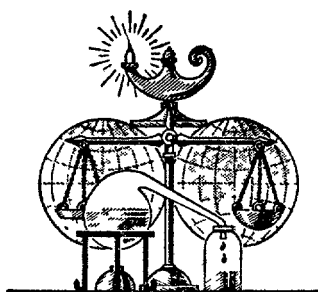


VOL. 10 REPRINT

1965



PURE and APPLIED CHEMISTRY

*The Official Journal of the
International Union of Pure and Applied Chemistry*

CHIMIE PURE et APPLIQUÉE

*Journal officiel de
l'Union internationale de Chimie pure et appliquée*

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International Union of Pure and Applied Chemistry
1966

THERMODYNAMIC AND KINETIC ASPECTS OF THE ELECTROCHEMICAL DOUBLE LAYER

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INTRODUCTION

An electric tension usually exists across the boundary between two phases, and if one of the phases is a fluid ionic conductor, part of that tension is located in an electrochemical double layer, in which ionic charges are displaced perpendicular to the phase boundary, so as to create two (or sometimes more than two) regions of space charge of different sign.

In many cases (*e.g.* if one phase is a metal, or if one of the charged layers is carried by ions adsorbed at the interface) one of the space charge layers may be treated as a good approximation as a surface charge, whereas for the layer in the ionic conductor the space charge character is essential.

The detailed, quantitative study of the electrochemical (also called electric) double layer is important, because it plays a role in all electrode processes, membrane phenomena (including biological membranes), the colloidal stability of suspensions, emulsions and foams, detergency, and in the behaviour of ionic macromolecules, such as nucleic acids and proteins, and even in the generation of thunderstorms. Quite apart from all these fields of application, double layers as such present interesting and challenging problems for the experimentalist and for the theoretician.

ORIGIN OF THE DOUBLE LAYER

The first problem in the study of electric double layers is the question of their origin. What is the direct cause of the spatial separation of the charges? In some cases, as in electrocapillary experiments or in many experiments on electrode reactions the answer is simple. It is the electric potential difference forced onto the systems from an outside source which determines the tension between the two phases, with the distribution of charges following as a secondary effect.

In other cases, however, where the double layer is formed spontaneously at the contact of the two phases (*e.g.* silver iodide and water) the answer is less simple, because the chemical preference of some of the ions for one of the phases or for the interface is the driving force and the final equilibrium is determined by the constancy of the electrochemical potential, $\bar{\mu} = \mu + zF\phi$, of these ions throughout the whole system.

In the final case, the double layer may be generated by dissociation as is the case for soap micelles or polyelectrolytes; this case differs from the formation of Debye-Hückel ionic atmospheres in simple electrolyte solutions only by the fact that a large number of unit charges are bound to a single particle.

THEORETICAL DESCRIPTION OF THE DOUBLE LAYER

For a complete theoretical description of the electrochemical double layer we would need to know:

(i) the distribution in space of the charge carriers, *i.e.* the ions in the solution phase and the ions (and electrons) in the solid phase;

(ii) the distribution in space of the orientation and polarization of the solvent molecules, or the local dielectric constant of the solvent and its orientation by non-electrostatic effects near the interface.

These two sets of data would completely determine such quantities as double layer charge, double layer tension, double layer capacity, and by straightforward thermodynamics the free energy of the double layer. If these data are known at different temperatures, or if calorimetric data are available, energy, entropy and other thermodynamic quantities can be derived.

Additional aspects are needed for the interpretation of the forces between overlapping double layers as is necessary for the understanding of colloid stability, equilibrium thickness of black soap films, and second virial coefficients in the Donnan equilibrium or light scattering.

Here one must know not only the free energy of the electrochemical double layers in interaction, but also forces or energies of a different nature, such as van der Waals forces (usually not considered to form part of double layer problematics) and the free energy connected with the solvent molecules (solvation, "icebergs", impenetrable layers *etc.*).

For the interpretation of kinetic data such as viscosity, sedimentation, diffusion and electrokinetics, free energy data are not sufficient. It is necessary to know the viscosity and even the mobility of the individual components in any point of the double layer, in order to be able to account for deformation and relaxation of the double layer.

Finally a further aspect of the double layer enters in the interpretation of electrode reactions, although in the theories used here the local potential at the ions which are closest to the interface gives sufficient information.

It is fairly obvious that our knowledge of the double layer is not as complete as could be desired and that shortcuts for different aspects have been sought. The choice of these shortcuts is frequently determined by the kind of experiment that is to be interpreted. We should consider the experiments as tools for the investigation of the double layer and a brief survey of these tools and their usefulness will be given.

METHODS OF INVESTIGATION OF THE DOUBLE LAYER

Chemical and electrochemical analysis are among the most straightforward methods for investigating double layers. Determination of the concentration (activity) of the potential-determining ions gives the *double layer tension* between the two phases in equilibrium directly from the Nernst-equation (1):

$$\Delta\phi = \Delta\phi_0 + \frac{RT}{z_1F} \ln \frac{a_1}{a_{1_0}} \quad (1)$$

where *i* indicates a potential-determining ion, of valence z_1 , present with activity a_1 in one phase and constant activity in the other. $\Delta\phi$ is the electric

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tension across the double layer and $\Delta\phi_0$ the electric tension across the double layer at the point of zero surface charge, which is reached at an activity a_{i_0} . R , T and F have their usual meaning.

If it is known which ions carry the *surface charge*, analytical determination of the adsorption of these ions gives the value of the charge. Determination of the (positive or negative) adsorption of ions contributing to the *space charge* gives similar information on this part of the double layer.

