densities are rather higher than those

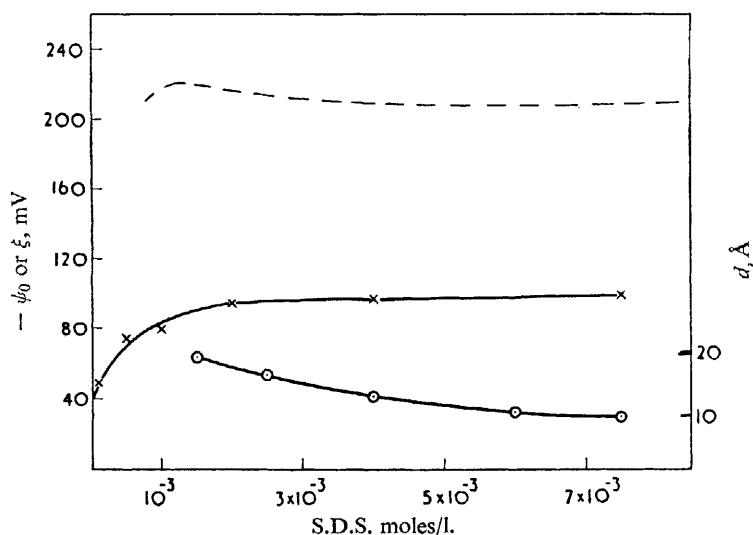


FIG. 4.—Comparison of ζ -potential with adsorption data on Gouy model for *n*-decane + S.D.S. with zero NaCl.

--- ψ_0 calculated from Cockbain's data; \times ζ -potential; d is the distance of the slipping plane from the charged surface.

discussed by Davies for the applicability of the Gouy model the salt concentrations are well within the required range. In all cases the ζ -potential is considerably lower than ψ_0 calculated in this way. This result has been found with other similar systems,^{22, 23} but in general the relation $\zeta \approx 0.55 \psi_0$ found by Davies and Rideal²³ for a number of cases is not obeyed well.

The effective distance d of the slipping plane from the charged surface on this model may be calculated from¹⁴

$$d = \kappa^{-1} \ln \left\{ \frac{(1 + \exp(e\psi_0/2kT))(1 + \exp(e\zeta/2kT))}{(1 + \exp(e\psi_0/2kT))(1 - \exp(e\zeta/2kT))} \right\}, \quad (2)$$

where κ^{-1} is the usual "thickness" of the double layer. The actual values of d (included in fig. 4 and 5) are not unrealistic, but clearly any hypothesis such as that the slipping plane is situated just outside the first layer of counterions must be abandoned if the Gouy model is applicable to this system. However, this model fails to explain a number of other features of the results such as the maxima in the ζ -potential curves in the presence of excess NaCl and the fact that ζ may increase whilst ψ_0 decreases and vice versa. If allowance were made for the modification of dielectric properties of water in the double layer according to the

calculations of Conway, Bockris and Ammar¹⁵ the general effect would be to make the numerical values of ζ somewhat higher and values of d rather smaller, but would not remove the difficulties just mentioned. Moreover, the considerations of Bolt¹⁶ concerning modifications to the Gouy equation arising from dielectric saturation, polarization of ions and ionic interactions in the double layer show that such effects tend to cancel one another and the simple Gouy equation remains surprisingly accurate over most of the experimental range covered.

