PROGRESS IN INTERFACIAL CHEMISTRY IN RELATION TO COLLOID STABILITY

J. Lyklema

Laboratory for Physical and Colloid Chemistry, Agricultural University,
De Dreijen 6, 6703 BC WAGENINGEN, The Netherlands.

Abstract – This paper describes a number of developments in the domain of
interfacial (electro-)chemistry that have repercussions on the understand-
ing of colloid stability. Under conditions of coagulation, the double
layers are almost entirely non-diffuse. Information on such double layers
is obtainable with the mercury-solution interface and much attention is
paid to the translation of this information to systems with which, as a
matter of routine, stability studies are done. The silver iodide system is
very suitable and as a special example the congruence issue of electrosorp-
tion is discussed. Insoluble oxides offer a number of specific problems
that require separate treatment. Furthermore, attention is paid to lyotro-
pic sequences, to structural contributions to stability and to the dynamics
of interaction.

INTRODUCTION

In this review lecture, I intend to pay attention to the relationships between the interfacial
properties of colloid particles and the stability of the corresponding sol against aggrega-
tion. Although it is one of the oldest and most important issues in stability studies, the
number of investigations that are sufficiently systematic and detailed to be useful are still
relatively limited. The reason is primarily, but not exclusively, of an experimental nature.
It is all too easy to measure sol stability in some system, provided it is not too concentra-
ted, and to investigate the effect of changes in conditions such as the addition of an adsor-
bable compound. However, it is very difficult to describe the interfacial alterations provoked
by such a change with satisfactory precision, partly because the particles are seldom well-
defined and well-characterized, and partly because small errors in the establishment of the
precise positions and orientations of adsorbed ions and neutral molecules may lead to consi-
derable uncertainties in the values of variables that are governing particle interaction.

A specific example may illustrate this. Under conditions of coagulation, the potential ϕ_d of
the diffuse double layer part (i.e. the part governing interaction) is of the order 10-20 mV,
even if the surface potential ϕ_o is several hundreds of mV. If a small error is made (either
because of a slightly incorrect theoretical picture or because the precise composition of the
inner layer is not known) in the computation of the potential drop $(\phi_o - \phi_d)$, this can lead to
large errors in ϕ_d, and these errors are even magnified in the stability criterion, because
the DLVO (1,2) expression for the critical coagulation concentration c_c:

$$c_c = \text{const.} \ \varepsilon^3 \frac{[\tanh \ (ze\phi_d/4kT)]^4}{A^2 z^6} \qquad (1)$$

at low ϕ_d may be replaced by

$$c_c = \text{const'} \frac{\varepsilon^3 \phi_d^4}{A^2 z^2} \qquad (2)$$

so that c_c is extremely sensitive to (errors in) ϕ_d. In eqs. (1) and (2), ε is the relative
dielectric permittivity of the medium, z the valence of the (symmetrical) electrolyte and A
the Hamaker-van der Waals "constant" (virtually it is a function of distance).

Because of this difficulty, there is a tendency to follow "escape routes". One of them is not
to worry about the precise inner layer composition and use the electrokinetic potential ζ as
the electric parameter characterizing the particle. Another escape is to perform adsorption
studies only on very well-defined systems like the mercury-solution interface. For our purpose
the first route has the principal disadvantage that the relation between ζ, ϕ_d and stability
has never been rigorously established. The second one has the drawback that stability studies
with mercury sols are very difficult to perform.

These considerations take us to the objective of the present study, namely to review the pro-
gress that has been made in the study of interfacial (electro-)chemistry with systems as well-
defined as possible, to analyze what from such investigations can be deduced for less well-

defined systems and to connect the information obtained with sol stability. Proceeding this way, the introduction of the electrokinetic potential as a primary parameter will be avoided.

APPROACH FROM THE STABILITY SIDE

The present state of stability theory is as follows.

The DLVO theory is now generally accepted as correct under the conditions for which it has been derived, in particular
- the sol must be dilute so that the potential (energy) of mean force may be replaced by the average potential (energy);
- no other interaction forces are operative besides van der Waals attraction and double layer repulsion;
- the geometry of the particles must be relatively simple (spheres, plates, cylinders, etc.);
- the double layers must be purely diffuse;
- upon overlap, the double layers relax sufficiently fast to remain in thermodynamic equilibrium.

Of these five requirements, some are a matter of choosing the system properly (sol concentration, particle size and shape, absence of polymeric additives), others have a more basic character (the relaxation process in double layers). In connection with our theme, let us first focus our attention to the consequences of the existence of diffuse character of the double layer. The dilemma is that diffuse double layers are now understood in much detail, but that under conditions of coagulation double layers are essentially non-diffuse. Extending and quantifying the pertaining argument in the introduction, for an AgI-sol in the regime of slow coagulation (pI $\sim$ 4, $c_{KNO_3} \sim 10^{-1}$ M), ϕ_o (following from Nernst's law) is $\sim$ -400 mV, but ϕ_d is only about -20 mV, as can be inferred from eq.(2), after substitution of reasonable values for A (3). Extrapolation of ζ-potentials, measured at lower c_{salt} to 10^{-1}M leads to comparable or lower values and improved interaction theories (such as a picture in which the differing distance of action between V_R and V_A is accounted for) tend to give even lower values for ϕ_d. The conclusion is that ϕ_d is only about 5% of ϕ_o. For the charge the situation is somewhat less extreme, but even in an electrolyte like KNO_3, containing a weakly specifically adsorbing cation, only about 35% of the counterions is in the diffuse layer. On the other hand, for bivalent counterions this fraction is again lower than 10% (4). (We shall return below to the greater adsorbability of bivalent ions.) For other systems, the situation is not different. For instance, on insoluble oxides surface charges σ_o of several tens of $\mu C/cm^2$ are easily obtained, but the diffuse charge σ_d (calculated from ϕ_d which, in turn, is inferred from electrokinetics or stability studies) is usually not more than a few $\mu C/cm^2$. Similar reasoning applies to systems where the charge is due to adsorption of ionized surfactants, and it follows also from more remote fields such as that of polyelectrolytes, where it is often found that theories do not work unless counterion condensation is accounted for.