Analytical techniques were used at an early stage of colloid chemistry by Freundlich, Joachimson and Ettisch¹ and by Pauli and Valkó², although at that stage separation between adsorbed ions and ions in solution was not always successful. More recently, after the pioneering work of Verwey and Kruyt³ and of de Bruyn⁴ a great deal of information about the double layer on silver iodide in water has been obtained in this way. As an example *Figure 1* shows the charge *vs.* tension curves⁵⁻⁷ at different concentrations of electrolyte, the charge being obtained from the adsorption of I^- or Ag^+ ions and the tension from a direct measurement with a silver-silver iodide electrode.

Very accurate information on double layers can be derived using *electrocapillary techniques* for the mercury-water interface. Due to the high degree of irreversibility of the possible electrode reactions, the double layer tension can be applied from an outside source and thus be known accurately. In older experiments the double layer charge was derived from Lippmann's⁸

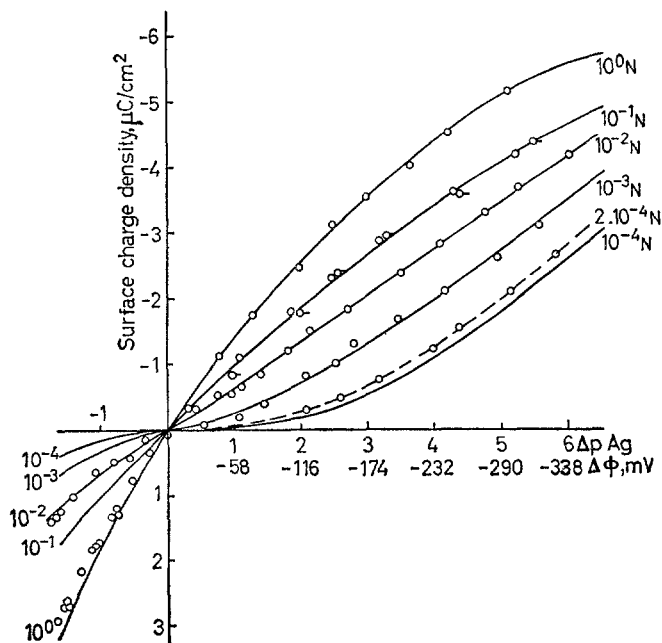


Figure 1. Surface charge density of silver iodide plotted against the double layer tension for different concentrations of electrolyte. Drawn curves are mixtures of KNO_3 and $NaNO_3$ in a molar ratio of 1:7 (van Laar), \circ $NaClO_4$ (Mackor) and $\circ-$ $NaNO_3$ (Mackor)

famous relation (2) between the interfacial tension γ , the surface charge density σ , and the double layer tension $\Delta\phi$:

$$\left(\frac{\partial \gamma}{\partial (\Delta\phi)} \right)_{\text{constant composition}} = -\sigma \quad (2)$$

In its integrated form (3) this equation gives the most straightforward expression for the free energy F of the double layer:

$$F(\Delta\phi) = \gamma - \gamma_0 = - \int_{\text{point of zero charge}}^{\Delta\phi} \sigma \, d(\Delta\phi) \quad (3)$$

In the hands of Frumkin^{9, 10} and others this method has yielded a great deal of information, including some on the influence of adsorbed organic substances. In other experiments Frumkin¹¹ has measured the surface charge directly as the amount of electricity necessary to bring a freshly formed mercury-water interface at a given double layer tension. However, at present the method of choice is the direct measurement of the *double layer capacity*, $\partial\sigma/\partial(\Delta\phi)$, using electronic methods and deriving σ (and if desired γ or F) by integration. Especially since Grahame's careful analysis¹² of the theory involved and his painstaking development of the experimental technique, this method has given information on rather detailed features of the double layer, such as the influence of the lyotropic series (small, much smaller than with silver iodide-water), on specific adsorption, dielectric saturation and water structure. As far as accuracy is concerned it provides very stringent tests for any theory, but its extension beyond the mercury-water case is not easy.

Somewhat similar data can be derived from the *surface pressure of ionized monolayers* and from the *surface tension* of solutions of *ionic surfactants*. In both cases the number of ionic molecules in the surface is known either analytically or by using the Gibbs adsorption equation (4):

$$\frac{\partial \gamma}{\partial \mu_i} = -\Gamma_i \quad (4)$$

where μ_i is the chemical potential of the species i and Γ_i its surface excess. If an estimate is made of the contribution that the non-ionized surface molecules would make to the surface free energy, the remaining surface free energy can be considered as the free energy of the electric double layer^{13, 14}. This quantity can also be calculated from the surface charge and a model for the double layer. The weak point in this method as compared with electrocapillary work is that the electric tension across the interface is often not known, or if it has been measured its relation to the double layer tension is not simple.

Double layers around polyelectrolyte molecules or detergent micelles are conveniently studied with the aid of light scattering or the *Donnan equilibrium*. The extrapolated Donnan osmotic pressure gives information on the molecular weight, but not on the double layer. In the same approximation,

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however, the unequal distribution of ions between the two phases is already related to the distribution of the counter charge between excess counter-ions and a shortage of co-ions^{15, 16}. This same distribution affects the light scattering at infinite dilution^{17, 18}. The second virial coefficients, both from light scattering and the Donnan pressure^{15, 16} are related to the interaction between pairs of particles, and in many cases, especially at high charge of the particles and low electrolyte content, this pair interaction is nearly exclusively determined by the repulsion between the double layers¹⁹.

Interaction between two or more double layers is of great importance in many other phenomena, such as the distance between platelike particles in Schiller layers²⁰, the thickness of black soap films²¹⁻²³ and the stability of lyophobic colloids^{24, 25}.

All the above-mentioned methods for the study of the double layer are essentially thermodynamic, *i.e.* they are based on *equilibrium* phenomena.

There is another group of phenomena, where shearing motions in the double layer are essential. These are the *electrokinetic phenomena* of which electrophoresis is the most widely known, but sedimentation potential, electro-osmosis and streaming potential are nearly equivalent sources of information.