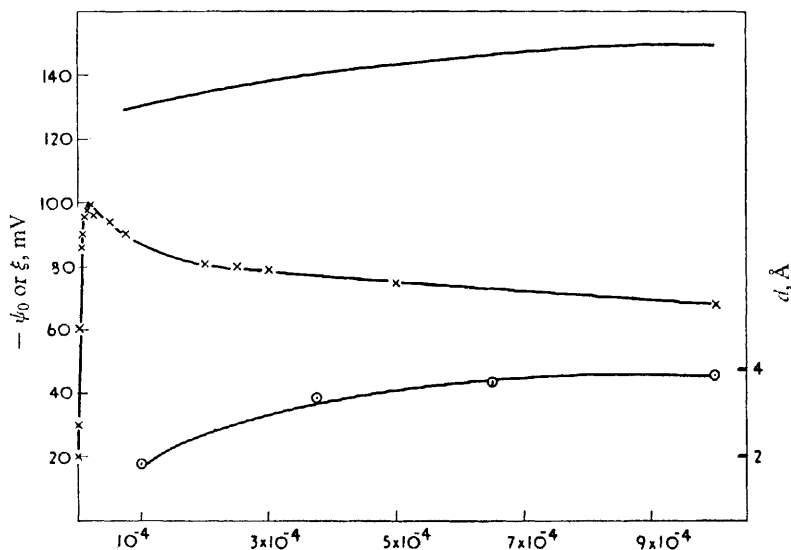


FIG. 5.

FIG. 5.—As for fig. 4; *n*-decane + S.D.S. with 10^{-1} M NaCl.

Haydon has carried out similar measurements to those reported here. This author rejects the idea of specific interactions as would be implied by use of the Stern model and attempts to overcome the difficulties arising from the simple Gouy theory by further modifications to the latter.¹⁷ It is noted that any evidence for the absence of specific interactions between ions in the bulk phase does not preclude the possibility of such interactions at an interface and the implications of an interpretation of the data according to the Stern model will now be examined.

INTERPRETATION OF THE RESULTS ON THE STERN MODEL

This model considers the distribution of counterions between the number of available positions in solution and the number of available adsorption sites upon the charged surface. The countercharge is thus divided into an adsorbed (Stern layer) charge σ_1 and the remaining diffuse layer charge σ_2 . The diffuse layer charge and the corresponding potential ψ_δ are related by the Gouy equation:

$$\sigma_2 = \frac{\sqrt{c}}{136} \sinh \left(\frac{e\psi_\delta}{2kT} \right), \quad (3)$$

where c is the electrolyte concentration, moles/l., ψ_G is in mV, and σ_2 , charge/Å². From the condition of electroneutrality over the whole double layer we have

$$\sigma = \sigma_1 + \sigma_2. \quad (4)$$

In the present system we consider adsorption of a cation into the Stern layer and the density of adsorption sites is put equal to the density of detergent molecules.

According to the assumptions of the theory,^{14, 18} the division of the countercharge is given by

$$\frac{\sigma_2}{\sigma} = \frac{1}{1 + (Mn/N) \exp(-W_i/kT)}, \quad (5)$$

where M is the molecular weight of water, N the Avogadro number and n is the number of ions per cm^3 in the bulk solution. W_i is the work of adsorption of the ion i into the Stern layer which may be considered to be divided up formally into electrostatic and chemical contributions. We take Stern's assumption that the electrostatic potential of the adsorbed ions is approximately equal to the diffuse-layer potential, so that

$$W_i = Z_i e \psi_\delta + \phi, \quad (6)$$

where Z_i is the valence (including sign) and ϕ is the specific chemical adsorption potential of i . One further relation of the Stern model is obtained from a consideration of the Stern layer condenser, viz.,

$$\sigma = \frac{\epsilon'}{4\pi\delta} (\psi_0 - \psi_\delta), \quad (7)$$

where δ is the thickness and ϵ' the effective dielectric constant of the Stern layer.