Apparently, it is a general feature that under conditions of destabilization the contribution of the diffuse double layer part is relatively small. This fact has a number of important consequences, of which we shall discuss the following.
1. Diffuse double layer theory, as initiated by Gouy (5) and Chapman (6) is based on the idealized Poisson-Boltzmann distribution, in which ion size effects and specific adsorption are neglected and in which for the ions no distinction is made between the average potential and the potential of mean force. Numerous attempts have been made to improve this theory. In principle, two alleys are open: (a) an ab initio treatment in which the mentioned defects are avoided as rigorously as possible, and (b) the more drastic procedure of splitting the double layer into an ideal diffuse part (obeying the PB distribution) and a non-diffuse or Stern layer (7,8) in which all deviations from ideality are compounded. The first approach is intellectually more satisfying, but the second is much more effective in stability studies, (i) because the various defects of the PB picture count heavily only in the first few layers near the surface, and (ii) because ϕ_d is so low that significant corrections are not needed. Actually, there are several highly sophisticated approaches to improve the Gouy theory but their impact on the insight in colloid stability has been small in view of the efforts put into them. Here, we can also learn from the double layer work with mercury, where the Gouy-Stern picture (with refinements in the non-diffuse part only) is used as a matter of routine and appears to work well. In passing, the historical note may be made that the Gouy theory antedates the Debye-Hückel theory by about a decade and that the Stern theory and the DH theory are contemporary. Debye and Hückel referred to Gouy's work only in a footnote.
2. DLVO-theory is worked out mainly for diffuse double layers (putting $\phi_o = \phi_d$) with ϕ_o so high that in eq.(1) the hyperbolic tangent approaches unity. However, we have now seen that ϕ_d is rather low so that eq.(2) does apply. The implication is that c_c is not proportional to z^{-6} but to z^{-2}. Historically, the very strong dependence of c_c on z is known as the (qualitative) rule of Schulze and Hardy (9,10) and DLVO-theory has interpreted it in terms of the z^{-6} power dependency according to eq.(1). This interpretation must now be replaced (11,12) by the following: the rule of Schulze and Hardy is the outcome of the combined direct action of z^2 in eq.(2) and the indirect effect due to the increasing specific adsorption with increasing counterion valency, leading to a lowering of ϕ_d^4. The coagulation concentration being more sensitive to the indirect action of z than to its direct ac-

tion, it is not surprising that the ratio between c_c of mono-, bivalent and trivalent coun- terions is never strictly 1 : 1/64 : 1/729, but deviates from this sequence by several tens of a percent, depending on the natures of the system and the counterion. A logarithmic de- pendence has also been suggested and shown to work reasonably well (13).

In this connection the lyotropic sequences may also be mentioned. Being specific effects, they must have their roots in the Stern layer. Although the effect of the nature of the counterion on c_c is much less pronounced than that of its valency, the latter is by no means negligible. Even for a relatively aspecific system like AgI, the c_c values for $LiNO_3$ and $RbNO_3$ differ by almost 30% (14) and these differences are reflected in the double layer capacitance (11).

3. The relative smallness of σ_d as compared with σ_o offers perspectives for the study of Stern layers. If we are able to measure σ_o and derive σ_d from stability, it is possible to calcu- late the Stern charge σ_s. Since $\sigma_d < \sigma_o$ (or even $\sigma_d \ll \sigma_o$), the quality of the stability measurement and the perfection of the theoretical picture are not very critical. In the introduction it was stated that studies on the composition of the interfacial layer of dispersed particles were bound to be much more difficult than those on mercury because of irreproducibilities inherent to the system. This drawback is to some extent offset by the above possibility, because with mercury it is quite difficult to measure Stern charges in- dependently.

APPROACH FROM THE DOUBLE LAYER SIDE

The mercury solution interface is the best available model system for double layer studies. The interface is smooth and easily renewable, so that contaminations can easily be avoided. Moreover, it is polarizable over a large potential range (depending on the presence of redu- cible substances) which means that ϕ_o can be applied and varied at will; it is an independent variable. Surface charges can be calculated either from electrocapillary curves (by differen- tiation according to the Lippmann equation) or by integration from the (differential) capa- citance, which can be directly measured with a bridge method.

Once $\sigma_o(\phi_o)$ curves are available under various conditions (ionic strength, pH, concentration of adsorptives) it is possible to obtain a rather detailed picture of the composition of the interfacial region, the Stern layer that is, using methods of interfacial thermodynamics in combination with electrochemical principles (15). In many instances it is possible to make rather precise statements on the mode of orientation and the factors responsible for interac- tion in organic and inorganic adsorbates and on the potential drop over the inner and outer Helmholtz layer (the two layers into which the Stern layer can be subdivided). It is a pity that direct verification of all of this information by stability studies is not (yet) possible.