The quantitative relations between the different electrokinetic phenomena have been clarified by the application of thermodynamics of irreversible processes^{26, 27}, although many of these relations have been derived from less general considerations²⁸.

Although interpretation of electrokinetic phenomena in terms of ζ -potential and "slipping plane" is an oversimplification, it is also obvious that electrokinetic effects do not only depend on the electrical structure of the double layer, but also on the distribution of viscosity in it.

A somewhat less direct method, but of the same nature as electrokinetics is the *electroviscous effect*^{29, 30}, *i.e.* the excess viscosity of a suspension due to the presence of a double layer. Another completely different group of non-equilibrium data on the double layer is formed by the *rates of electrode reactions*. Such a rate is, among other things, determined by the electric potential (*e.g.* with respect to the liquid far from the interface) of the ions which actually take part in the reaction, that is, the ions in close proximity to the interface, and consequently it gives information on this potential.

It is rather unfortunate that electrochemists have proposed³¹ to call this potential, ζ -potential or electrokinetic potential, although numerically and conceptually it differs from what colloid chemists have long called ζ - or electrokinetic potential.

INTERPRETATION OF EXPERIMENTS

As mentioned before, experimental data are as a rule interpreted by using a simplified model of the double layer. Simplifications which have been frequently used are the assumption of a continuously smeared-out surface charge and space charge, a fixed dielectric constant all through the double layer, partial dissociation of the surface molecules (often in combination with ideal behaviour of the dissociated ions), a constant viscosity (up to a sharp "slipping plane") and solvation in one form or another.

Simplification is not at all an unjustified procedure as testified by the success of many of these simple theories, but from time to time one has to be aware of its limitations.

The model still most frequently used for the interpretation of analytical and electrochemical data is the Gouy-Chapman double layer, based on the complete Poisson-Boltzmann equation, combined if necessary with a molecular condenser or Stern-layer to take ion-size and specific adsorption into account. This model is sometimes extended by assuming partial dissociation in the surface layer, the association then being a particular form of Stern adsorption. In recent years this model has been refined by taking the discreteness of the surface charge and that of the Stern-layer into account.

Interaction between double layers is often interpreted in terms of interaction between the tails of Gouy-Chapman distributions, or in terms of simple Donnan equilibria. Added to these are long range van der Waals attractive forces, short range Born repulsions and repulsions based on solvation layers.

In the interpretation of electrokinetics a slipping plane is nearly always involved. It may or may not coincide with the Stern layer. In this case partial dissociation refers to all ions within the slipping plane, irrespective of the forces by which they are held there. Sometimes an extra surface conductance of more or less obscure origin is also introduced.

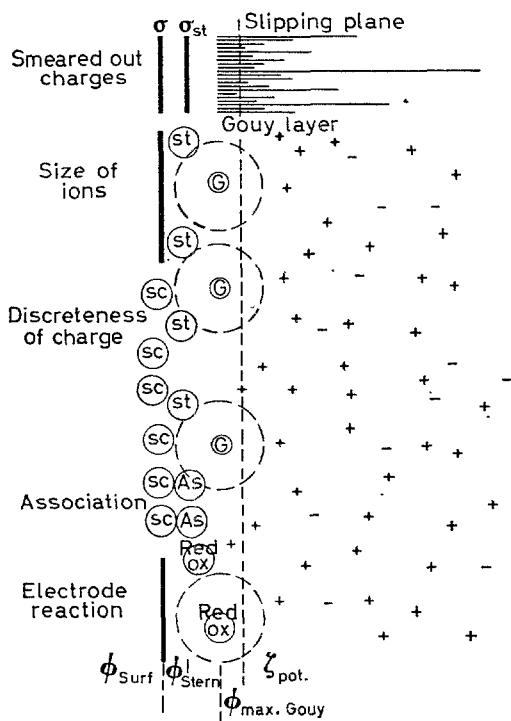


Figure 2. Different approximations and assumptions used in double layer models

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In the field of electrode reactions the most obvious assumption is that the reacting ions are situated in the Stern layer or at the inner boundary of the Gouy layer.

Figure 2, in which some of the assumptions used have been illustrated, may help to visualize the situations.

PROBLEMS OF SPECIAL INTEREST

I should like to discuss a few specific points which are of major interest for the actual research on double layers.

Discreteness of charge

The first point concerns the influence of the discreteness of charge or fluctuation term. Esin and Shikov³² and Ershler³³ have pointed out that the electric field in a condenser with smeared-out charge layers differs from that when the same average charge density is concentrated in finite discrete charges placed at discrete, regular or irregular distances. The simplest way to visualize this is to realise that the electric field is completely confined between the smeared-out charges, but penetrates through the openings in the discrete charge pattern as represented schematically in *Figure 3*. It is obvious that the energy of interaction may differ in the two cases, and that this difference is affected by the actual arrangement of the charges. A quantitative estimate shows that the difference with the smeared-out case may be several times kT , and thus large enough to affect, *e.g.* the adsorption of ions in the Stern layer and therefore such things as the total double layer capacity or the repulsion between two double layers³⁴⁻³⁶.

Overbeek and Stigter³⁷ have applied the same idea in the calculation

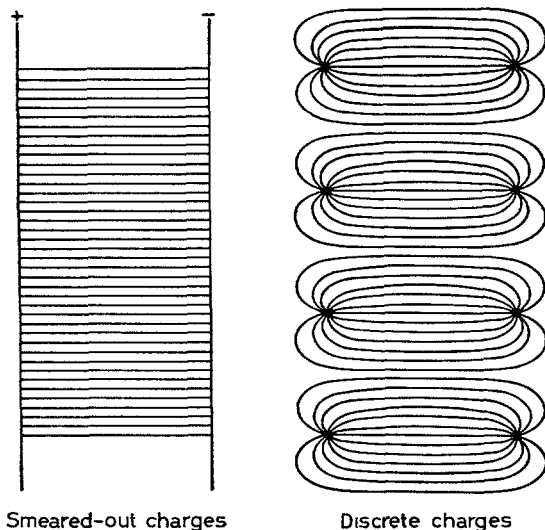


Figure 3. Difference in the fieldlines between smeared-out charges and discrete charges

of the free energy of micellization of detergent ions. Levine, Mingins and Bell^{35,36} have worked on this effect in considerable detail and have ascribed to it among other things the decrease of colloidal stability, which accompanies^{38, 39} an increase in surface charge density.