On comparing the present results with surface potential data (ΔV) for sulphate monolayers it is found that the Stern model (with $\zeta = \psi_\delta$) applied to both systems explains certain features which seem to be inexplicable on the Gouy theory. Thus, maxima in ΔV against A curves (where A is the area per detergent ion) have been reported for octadecyl sulphate on 10^{-2} M and 10^{-1} M HCl and NaCl at the A/W and O/W interfaces by Phillips and Rideal.³ The maxima occur at $75 \pm 10 \text{ \AA}^2$. Pethica and Few² also found ΔV maxima at $A = 63\text{--}70 \text{ \AA}^2$ for octadecyl sulphate on NaCl and for S.D.S. with 0.146 M NaCl ($A = 70 \text{ \AA}^2$) and without added salt ($A = 60 \text{ \AA}^2$) at the A/W interface. Phillips and Rideal³ (quoting unpublished results of Haydon and Phillips) report no maximum for S.D.S. at the O/W interface in the absence of excess NaCl. This latter corresponds to the fact that we find no maximum in the ζ -potential in the absence of excess NaCl. On extrapolating the adsorption curve of fig. 3 to slightly lower concentrations, it is found that the maximum in ζ occurs at $A = 70 \text{ \AA}^2$ in excellent agreement with the position of the maxima in the various ΔV against A curves quoted above. Although there is no adsorption curve for the 10^{-2} M NaCl case, we may estimate by interpolation that the value of ϕ (see below) at the ζ -potential maximum is between $-4kT$ and $-5kT$ from which it is calculated that this maximum also occurs in the range $A = 60\text{--}90 \text{ \AA}^2$.

In the interpretation of surface potential data, it is usual to write ΔV as the sum of a molecular dipole term and the electrostatic potential at the charged interface,

$$\Delta V = 4\pi\mu_D\sigma + \psi_0, \quad (8)$$

where μ_D is the net dipole moment per ion (cm). Phillips and Rideal³ follow Davies¹³ and assume a complete Gouy counterion distribution so that the Gouy potential ψ_G calculated from the total charge σ is substituted for ψ_0 and eqn. (8) becomes on differentiation,

$$\left(\frac{\partial\Delta V}{\partial\sigma}\right)_c = 4\pi\sigma\left(\frac{\partial\mu_D}{\partial\sigma}\right)_c + 4\pi\mu_D + \left(\frac{\partial\psi_\delta}{\partial\sigma}\right)_c. \quad (9)$$

Since $(\partial\psi_G/\partial\sigma)_c$ is positive always, it is necessary to postulate a rather drastic variation of μ_D with σ in order to explain the change of sign of $(\partial\Delta V/\partial\sigma)_c$. Although a change in the resultant dipole moment of the molecules is expected when they approach a close-packed density, it is surprising that μ_D varies rapidly with

σ at $A \sim 70 \text{ \AA}^2$. A more natural explanation of the ΔV maximum follows from an application of the Stern treatment. Thus from eqn. (7) and (8) we have

$$\Delta V = 4\pi\mu_D\sigma + (4\pi\delta\sigma/\epsilon') + \psi_\delta, \quad (10)$$

which on differentiation yields

$$\left(\frac{\partial(\Delta V)}{\partial\sigma}\right)_c = 4\pi\left\{\sigma\left(\frac{\partial\mu_D}{\partial\sigma}\right)_c + \mu_D + \delta/\epsilon'\right\} + \left(\frac{\partial\psi_\delta}{\partial\sigma}\right)_c, \quad (11)$$

where it is assumed that δ/ϵ' is invariant with σ at constant total salt concentration. This assumption has been shown to be justified in the absence of counterion penetration² and is a fair assumption in the ranges of σ and c of interest here. The shape of the ΔV against σ curve thus reflects that of the ψ_δ against σ relation and the close correspondence of the position of the maxima in the two cases indicates that the sum of the terms in the bracket in eqn. (11) is small.

Thus, on the Gouy model, the ΔV maximum is explained as a change in the dipole contribution; however, a corresponding maximum occurs in ζ -potential curves involving no dipole term. The maximum in ζ leading to a decreasing ζ -potential whilst σ (and presumably ψ_0) increases (see fig. 5) has been regarded¹ as an anomaly on the Gouy theory. The Stern model, however, readily admits of this situation since it is seen from eqn. (7) that σ must increase only with the difference ($\psi_0 - \psi_\delta$) and depending upon the variation of ϕ this may take the form of ζ decreasing whilst σ increases.