Accepting this situation, the question of generalization automatically presents itself. Can the information obtained with the Hg system mutatis mutandis be applied to systems for which stability measurements *are* feasible? Within some limits, the answer is positive, as we shall now illustrate by comparing some data for Hg with the corresponding data for AgI which, in turn, is a suitable system for stability studies (insoluble oxides exhibit a number of speci- fic features that will be discussed separately below). On AgI, $\sigma_o(\phi_o)$ curves can be obtained either by potentiometric titration or by bridge measurement (16). The surface charge is de- fined as:

$$\sigma_o \equiv F(\Gamma_{Ag^+} - \Gamma_{I^-}) \tag{3}$$

where Γ_i stands for the surface excess of i and F is the Faraday. The AgI-solution interface being reversible, ϕ_o can be obtained, except for a constant, by Nernst's law:

$$d\phi_o = -\frac{RT}{F} \, dpAg \tag{4}$$

or, after integration, choosing the point of zero charge (p.z.c.) in the absence of specific adsorption as the reference point,

$$\phi_o = -\frac{RT}{F} \, (pAg - pAg^o) \tag{5}$$

As a first example, fig. 1 shows that $\sigma_o(\phi_o)$ curves on mercury and silver iodide are rather similar, notwithstanding the substantial differences with respect to nature, electrical pro- perties and geometry of the two materials, the differences between the charge-determining me- chanisms and the principal distinction that one interface is polarizable, whereas the other is reversible. Differences between the two curves are quantitative rather than qualitative and must be due to specific properties of these two systems.

Another quantitative difference concerns the lyotropic sequences. At given negative ϕ_o in both systems σ_o increases in the order:

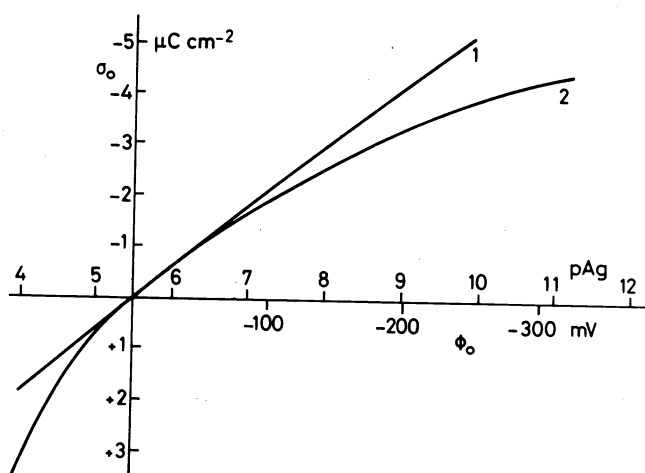$$\sigma_o(Li^+) < \sigma_o(Na^+) < \sigma_o(K^+) < \sigma_o(Rb^+) \tag{6}$$

Fig. 1. Comparison of $\sigma_o(\phi_o)$ curves on mercury (curve 1) (Ref.17) and silver iodide (curve 2) (18). Electrolyte: 10^{-1} M KF.

but the extent of specificity is much more pronounced on AgI than on Hg: on AgI, the relative difference between $\sigma_o(Rb^+)$ and $\sigma_o(Li^+)$ is about 10 times as high as it is on Hg. (Actually, the differences on Hg are so small that, if the differences on AgI would have been of the same order, they would have been experimentally undetectable). The lyotropic sequence in σ_o is *inversely* reflected in the corresponding sequence in the stability, that is: sols with the highest σ_o have the lowest coagulation concentration. This is obviously due to specific adsorption which at given ϕ_o simultaneously leads to low ϕ_d values and to high surface charges. From all of this, it can be predicted that if the stability of Hg sols could be measured, there would be very little specificity with respect to the alkali ions.
Later in this paper, we shall return to the lyotropic series.

Double layer properties in the presence of organic adsorbates are of particular interest for stability studies because of the numerous attempts to modify the electrostatic repulsion energy by changing the double layer structure. The concomitant change of the van der Waals attraction is as a rule several orders less, because (i) the bulk mole fraction of the organic additive is usually small, and (ii) the Hamaker constant is only moderately sensitive to the replacement of water as the solvent by organic fluids.

Concerning the interfacial electrochemistry, detailed pictures have again been developed for the mercury system, whereas for dispersed particles the corresponding information is much more limited. In the latter case typical procedures of analysis are direct measurements of the adsorbed amount and electrokinetic studies, in combination with estimations of c_c or rates of coagulation. As $\zeta \sim \phi_d$, in this way little insight is obtained on the composition and electrical properties of the Stern layer. On the other hand, with dispersed systems direct measurement of the adsorption of the organic compound Γ_A is usually analytically feasible, whereas on mercury this is not usually the case, the total surface area of a mercury drop being too small to lead to detectable depletion of the bulk.

In many cases, $\sigma_o(\phi_o)$ curves on marcury in the presence of varying amounts of an organic adsorbate A have the appearance of fig. 2. Three features are generally observable:
(a) With increasing concentration c_A the slope decreases.
(b) The p.z.c. shifts to the left.
(c) There is a common intersection point (c.i.p.) that is characterized by the values σ_{om} and ϕ_{om}.
Feature (a) points to a reduction of differential double layer capacitance,

$$C = (\partial\sigma_o/\partial\phi_o)_{\mu_A} \qquad\qquad (7)$$

which in decimolar swamping electrolytes equals the Stern capacitance C_s. This quantity is determined by the quotient ε^s/d of the dielectric permittivity in that layer over the layer thickness and by the amount of countercharge, specifically adsorbed in the Stern layer. All of these quantities tend to decrease if water is replaced by an organic substance, which explains feature (a). Later additions are less effective than the earlier ones, due to saturation of the interface.