Nevertheless, the situation is not yet satisfactory. Of course, insofar as the charges are carried by ions they are indeed discrete, but the calculations are so sensitive to the actual assumptions about the pattern of the charges, dielectric constants, *etc.*, that it is not certain that the effects which can be explained qualitatively by the influence of the discreteness of charge also follow quantitatively from it. It would be important to have more data of high accuracy covering wide variations of circumstances (especially the surface charge density) to test the quantitative formulations of the discreteness of charge effect.

Incomplete dissociation

The next point is that of partial dissociation. The behaviour of colloidal electrolytes (polyelectrolytes, detergent micelles) has often been interpreted in terms of partial dissociation of the surface "salt-groups". Examples are: the influence of the double layers in light scattering⁴⁰⁻⁴², thermodynamic treatments of micelle formation in solutions of ionic detergents^{43, 44}, or Donnan equilibria and Donnan electromotive force^{45, 46}.

In the cases cited above and in many others the supposed association is one between Na^+ ions and sulphate, sulphonate or carboxyl groups or between other ions for which low molecular weight analogues do not give any indication of less than complete dissociation. Therefore incomplete dissociation of colloidal electrolytes of this nature is already *a priori* somewhat improbable. Moreover, the law of mass action does not apply at all, which destroys much of the usefulness of the concept of partial dissociation. This is very clearly shown in Klaarenbeek's measurements⁴⁷ on the salt distribution in membrane equilibria of gum arabic in potassium bromide solutions. If these measurements are interpreted using the classical Donnan theory, the degree of dissociation of the potassium salt of gum arabic ($\text{RCOO}^- \text{K}^+$) increases with increasing concentration of K^+ ions—just opposite to what the law of mass action would require. (*Table 1*).

It is much more attractive to attempt an interpretation based on complete dissociation and taking electrostatic effects carefully into account. As

Table 1. Salt distribution in membrane equilibria expressed as equiv. Br^- expelled from the gum arabic solution per equiv. gum arabic and degree of dissociation calculated from it

Concentration KBr in outside solution (equiv./l.)	Br^- expelled per equiv. gum arabic (equiv.)	"Degree of dissociation"
0.00108	0.115	0.23
0.01	0.19	0.38
0.1	0.32	0.64
1.0	0.50	1.0

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Klaarenbeek has pointed out, the qualitative interpretation of *Table 1* is quite simple. Gum arabic, being a negatively charged polyion, attracts cations and repels anions electrostatically, the local concentrations being proportional to a Boltzmann factor, $\exp(-z_i F \phi / RT)$, where ϕ is the local potential. In the classical Donnan approach ϕ is the *average* potential of the colloidal solution ($\phi = 0$ in the outside solution) and is low when the colloid concentration is low. In that case (considering univalent electrolytes), $\exp(+F\phi/RT)$ and $\exp(-F\phi/RT)$ are sufficiently approximated as $(1 + F\phi/RT)$, and $(1 - F\phi/RT)$, which means that the expulsion of co-ions is just as large as the excess of counter-ions, both being equal to half the charge of the colloid. If one considers individual particles, however, the potential in the neighbourhood of a particle remains high even at low colloid concentration, and the positive exponential goes up much faster than the negative one goes down. This dissymmetry causes the expulsion of co-ions to be less than one half of the colloid charge. The effect is most pronounced at low electrolyte concentration, because then the double layer potentials are highest, as shown in *Table 1*. *Figure 4* may illustrate this effect. Further quantitative development of this approach explains a relatively smaller expulsion of co-ions at higher polyelectrolyte concentration, and explains the Donnan osmotic pressure as mainly caused by the electrostatic repulsion between overlapping double layers around the individual particles.

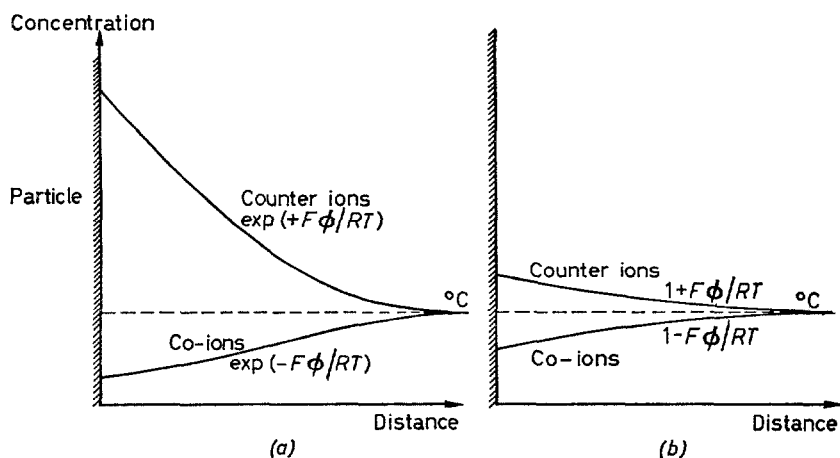


Figure 4. Distribution of ions in electric field around a particle.
 (a) Low electrolyte content, high charge density, high potentials;
 (b) high electrolyte content, low charge density, low potentials