The present alternatives to the application of a model of the Stern type to these systems appear to be either to modify the Gouy theory to such an extent that it can account for the maxima in both ΔV and ζ curves and thus allow a negative $(\partial\psi_G/\partial\sigma)_c$, or to reject the ζ -potential as a means of obtaining adsorption data. However, it has been shown above that with ζ equated to ψ_δ of the Stern theory, a close correspondence between the maxima obtained in two quite distinct types of experiment is obtained and the model is thus regarded as worthy of further consideration.

Unfortunately, there are not sufficient equations in the Stern theory to allow calculation of σ_2 and ϕ independently, so that a direct test of the assumption that the slipping plane corresponds to the plane of separation of the Stern and Gouy layers (i.e., $d = \delta$) is not possible without an independent method of calculating ϕ . For adsorption at the mercury/electrolyte interface, Grahame¹⁸ has calculated this parameter but his assumptions have been criticized.²⁰ In the type of system of interest here some assumption in addition to those of the Stern theory must be made, and it seems that at present two approaches are possible. Pethica¹⁹ assumes that ϕ is invariant with salt concentration so that the ratio σ_2/σ and hence ϕ may be calculated from monolayer results from the variation of ΔV with total salt concentration. The appropriate assumption in the present work is that $\zeta = \psi_\delta$ (and hence $\sigma'_2 = \sigma_2$) and values of ϕ so calculated are presented in fig. 6. Pethica¹⁹ calculates for octadecyl sulphate monolayers at the A/W interface that ϕ ranges from about $-6kT$ at 5.5×10^{-3} charge/ \AA^2 to about $-9kT$ at 3.3×10^{-2} charge/ \AA^2 . Both methods thus agree that ϕ becomes more negative as the surface-charge density increases, with constant total salt concentration, and both assumptions lead to values of about the same order of magnitude.

The variation of the specific adsorption potential may be qualitatively explained by recalling that the Stern equations are derived assuming ideality in the adsorbed state, whereas there are probably appreciable repulsive interactions in the present system. On the reasonable assumption that the interactions between (neutral) ion pairs are negligible compared with those between unpaired detergent ions, one may expect $|\phi|$ to decrease smoothly as the net charge σ_2 of the adsorbed layers increases. This is shown in fig. 6 when ϕ is plotted as a function of σ_2 for the two cases together, and the apparent arbitrariness of the variation of ϕ with σ and salt concentration largely disappears.

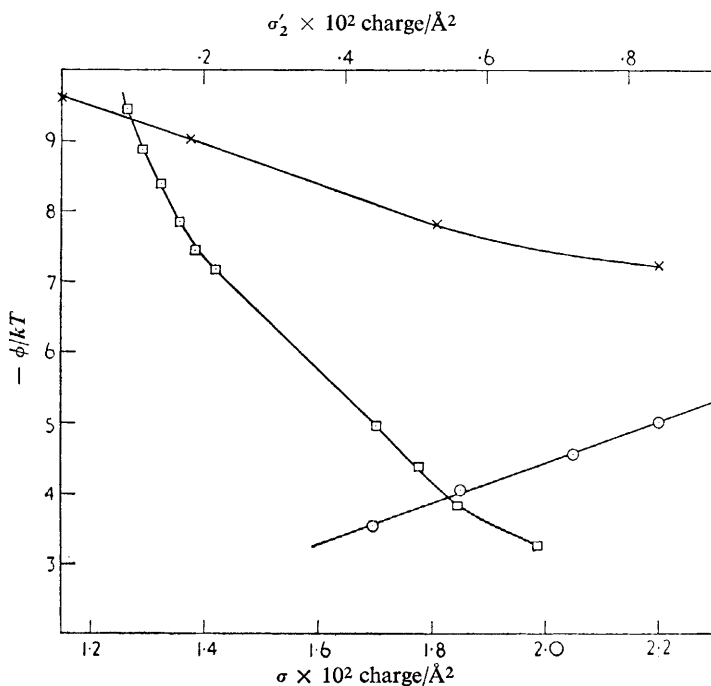


FIG. 6.—Relations for the specific adsorption potential ϕ calculated from the Stern model assuming $\psi_G = \zeta$.