Feature (b) is due to the replacement of H_2O dipoles by organic molecules. From model considerations that we shall not repeat here it is likely that in the absence of organic additives at the p.z.c. the water molecules are oriented in such a way that there is a net negative excess in the Stern layer on the mercury side. If this layer is replaced by groups that are uncharged or oriented in the same fashion, albeit with a lower net moment, the surface becomes
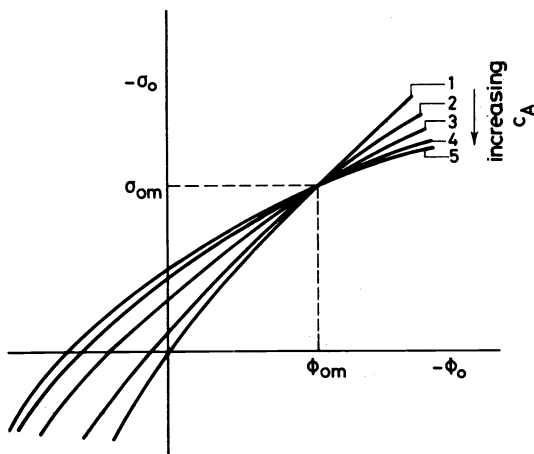
Fig. 2. Often found general appearance of $\sigma_o(\phi_o)$ curves in the presence of increasing concentrations c_A of organic additives. Electrolyte: 10^{-1} M KNO_3.

more positive upon adsorption. Obviously, the magnitude of the shift is a measure of the mode of adsorption and shifts in the negative direction are also sometimes observed.

The c.i.p. (feature c) can be identified with the point where the adsorption Γ_A of A is a maximum as a function of ϕ_o or σ_o. That such a maximum is likely to occur follows from the following physical reasoning: water having a higher dipole moment than the majority of the organic molecules, the competition will always end favourably for the water at very negative and at very positive σ_o, so that at some intermediate value the chances of A to compete with H_2O are a maximum. If the energy of the dipoles in the Stern layer field $(\vec{\mu}.\vec{E})$ would be the only interaction contribution, this maximum would coincide with the p.z.c. but the situation is of course much more complex. Thermodynamically, it follows immediately from Gibbs' law, after cross-differentiation and subsequent integration, that:

$$\Gamma_A - \Gamma_{Am} = - \int_{\phi_{om}}^{\phi_o} \left(\frac{\partial \sigma_o}{\partial \mu_A}\right)_{\phi_o} d\phi_o \tag{8}$$

where
    Γ_{Am} is the maximum value of Γ_A and μ_A the chemical potential of A. Starting at the common intersection point in fig. 2 and integrating to the right, $d\phi_o < 0$ and $(\partial \sigma_o/\partial \mu_A)_{\phi_o} < 0$, hence the RHS of eq.(8) is negative. So it is on the left side of the c.i.p.. Hence Γ_A is always less than Γ_{Am} except at the c.i.p. where the two are equal.

In passing we note that the sharpness of the c.i.p. is a measure of the shift of the adsorption maximum with coverage. If all adsorbing molecules have similar orientations and interactions at every degree of occupancy, this maximum does not shift with Γ_A and the c.i.p. is sharp.

This brief review takes us automatically to the recurring issue of generalization. We are now in the fortunate position that with AgI as the charge carrier qualitatively the same features have also been obtained and that this information has been amplified with data from direct adsorption and/or stability measurements that are unavailable for mercury. A few examples may illustrate this.

A relatively well-studied organic adsorbate is n-butanol in 10^{-1} N HCl. With mercury a picture like fig. 2 is obtained with $\sigma_{om} = -2.0$ $\mu C/cm^2$ and $\phi_{om} = -64$ mV with respect to the p.z.c. in the absence of adsorbate. The maximum shift of the p.z.c. is +240 mV (19). For AgI, the same picture is obtained, except for quantitative differences with respect to the parameters that in this case are: $\sigma_{om} = -1.05$ $\mu C/cm^2$, $\phi_{om} = -70$ mV and the maximum shift of the p.z.c. = +161 mV (20).

More detailed studies (among them a comparison with other alcohols) and theoretical arguments have led to the conclusion that on mercury n-BuOH molecules orient with their hydrophobic moiety towards the surface (21). This is also the case for AgI (20,22). As the OH-group of BuOH is rather far from the surface, these groups are not strongly preferentially oriented, so that upon replacement of water by BuOH virtually a polarized layer is replaced by an apolar one. Experiments with ethylene glycol (EG) as the organic additive confirm this: EG molecules orient with a net dipole moment, pointing with the negative end both to Hg and AgI, so that in this case the shift is considerably smaller than with n-BuOH (23,24).

The presumption that n-BuOH molecules adsorb with their hydrophilic groups towards the aqueous phase has implications for stability. Silver iodide has a relatively hydrophobic surface, as may be inferred from contact angle measurements (25) and the hydrophobic bonding of certain organic molecules (16). Adsorption of n-BuOH hydrophilizes the surface. Uncovered AgI prefers Rb^+ ions over Li^+ ions (see eq.(6)), but on a surface exposing OH-groups this preference is
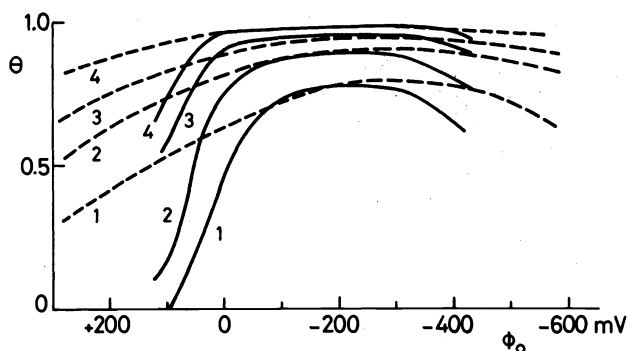
Fig. 3. Adsorption expressed as $\theta_A = \Gamma_A/\Gamma_{Am}$ of tetrabutyl ammonium (TBuA$^+$) ions on mercury (---) (ref.(27)) and silver iodide (——) (28) as obtained from $\sigma_0(\phi_0)$ curves at the following concentrations c_A of the organic substance. 1: 3×10^{-5} m ; 2: 10^{-4} m ; 3: 3×10^{-4} m ; 4: 10^{-3} m .

the other way round, as will be discussed in more detail below. Therefore, the lyotropic sequence in the critical coagulation concentration should also invert, and experiment has corroborated this expectation (26).