A very similar approach has proved to be applicable to the light scattering by detergent micelles. The authors cited previously⁴⁰⁻⁴² have in essence used the second virial coefficient in light scattering to determine a degree of dissociation (assuming ideal behaviour of the free particles) and used this degree of dissociation to calculate the relative composition of the micelle, the knowledge of which is necessary to estimate its optical effect. Vrij⁴⁸ has pointed out that the situation in light scattering is analogous to that in the Donnan equilibrium. Not only does the Donnan osmotic pressure appear

explicitly in the expression for light scattering as derived by the fluctuation method, but it should also be noted that the scattering particle is not the poly-ion (or ionic micelle) with an equivalent amount of counter-ions, but subtracted from this should be the electrolyte pushed away by the double layer field (negative adsorption). Just as in the Donnan equilibrium, this negative adsorption corresponds to half of the particle charge for low potentials, but to less than half for high potentials. The negative adsorption can either be determined separately in a membrane equilibrium experiment, or the effect of negative adsorption on light scattering can be nullified by extrapolating to a supporting electrolyte, which, when dissolved in the solvent (water), does not modify its index of refraction.

Applying these ideas, Overbeek, Vrij and Huisman⁴⁹ found negative adsorptions as given in *Table 2* from very accurate measurements of the light

Table 2. Negative adsorption of sodium halides (NaX) on micelles of NaDS, derived from light scattering experiments. Calculated values are according to Gouy theory. "Degree of dissociation" is derived from the same experimental data, but assuming ideal behaviour of the dissociated ions. Experimental and calculated second virial coefficients, *B*, defined from the equation:
Donnan osmotic pressure = $\pi = RT (g/M + B g^2)$ in which *g* is the concentration of micellar soap in g/ml

Solvent	Negative adsorption (moles per mole micellar soap)		"Degree of dis- sociation" (per cent)	Second virial coefficient (ml/g × 10 ³)	
	Exp.	Calc.		Exp.	Calc.
Water	—	0.135	27	9.24	12.75
0.01 M NaX	0.15	0.129	30	4.10	5.12
0.03 M NaX	0.14	0.130	28	1.95	2.44
0.1 M NaX	0.15 ⁵	0.149	31	0.60	0.68
0.3 M NaX	0.24	0.216	48	0.23	0.26

scattering of sodium dodecylsulphate (NaDS) in solutions of various concentrations of sodium halides. The experimental figures are in good agreement with negative adsorptions as calculated on the basis of a simple Gouy-Chapman double layer assuming complete dissociation of the sulphate groups. Moreover, the second virial coefficients, calculated from the interaction of two Gouy double layers, are in reasonable agreement with the experimental ones, although a systematic difference of about 25 per cent remains to be explained. The agreement between calculated and observed values for micellar solutions of the lower sodium alkylsulphates (C₈, C₉, C₁₀ and C₁₁) is at least as good as for NaDS.

The conclusion that in many cases ion-binding is purely electrostatic and non-localized is supported by data on proton magnetic resonance⁵⁰, Raman spectra⁵¹, activity coefficients⁵² and on the additivity of partial molal volumes⁵³.

Adhering water layer, slipping plane

As mentioned before the idea of partial dissociation is also applied to electrophoresis and to electrokinetic phenomena in general. As Freundlich⁵⁴

has already pointed out, it is necessary to assume that a layer of solvent adheres to the particle and that only part of the potential drop in the double layer, the “ ζ -potential”, occurs in the mobile part of the liquid and contributes to electrokinetics. In this picture the ions in this stagnant layer move bodily with the particle and as far as electrokinetics is concerned, they are “bound”. Considering these ions as bound may even help to locate the “slipping plane”. The crucial point here is of course: is there a sharp separation between mobile and stagnant liquid, and, if so, where is it located? It is remarkable that, although a very large number of different electrokinetic experiments have been done, so very little is known about this slipping plane. Eversole *et al.*⁵⁵ have calculated the distance between the slipping plane and the interface from the ζ -concentration relation for glass or ceramics water systems. Assuming a Gouy-type double layer, they found that the thickness of the stagnant layer varies between 8 and 63 Å, and varies in a rather unpredictable way between different series of experiments. In such a case the stagnant layer simply serves to cover our lack of understanding.

Lyklema and Overbeek⁵⁶ have suggested that instead of a sharp separation between stagnant and mobile liquid there is a gradual transition from very high viscosity near the actual interface to normal viscosity farther away in the double layer. This gradual change in viscosity could be due to the general phenomenon of increase in viscosity in the electric field of the double layer. Unfortunately the absolute magnitude of this “viscoelectric” effect for water is not known and several authors have suggested that it is much smaller than Lyklema and Overbeek assumed in their paper.

Whatever the true situation is, two recent cases can be mentioned in which it is made very probable that the layer of water adhering to a highly charged interface is only one or a very few molecules thick. Mysels and Cox⁵⁷ and Lyklema, Scholten and Mysels⁵⁸ measured the relation between the thickness, δ , of a film drawn from a detergent solution and the velocity, v , of drawing. According to the quantitative hydrodynamic treatment by Frankel⁵⁹ the relation between δ and v is:

$$\frac{\delta}{(v)^{2/3}} = 1.88 \frac{\eta^{2/3}}{\gamma^{1/6}(\rho g)^{1/2}} \quad (5)$$

where η is the viscosity of the liquid in the film, γ its surface tension, ρ the density of the solution and g the acceleration of gravity. This equation has been derived assuming that the viscosity is equal to η over the whole thickness of the film. In these experiments relation (5) has been proved to be correct over a large range of values of δ and v , and this implies that the viscosity has its normal value all through the film. As a matter of fact, these experiments, one of which is illustrated in *Figure 5*, point to a rigid layer of 16 ± 8 Å thickness at both faces of the film. This includes the thickness of the rigid detergent layer, which is estimated at 16 Å. Consequently the thickness of the rigidified water layer is 0 ± 8 Å. This is a case where the surface charge density is very high on account of the close packing of the detergent molecules.