× S.D.S. in water; ○ S.D.S. in 10^{-1} M NaCl;
 □ the two cases plotted together as a function of σ_2 .

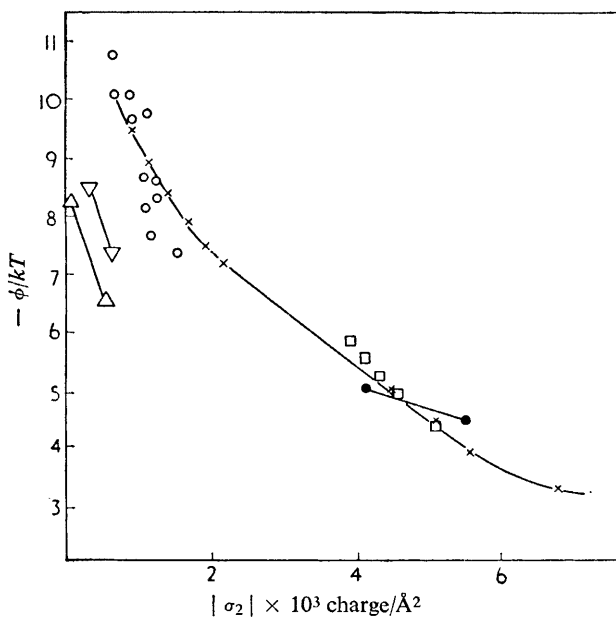


FIG. 7.—Specific adsorption potential as a function of σ_2 , for various systems.

×, S.D.S. present work; ○, sodium octadecyl sulphate monolayers;¹⁹
 □, S.D.S. micelles;²² △, albumin;²³ ▽, haemoglobin;²³ ●, CTA.

There is very little published work with which the present calculations of the specific adsorption potential may be compared. The available data are included in fig. 7. That for octadecyl sulphate is calculated from the monolayer results of Pethica¹⁹ by the methods mentioned above, and includes points taken from the range $\text{NaCl} = 3.16 \times 10^{-3}$ – 3.16×10^{-2} M and $\sigma = 5.5 \times 10^{-3}$ – 4.10^{-2} charge/Å². The data for S.D.S. micelles is obtained from the results of Stigter and Mysels,²² who obtained σ_2 from electrophoresis and the total micellar charge from light-scattering measurements. In this case, σ varies only slightly ($\sim 1.35 \times 10^{-2}$ – 1.55×10^{-2} charge/Å²) whilst the total salt concentration is varied from the c.m.c. in pure water ($\sim 8 \times 10^{-3}$ M) to 10^{-1} M NaCl. Also included on fig. 7 are results for two proteins ($c = 10^{-2}$ M) and the cationic detergent cetyl trimethyl ammonium chloride (CTA) ($c = 5 \times 10^{-2}$ M) calculated from the isolated points given by Davies and Rideal.²³

Thus in all cases, $|\phi|$ decreases with increasing $|\sigma_2|$. No such regularity appears when the results are plotted as a function of the total charge; for S.D.S. micelles σ is almost constant whilst ϕ varies, and in the octadecyl sulphate case ϕ exhibits a maximum with increasing σ . Considering that the three sets of results for the sulphates are obtained from quite distinct experimental and analytical techniques, the agreement between them is remarkably good. The adsorption potentials for the proteins are fairly close together and far removed from those for CTA.

The analysis given above will be tested further as more data are obtained for other systems. If the large variation of ϕ with the net charge of the adsorbed layer is confirmed, then the need for a modified Stern approach is indicated, based on likely non-ideal adsorption isotherms.

I am indebted to Dr. B. A. Pethica for making available to me the results of his calculations of the specific adsorption potential and to Mrs. M. E. Gale for experimental assistance.

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