Another group of substances showing a qualitatively new feature are tetraalkyl ammonium (TAA$^+$) ions, in the presence of which the double layer properties on Hg and AgI have now been systematically studied. Also with these ions $\sigma_0(\phi_0)$ graphs like those in fig. 2 have been obtained. The inference is that at potentials more negative than ϕ_{om} such ions are desorbed from the surface by rendering it more negative. It is against all intuition that strengthening the Coulombic attraction between surface and counterion leads to desorption of the latter. The explanation is that the adsorption of TAA$^+$ ions is by no means solely governed by purely Coulombic forces but also by hydrophobic bonding. With increasingly negative ϕ_0 not only the Coulombic attraction energy $F\phi^S$ (ϕ^S being the potential at the locus of adsorption) increases but also the attraction energy ($\vec{\mu}.\vec{E}$) of water dipoles displacing a TAA$^+$ molecule. Apparently, at very negative ϕ_0 the latter contribution prevails.

Fig. 3 gives experimental data illustrating the adsorption maxima of tetrabutyl ammonium ions on mercury and silver iodide. The qualitative similarity between the two systems is again noted, although quantitatively TBuA$^+$ ions are more readily desorbed by changes of ϕ_0 from AgI than from Hg. This is probably related to the more hydrophobic nature of AgI and to differences in the charging mechanisms, a matter that will now not be further discussed.

However, there is another interesting feature in fig. 3. At sufficiently positive ϕ_0, curve 1 for AgI approaches zero. This means that curve 1 is an *absolute* curve, in contradistinction to all other curves, that can only relate Γ_A to Γ_{Am}. In addition, silver iodide suspensions have sufficiently high surface areas to allow direct absolute measurement of Γ_A. The outcome of such measurements agrees satisfactorily with those starting from eq.(8), and this is a gratifying confirmation of the applicability of Gibbs' adsorption law to the AgI solution interface (29).

Many of these important conclusions could not have been drawn without experiments involving the AgI system.

THE CONGRUENCE ISSUE

The previous discussion takes us to a closer inspection of the forces responsible for the adsorption of organic additives. The few examples given have already shown that "simple" interpretations are usually inadequate. By "simple" we mean interpretation of ion adsorption in terms of Coulombic energy only, of polar molecules in terms of isolated dipoles only, and of more complex molecules such as surfactants, in terms of additive contributions of the various parts of the molecule. On the other hand, for practical purposes it is often useful to know approximately what the most important factor is. In the realm of mercury interfacial electrochemistry, a procedure known as *"congruence analysis"* is relatively familiar; it allows a first orientation with respect to the dominating interaction contribution and an assessment of the deviations from this predominant behaviour. Such an analysis can also be carried out with disperse systems. Basically, the principle is as follows.

The standard free energy of adsorption $\Delta_{ads}G_A^O$ of some organic compound A is really the free energy of exchange of A against the n molecules of, say, water that are displaced by A. It consists of a chemical and an electrical part:

$$\Delta_{ads}G_A^O \equiv \Delta_{ads}G_{Achem}^O + \Delta_{ads}G_{Ael}^O \tag{9}$$

Splitting up eq.(9) is thermodynamically inoperable; the only way of using this equation is by specifying $\Delta_{ads} G^O_{el}$ as well as possible and then use eq.(9) as the defining expression for $\Delta_{ads} G^O_{chem}$.

$\Delta_{ads} G^O_{el}$ consists of various contributions, viz. terms proportional to ϕ^s, terms proportional to the derivative of ϕ^s with respect to distance (i.e., to the field strength E^s), terms proportional to the second derivative, etc. These terms correspond to adsorption of ions, dipoles, quadrupoles, etc., respectively. If we specify only the two first ones,

$$\Delta_{ads} G^O_{el} = zF\phi^s + \sum_j \Delta n_j \, (\vec{\mu}_j \cdot \vec{E}^s) \tag{10}$$

the quadrupole and higher contributions are by definition included in $\Delta_{ads} G^O_{chem}$. In eq.(10) Δn_j is the change in the number n_j of solvent dipoles due to adsorption. According to Gauss' law, E^s may be replaced by $\sigma^O/\epsilon^s \epsilon_o$, where ϵ_o is the permittivity of free space and ϵ^s the relative dielectric constant of the Stern layer. If θ_j is the angle between the normal and the direction of the dipole moment of j, one can write

$$\Delta_{ads} G^O_{el} = zF\phi^s + \sum_j \Delta n_j \, \mu_j \sigma^O \cos \theta_j / \epsilon^s \epsilon_o \tag{11}$$

showing that $\Delta_{ads} G^O_{el}$ consists of a contribution depending on the potential (more precisely: the potential of the inner Helmholtz plane) and a contribution depending on the charge. We repeat that the two terms in eq.(11) are in principle always both needed. However, idealized abstractions from reality can be imagined in which either the first or the second term is negligible. If the first term is negligible, $\Delta_{ads} G^O_{el}$ is solely determined by σ^O (and not by the potential). A system obeying this requirement is called "*charge congruent*". If the second term is negligible and if the additional assumption is made that ϕ_o and ϕ^s are related in a way that is independent of ϕ_o, $\Delta_{ads} G^O_{el}$ is exclusively determined by ϕ_o (and not by σ_o), and the system is called "*potential congruent*". (Incidentally, the relationship between ϕ^s and ϕ_o is determined by the field strength in the inner Helmholtz layer, which according to Gauss is governed by σ_o.)