The notion that the adhering water layer is very thin is strikingly confirmed by Stigter's recent comprehensive analysis⁶⁰ of flow in micellar

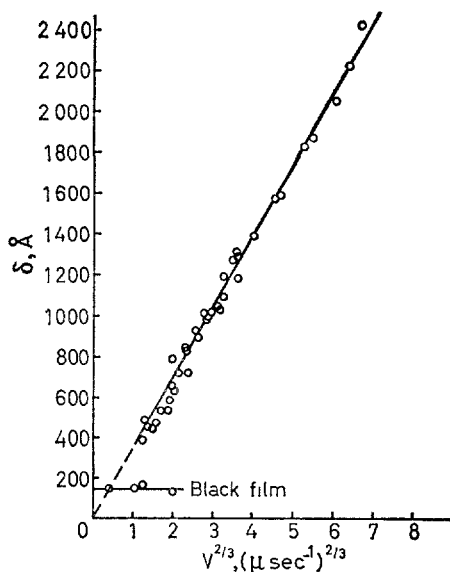


Figure 5. Film thickness, δ , as a function of its rate of formation, V . Films made of 0.0027 M NaDS, 0.00062 M dodecyl alcohol and 0.1 M LiCl

solutions. From a straightforward interpretation of the intrinsic viscosity of micellar solutions by the Einstein equation, taking the contribution of the electroviscous effect into account, Stigter concludes that a micelle of NaDS behaves as a rigid particle in which the hydrocarbon core is surrounded by a fixed layer of 4 Å (± 1 Å) thickness. This thickness agrees quite well with the length of the hydrated sulphate end-group which is estimated at 4.3 Å. It may thus be concluded that *the surface of shear (slipping plane) coincides within 1 Å with the surface enveloping the hydrated end-groups*. For micelles of dodecylammonium chloride a similar conclusion applies. Data on self-diffusion of micelles of NaDS, in which the diffusion constant is interpreted as:

$$D = \frac{kT}{6\pi\eta r} S \left(1 + a \left(\frac{F\zeta}{RT} \right)^2 \dots \right) \quad (6)$$

also confirm that the adhering water layer is thin. In equation (6) r is the radius of the micelle + adhering water, S is a shape factor, deviating from 1 if the micelle is not spherical, and a is the constant for the electroviscous effect, derived from Booth's calculation⁶¹ of the relaxation effect for sedimentation.

Although the adhering layer is found to be at most a very few water molecules thick this layer contains about half of the counter-ions, as follows from further calculations by Stigter based on the electrophoretic mobility and on the conductivity of the micellar solutions. These "bound" counter-ions find a natural place between the head groups of the detergent molecules. Elaborating this model in more detail, Stigter⁶⁰ proves that such a high fraction of counter-ions can be present in the adhering water layer solely

on the basis of electrostatic effects. Specific adsorption potentials for Na^+ or for Cl^- ions are only $0.5 RT$ per mole or less.

The success of Stigter's approach is doubtlessly due to the fact that for these detergent micelles a great variety of thermodynamic and hydrodynamic data are available, and that he has attempted to fit all these data in one model of the micelle and its double layer.

Interaction of double layers; role of solvation.

At this stage it is interesting to discuss the data on the interaction of two double layers, mainly investigated by determining the thickness of "black" detergent films. For low concentrations of electrolyte and high surface charge, equilibrium film thicknesses obtained by various authors⁶²⁻⁶⁴ and for various detergents agree rather well with values calculated on the basis of repulsion between two Gouy layers combined with van der Waals forces. *Figure 6*, taken from Scheludko's work⁶³, illustrates this point.

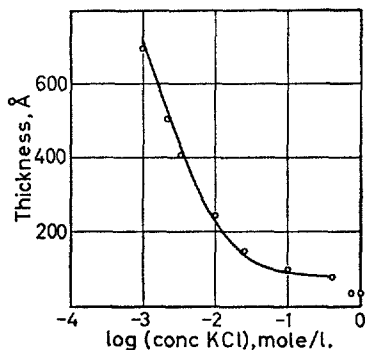


Figure 6. Thickness of equilibrium films of sodium oleate ($10^{-3}M$) in various concentrations of KCl at $21^{\circ}C$. Experiments represented by circles; the drawn line is calculated for Gouy-Chapman double layers with a surface potential of 70 mV and a Hamaker constant A of $7.5 \times 10^{-13} \text{ erg}$

For high concentrations of electrolyte, and thus for thin double layers, the situation is less clear. Deryaguin⁶⁵ suggested thirty years ago that relatively thick layers of water are so tenaciously fixed near the interface that they are not pushed away by the usual hydrostatic and intermolecular forces acting in films. In more recent experiments^{62, 66} he has estimated the thickness of these water layers at about $50\text{--}70 \text{ \AA}$ on each half of the film with the consequence that the equilibrium film thickness does not descend below about 120 \AA even at high salt content and/or low surface charge density.

There are, however, a number of results obtained by other authors in which the existence of stable thinner films is claimed. Corkill *et al.*⁶⁷ have found films of NaDS in $0.1 M \text{ Na}_2\text{SO}_4$ of thickness of about 55 \AA (aqueous core $20\text{--}25 \text{ \AA}$). In Scheludko's work⁶³ shown in *Figure 6*, sodium oleate films occur which are about 80 \AA thick and at about $1 M$ salt films of about 40 \AA are seen, which cannot contain much more than two monolayers of

oleate, with very little water in between. In recent experiments by Corkill, Goodman and Ogden⁶⁸ on films with uncharged surface layers, aqueous cores with a thickness of 22–47 Å have been found. Similar results, *i.e.* very thin films of ionic and non-ionic detergents, have been obtained by Duyvis⁶⁴ and van der Waarde⁶⁹. These measurements are very delicate. The thickness of the films is determined by optical methods, usually by the reflection coefficient for visible light, which is of the order of a few tenths of a percent, so that accurate measurements are difficult.

The interpretation of the reflection in terms of film composition and structure is not without some ambiguity because of the essential inhomogeneity of the films.

Fortunately the question as to whether the ultimate thickness of the film is influenced by the presence of relatively thick solvation layers is considered to be important by all concerned and it can reasonably be expected that the experimental controversy will be solved within the next few years.

On the theoretical side one should consider whether thick solvation layers found in the interaction of double layers are compatible with virtually no solvation in (electro) kinetics. In principle, of course, different properties are involved. In electrokinetics the *mobility* of the surface water is considered and in the interaction it is the *free energy* of surface water which is important. It is, however, difficult to see how a rather sensitive property like viscosity can remain unaffected by a relatively strong binding.

CONCLUSION

Summarizing the situation concerning the electrochemical double layer at this time, the theoretical developments are on the whole ahead of the experimental data, with the exception that a good theory of solvation is still lacking. The most important tasks for the near future are set out below.

(i) Very accurate data on the double layer capacity of mercury–water and if possible similar data for other systems, *e.g.* metal–water, AgI–water, *etc.*, should be obtained, with the main purpose of getting better information on the discreteness of charge effect.

(ii) Electrophoresis, conductivity and other electrokinetic phenomena for a variety of substances, *e.g.* metals, silver halides, barium sulphate, soaps, latex, emulsions and polyelectrolytes, should be measured in order to see whether Stigter's conclusion of the extreme proximity of the "slipping plane" and the interface is confirmed. Glass and quartz are less suitable on account of possible swelling of the surface layers.

(iii) In the field of double layer interactions the existing experimental discrepancies should be removed. A particularly important region is that of low charge and/or high electrolyte content. Application of a variety of methods, not only reflection measurements on films, but also light scattering⁷⁰ of films, infrared absorption, radioactive tracing⁶⁷, optical polarization measurements⁶⁸, and also second virial coefficients in Donnan equilibria or light scattering, should then not only increase our understanding of thin films and foams, but give the fundamental basis for considerations of colloid stability, coalescence of emulsions, flotation, wetting and other phenomena of scientific and practical interest.

References

- ¹ H Freundlich, K Joachimson, and G Ettusch *Z Physik Chem (Leipzig)* **A 141**, 249 (1929).
- ² W Pauli and E Valko *Elektrochemie der Kolloide*, p 289 Verlag Julius Springer, Vienna (1929)
- ³ E J W Verwey and H R Kruyt *Z Physik Chem (Leipzig)* **A 167**, 149 (1934)
- ⁴ H de Bruyn Thesis, Utrecht (1938), *Rec Trav Chim* **61**, 21 (1942)
- ⁵ E L Mackor *Rec Trav Chim* **70**, 763 (1951)
- ⁶ J W A van Laar Thesis, Utrecht (1952)
- ⁷ J Lyklema and J Th G Overbeek *J Colloid Sci* **16**, 595 (1961)
- ⁸ G Lippmann *Ann Chim et Phys* **5**, 494 (1875)
- ⁹ A Frumkin *Ergeb Exakt Naturw* **7**, 235 (1928)
- ¹⁰ M Proskurnin and A Frumkin *Trans Faraday Soc* **31**, 110 (1935)
- ¹¹ A Frumkin *Z Physik Chem (Leipzig)*, **103**, 55 (1923)
- ¹² D C Grahame *Chem Rev* **41**, 441 (1947), *J Am Chem Soc* **80**, 4201 (1958)
- ¹³ Th A J Payens *Philips Res Rep*, **10**, 425 (1955)
- ¹⁴ J T Davies and E K Rideal *Interfacial Phenomena*, pp 95, 106 ff, 237 Academic Press, New York and London (1963)
- ¹⁵ F Klaarenbeek Thesis, Utrecht (1946)
- ¹⁶ J Th G Overbeek *Progress in Biophysics and Biophysical Chemistry*, **6**, 58 (1956)
- ¹⁷ A Vrij and J Th G Overbeek *J Colloid Sci* **17**, 570 (1962)
- ¹⁸ H F Huisman *Proc Koninkl Ned Akad Wetenschap* **B 67**, 367, 376, 388, 407 (1964)
- ¹⁹ A Vrij Thesis, Utrecht (1959)
- ²⁰ P Bergmann, P Low-Beer and H Zocher *Z Physik Chem (Leipzig)*, **A 181**, 301 (1938)
- ²¹ B V Deryagun and A S Titevskaia *Discussions Faraday Soc* **13**, 32 (1954)
- ²² A J de Vries *Rec Trav Chim* **77**, 383 (1958)
- ²³ J A Kitchener In J F Danielli K G A Pankhurst and A C Riddiford *Recent Progress in Surface Science*, Vol 1, p 51 Academic Press, New York and London (1964)
- ²⁴ B V Deryagun and L Landau *Acta Phys -chim URSS*, **14**, 633 (1941)
- ²⁵ E J W Verwey and J Th G Overbeek *Theory of the Stability of Lyophobic Colloids* Elsevier, Amsterdam (1948)
- ²⁶ P Mazur and J Th G Overbeek *Rec Trav Chim* **70**, 83 (1951)
- ²⁷ S R de Groot, P Mazur, and J Th G Overbeek *J Chem Phys* **20**, 1825 (1952)
- ²⁸ U Saxen *Wied Ann* **47**, 46 (1892)
- ²⁹ M von Smoluchowski *Kolloid-Z* **18**, 194 (1916)
- ³⁰ F Booth *Nature* **161**, 83 (1948), *Proc Roy Soc (Lond)*, **A 203**, 533 (1950)
- ³¹ P van Rijsselberghe *Electrochim Acta* **9**, 1343, 1365 (1964)
- ³² O Esin and V Shikov *Zh Fiz Khim* **17**, 236 (1943)
- ³³ B V Ershler *Zh Fiz Khim* **20**, 679 (1946)
- ³⁴ A L Loeb *J Colloid Sci* **6**, 75 (1951)
- ³⁵ S Levine and G M Bell *J Colloid Sci* **17**, 838 (1962), *J Phys Chem* **67**, 1408 (1963)
- ³⁶ S Levine, J Mingins and G M Bell *J Phys Chem* **67**, 2095 (1963)
- ³⁷ J Th G Overbeek and D Stigter *Rec Trav Chim* **75**, 1263 (1956)
- ³⁸ B Težek, E Matjevic and K F Schulz *J Phys Chem* **55**, 1567 (1951), **59**, 769 (1955)
- ³⁹ H R Kruyt and M A M Klompé *Kolloidbehefte*, **54**, 484 (1943)
- ⁴⁰ W Prins and J J Hermans *Proc Koninkl Ned Akad Wetenschap* **B 59**, 162, 298 (1956)
- ⁴¹ L H Princen and K J Mysels *J Colloid Sci* **12**, 594 (1957)
- ⁴² S P Wasik and W D Hubbard *J Res Nat Bur Std A* **68** No 4, 359 (1964)
- ⁴³ G S Hartley *Aqueous solutions of paraffin salts*, p 27 Hermann et Cie, Paris (1936)
- ⁴⁴ K Shinoda *Preprint B/IV, 3* 4th International Congress on Surface Active Substances, Brussels (1964)
- ⁴⁵ R Azuma and N Kameyama *Phil Mag* **50**, 1264 (1925)
- ⁴⁶ G S Adair and M E Adair *Trans Faraday Soc* **31**, 130 (1935)
- ⁴⁷ F Klaarenbeek Thesis Utrecht (1946) Cited from J Th G Overbeek, *Progress in Biophysics and Biophysical Chemistry*, Vol 6 p 58 72 (1956)
- ⁴⁸ (a) A Vrij Thesis Utrecht (1959)
- (b) A Vrij and J Th G Overbeek *J Colloid Sci* **17**, 570 (1962)
- ⁴⁹ (a) J Th G Overbeek, A Vrij and H F Huisman *Proceedings Interdisciplinary Conference on Electromagnetic Scattering* p 321 Pergamon Press, London and New York (1963)
- (b) H F Huisman *Proc Koninkl Ned Akad Wetenschap* **B 67**, 367, 376, 388, 407 (1964)
- ⁵⁰ L Kotin and M Nagasawa *J Am Chem Soc* **83**, 1026 (1961)
- ⁵¹ S Lapanje and S A Rice *J Am Chem Soc* **83**, 496 (1961)
- ⁵² S Lapanje, J Haebig, H T Davis and S A Rice *J Am Chem Soc* **83**, 1590 (1961)
- ⁵³ P Mukerjee *J Phys Chem* **66**, 943 (1962)
- ⁵⁴ H Freundlich *Kapillarchemie*, p 244 Akademische Verlagsgesellschaft, Leipzig (1909)