Congruency with respect to charge or potential can be inferred from adsorption isotherms in the following way. If some system is charge congruent, the isotherm can be written as

$$f(\theta) = c_A \cdot F(\sigma_o) \tag{12}$$

where $f(\theta)$ is some function of the degree of occupancy and $F(\sigma_o)$ is a function containing besides the chemical free energy of adsorption a term depending only on σ_o (and not on ϕ_o). For instance, for Langmuir adsorption $f(\theta) = \theta/(1-\theta)$ and $F(\sigma_o) = \exp.(-\Delta_{ads} G^O_A/RT)$, with $\Delta_{ads} G^O_A$ given by eq.(9) and the second term of eq.(11).

If now eq.(12) is (semi-)logarithmically plotted, isotherms at different σ_o values have the same shape, i.e., they are *isomorphous* or *congruent*. It follows that they can be made to merge by shifting them along the $\log c_A$ axis by an amount depending on the difference between the σ_o values.

Similar reasoning applies for potential congruency; instead of eq.(12) the isotherm reads then:

$$f(\theta) = c_A \cdot G(\phi_o) \tag{13}$$

where $G(\phi_o)$ is some function of ϕ_o (but not of σ_o).

For disperse systems, congruence analyses have hitherto only sparingly been carried out. One of the reasons is that to that end many data at many values of c_A, σ_o and ϕ_o are needed and that these data must be of high precision. A recent example concerns the adsorption of TAA$^+$ ions on silver iodide, mentioned before (28,29). It appeared that, according to expectation, this adsorption was neither perfectly charge- nor perfectly potential congruent, but that charge congruency was much better obeyed. In view of the discussion given, this underscores that dipole exchange is a more important contribution to the adsorption process than ionic attraction; it supports the picture given in the previous section to interpret the occurrence of an adsorption maximum (fig. 3).

It is hoped that in the near future more of such analyses with other adsorbates and different adsorbents will be carried out.

INTERFACIAL ELECTROCHEMISTRY OF OXIDES

The previous discussion has shown that many features, observable with the mercury-solution interface, recur with silver iodide, proving the qualitative generality of those features. Extensions to other insoluble inorganic materials remain desirable. A special category is that of oxides. For those substances the surface charge

$$\sigma_o \equiv F(\Gamma_{H^+} - \Gamma_{OH^-}) \tag{14}$$

can be plotted as a function of pH, but the ensuing curves do by no means resemble those on AgI as fig. 4 illustrates. Typically, the curves are steep and convex toward the abscissa axis.
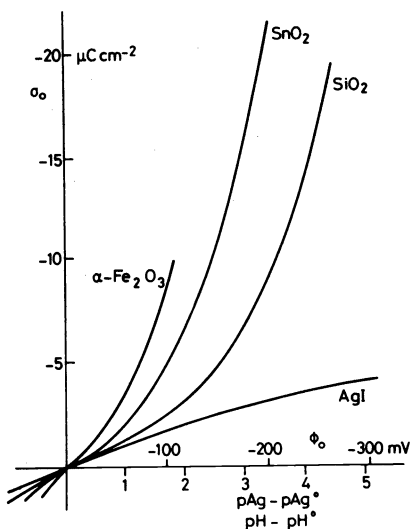
Fig. 4. Surface charge as a function of the negative logarithm of the poten-
tial determining ion concentration, measured with respect to the point of
zero charge in decimolar KNO_3 or KCl. Data taken from refs.(16,30-32).

The surface charge can easily attain values of several tens of $\mu C \cdot cm^{-2}$ or even exceed $100\,\mu C \cdot cm^{-2}$.
All of this is characteristic of all insoluble oxides. Notwithstanding the very high σ_o, these
sols are not particularly stable. For instance, for (positively charged) Fe_2O_3 sols long ago
Freundlich (23) reported critical coagulation concentrations for (1-1) electrolytes around 10
$mMol \cdot l^{-1}$, which is a factor 10 lower than c_c for (negatively charged) AgI sols and the same
electrolytes. More recently, these data were confirmed and extended (34,35). For other oxides
the situation is not different, except for a few particular cases (some silica sols are par-
ticularly stable (36,37), but this has a different origin (38)).

Because of eq.(1), it follows that on oxides a very large proportion (from 80% to more than
99%) of the countercharge must reside at the inner side of the outer Helmholtz plane. There
are two theories to account for this phenomenon: the *site binding* model and the *porous double
layer* model.

The site binding picture describes the binding of potential determining and other ions onto
specific surface sites in terms of equilibrium constants (pK's) (39). It can explain several
features, such as the shapes of the curves near the p.z.c., specific ionic effects, and the
theory offers also an easy interpretation of the value of the p.z.c. However, it has one funda-
mental flaw, viz. that it can not account for the fact that σ_o sometimes exceeds the maximum
attainable surface charge if all surface groups would be dissociated.

The alternative porous double layer picture attributes the excessively high surface charge to
penetration into the solid (40). One of the arguments is that the more porous the oxides are,
the higher their surface charges. An elaboration for the charge-potential distribution inside
the solid has been given.

The two theories are not conflicting but complementary. The porous double layer picture has
not been elaborated to give σ_o(pH) curves, but this can be remedied by combining it with the
site binding theory, a combination that we are now developing. The peculiar properties of
oxides have of course also their repercussions with respect to the interfacial electrochem-
istry and its relation to sol stability. As a trend, adsorption of organic molecules influen-
ces σ_o(pH) curves very little (because the charge accumulated inside the solid is not affec-
ted) (41,42). Therefore, such materials are not so suitable to carry out congruence tests.