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- ⁵⁵ (a) W. G. Eversole and P. H. Lahr. *J. Chem. Phys.* **9**, 530 (1941).
⁵⁵ (b) W. G. Eversole and W. W. Boardman. *J. Chem. Phys.* **9**, 798 (1941).
⁵⁶ J. Lyklema and J. Th. G. Overbeek. *J. Colloid Sci.* **16**, 501 (1961).
⁵⁷ K. J. Mysels and M. C. Cox, *J. Colloid Sci.* **17**, 136 (1962).
⁵⁸ J. Lyklema. *Rec. Trav. Chim.* **81**, 890 (1962).
J. Lyklema, P. C. Scholten, and K. J. Mysels. *J. Phys. Chem.* **69**, 116 (1965).
⁵⁹ K. J. Mysels, K. Shinoda, and S. Frankel. *Soap films—Studies of their Thinning and a Bibliography*, Chapter V. Pergamon Press, New York (1959).
⁶⁰ D. Stigter. *Preprint B/IV*, 2. Proceedings 4th International Congress on Surface Active Substances, Brussels (1964).
⁶¹ F. Booth, *J. Chem. Phys.* **22**, 1956 (1954).
⁶² B. V. Deryaguin, A. S. Titijevskaja, I. I. Abricossova, and A. D. Malkina. *Discussions Faraday Soc.* **18**, 24 (1954).
⁶³ A. Scheludko. *Proc. Koninkl. Ned. Akad. Wetenschap.* **B 65**, 97 (1962).
⁶⁴ E. M. Duyvis. Thesis, Utrecht, p. 85 (1962).
⁶⁵ (a) B. V. Deryaguin. *Z. Physik* **34**, 657 (1933).
(b) B. V. Deryaguin and M. Kussakov. *Acta Phys. chim. USSR* **10**, 25, 153 (1939).
⁶⁶ (a) B. V. Deryaguin, A. S. Titijevskaja, and V. X. Vybornova. *Kolloidn. Zh.* **22**, 398 (1960).
(b) B. V. Deryaguin, A. V. Gorodetskaja, A. S. Titijevskaja and V. N. Jasjin. *Kolloidn. Zh.* **25**, 535 (1961).
⁶⁷ J. M. Corkill, J. F. Goodman, D. R. Haisman, and S. P. Harrold. *Trans. Faraday Soc.* **57**, 821 (1961).
⁶⁸ J. M. Corkill, J. F. Goodman, and C. P. Ogden. *Trans. Faraday Soc.* **61**, 583 (1965).
⁶⁹ K. van der Waarde. Private communication.
⁷⁰ A. Vrij. *J. Colloid Sci.* **19**, 1 (1964).



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