LYOTROPIC SEQUENCES

As a trend, lyotropic sequences are now well understood and the principle of the explanation
has been given above: if of two ions a and b of the same valency   a adsorbs more strongly
than b, this must be due to other than purely Coulombic forces, i.e., by specific interaction.
The stronger the specific adsorption, the lower ϕ_d and the higher σ_o at given ϕ_o or at given
concentration of p.d. ions in solution.

How the sequences are depends on the nature of the surface. For instance, both on (negatively
charged) mercury and silver iodide Rb^+ ions adsorb more strongly than Li^+ ones, leading to
sequence eq.(6) in the surface charge and to the reverse order in the critical coagulation
concentration. However, on haematite (α-Fe_2O_3) it is the other way round (32,35). Apparently
the sequence depends on the nature of the surface, that is: on the nature of the surface
groups.

Basically, the explanation in terms of ion size effects is derived from the corresponding in-
teraction in solution. Consider a small anion a and a big one A, and a small cation k and a
big one K, and analyse their *non*-electrical interaction, i.e., their interaction by other than
Coulombic forces. Relatively speaking, the ak interaction is strong since both ions are sur-
rounded by strongly oriented hydration sheaths. So is the AK interaction, because of hydropho-
bic bonding. Relatively weak are the Ak and aK interactions. This trend is reflected in the
logarithms of the activity coefficients log $\gamma_{\pm}$ which tend to be more negative for ak and AK
pairs than for Ak and aK ones. For example, in 1 molal aqueous solutions at room temperature
the values of $a_{\pm}$ for LiOH, CsI, LiI and CsOH are 0.554, 0.532, 0.907 and 0.780, respectively
(43), corresponding with the ak, AK, Ak and aK character of the various pairs in this order.

Translated in terms of surfaces, the distinction can be made between low energy surfaces (i.e.
surfaces with big ions on the surface or no charges at all) and high energy surfaces (small
ions on the surface or at least the charge is strongly concentrated). Negatively charged sil-
ver iodide is an example of the former category, because the big I ions are the outer ions
and haematite is an example of the latter. We recall that on AgI the lyotropic series reverses
itself if the particles are covered by BuOH so that the small OH ions are now exposed to the
solution. Dumont and Watillon (44) prepared two samples of rutile (TiO_2), a high energy one
and a low energy one, and proved that the lyotropic sequence was different. Healy et al. (45)
reported great differences in the coagulation behaviour of amphoteric latices between electro-
lytes containing Cs^+ and Li^+ or K^+ as the cation. Many more examples can be given, and there
are also exceptions. Heterogeneity of the surfaces may blur the trends. Special mentioning
deserves Pearson's attempt to interpret and classify these kinds of interactions in terms of
"hard" and "soft" acids and bases, i.e., measures for the strength of electron donor or
-accepting tendency (46).

The interpretation of lyotropic series demands an argument involving the notion "structure",
and this takes us automatically to the interesting topical issue of "structural forces".

STRUCTURAL FORCES

Over and again, examples have been reported of stability studies where (in the absence of com-
plicating factors like polymeric adsorbates) the DLVO theory was unable to explain the re-
sults. In several cases the occurrence of structural forces due to hydration layers has been
invoked to make the ends meet. Almost equally often, these arguments have been refuted, and
the controversial matter is still under dispute. For a recent discussion see ref.(47).

One of the main reasons for the confusion is that the issue is not properly formulated. Expe-
rimentally, structural forces represent by definition everything that can not be understood
otherwise, and theoretically they are everything that goes beyond DLVO. In this way, "struc-
tural forces" constitute a kind of waste basket which is not the most appropriate way to de-
fine new concepts. Theoretically, the problem is that the notion "structure" requires defini-
tion before we can speak of structural forces.

Structure in fluids is perhaps a somewhat anthropomorphic notion, but there is one way to de-
fine it operationally, that is: in terms of quantities that do reflect the (statistically
averaged) ordering and are measurable. These quantities are the distribution functions
$g^{(h)}(\vec{r}_1, \vec{r}_2, \ldots \vec{r}_h)$ with the pair distribution function in a simple fluid $g(r)$ as the most
familiar example. Distribution functions reflect the extent of "organisation" in a fluid and
are experimentally accessible from X-ray scattering (visible light scattering if distribution
functions on the scale of colloid particles are studied). To define structure near interfaces,
we need the corresponding $g(z)$ distribution functions if z is the distance from the surface.
Hitherto no such measurements have been reported, but there are many computer simulations (48).
If $g(z)$ is known, the number density distribution $\rho(z)$ can be computed and hence the surface
excess:

$$\Gamma_i = \int_0^\infty \rho_i(z)\,dz \qquad (15)$$

where the subscript i refers to component i. Obviously, in multicomponent systems a complica-
ted matrix of distribution functions is required and in that case also a set of functions
$\rho_i(z)$ is needed.

The interfacial excess Gibbs energy per unit area,

$$G^\sigma = \sum_i \mu_i \Gamma_i \qquad (16)$$

can be derived from (15). Suppose now that i refers to the solvent (water), then, if upon ap-
proach of a second particle the distribution $\rho_i(z)$ is altered (i.e. if $\rho_i(z)$ has to be re-
placed by $\rho_i(z,H)$ if H is the interparticle distance), the Gibbs energy of the system is
changed which means that work has to be done to bring the particles closer together. Experi-
mentally this would be felt as a "hydration force".

A hydration force, however, is not the paradigm of a structural force, because all other in-
teraction forces can be calculated along the same lines. The reasoning applies equally well
if i is a low molecular weight organic substance (49) or if it is an ion. Actually, the DLVO-

theory is based on the same principle, the elaboration being that $\rho_i(z)$ is calculated for diffusely distributed space charges as a function of particle distance. Hence, we recognize DLVO-type electrostatic repulsion as a particular kind of structural force.

Having shown that solvent structure interaction forces can be rationally defined and incorporated in a more integrated approach to colloid stability, the question presents itself whether or not such forces have now been unambiguously proved to exist. The collected evidence of the last years is that the answer is positive, but that the range of action is short and comparable with the persistence- or correlation length, a fact that is intuitively anticipated. The most straightforward evidence stems of course from direct measurement of the interaction force and these experiments have now been perfected down to interaction distances of a few tenths of a nm for mica, which is molecularly smooth on that scale (50). Special mentioning deserve experiments by Pashley (51,52) who beyond doubt proved the occurrence of exponentially decaying short range forces (in addition to DLVO interactions, which appeared to work well at larger distances of separation). Typically, these forces which have a repulsive character require a given minimum amount of counterions bound to the surface, so that the association of these forces with the hydration of these ions is almost automatically made. The decay length is of the order of 1 nm, i.e., of a few molecular diameters. Independently, exponentially decaying additional forces have been reported for glass and quartz by Rabinovich et al. (48), so that their existence appears now well-established.

Further penetration in this domain is one of the most interesting challenges of interfacial chemistry.

DYNAMIC ASPECTS

Almost simultaneously with the growing insight in the fine structure of the Stern layer there has been developing a better recognition of the dynamics of the interaction processes. It is not the subject matter of this present paper, but it deserves a brief discussion because it is important and related to interfacial (electro-)chemistry.

The classical interpretation of interaction is based on the assumption of thermodynamic equilibrium, implying that the changes in double layer structure due to a collision between two colloidal particles is a reversible process. In statistical terms: upon interaction, the system is continuously in its most probable state. This assumption is not only made in the DLVO-theory, but also in the various theories of steric stabilization, in those on the effect of low molecular weight adsorbates and actually also underlies the discussion of structural forces, as outlined in the previous section. Also the so-called charge regulation interaction (53) belongs to this category.

However, the establishment of equilibrium is not automatically warranted, because it requires transport processes involving ions and molecules, and these processes have a finite relaxation time. If one of these relaxation times is long as compared with that of the encounter time, the corresponding part of the equilibrium is not attained.

In a special sense, this problem is very old. In the DLVO-theory it is the basis for the distinction between interaction at constant charge and at constant potential (1). Later work has shown that, depending on the system, various intermediate cases are possible with only parts of the double layers relaxed during interaction. For silver iodide, which is the classical example of a constant potential interaction case, it nowadays seems more likely that interaction takes place at constant total surface charge but variable surface charge density distribution (54). Similar questions arise with respect to the effects of adsorption of low molecular weight molecules (do the molecules have time enough to adjust to the changing conditions?), of polymers (to which extent can the segment distribution over trains, loops and tails adjust itself?), and to the hydration forces. Resolving these problems is another challenge of the joint field of interfacial chemistry and colloid stability.

REFERENCES

1. E.J.W. Verwey and J.Th.G. Overbeek, Theory of the Stability of Lyophobic Colloids, Elsevier, Amsterdam (1948), p. 118.
2. B.V. Deryagin and L. Landau, Acta Physicochim. URSS 14, 633 (1941).
3. J. Lyklema, J.Colloid Interface Sci. 58, 242 (1977).
4. J. Lyklema and J.N. de Wit, J.Electroanal.Chem. 65, 443 (1975).
5. G. Gouy, J.Phys. 9 (4), 457 (1910).
6. D.L. Chapman, Phil.Mag. 25 (6), 475 (1913); Ann.Phys. 7 (9), 129 (1917).
7. O. Stern, Z.Electrochem. 30, 588 (1924).
8. D.C. Grahame, Chem.Revs. 41, 441 (1947).
9. H. Schulze, J.Prakt.Chem. 25 (2), 431 (1882); 27, 320 (1883).
10. W.B. Hardy, Proc.Roy.Soc.London 66, 110 (1900); Z.physik.Chem. 33, 385 (1900).
11. J. Lyklema, Croat.Chem.Acta 42, 151 (1970).
12. J.Th.G. Overbeek, Pure Appl.Chem. 52, 1151 (1980).
13. B. Težak, Z.physik.Chem. 191A, 270 (1942); J.Phys.Chem. 57, 301 (1953).
14. H.R. Kruyt and M.A.M. Klompé, Kolloid-Beihefte 54, 484 (1942).

15. R. Parsons, in Comprehensive Treatise of Electrochemistry (J.O'M. Bockris, E. Yeager and B.E. Conway, Eds.), Vol.1, Plenum Publ.Cy., New York (1980) p. 1.
16. B.H. Bijsterbosch and J. Lyklema, Advan.Colloid Interface Sci. 9, 147 (1978).
17. Integration of capacitance data in ref.(8).
18. J. Lijklema, Thesis, State Univ. of Utrecht (1957).
19. E. Blomgren, J.O'M. Bockris and C. Jesch, J.Phys.Chem. 65, 2000 (1961)
20. B.H. Bijsterbosch and J. Lyklema, J.Colloid Sci. 20, 665 (1965).
21. J.O'M. Bockris, M.A.V. Devanathan and K. Müller, Proc.Roy.Soc.London A274, 55 (1963).
22. B.H. Bijsterbosch and J. Lyklema, Proc.4th Int.Congress Surface Activity (Brussels 1964), Vol.II, Gordon & Breach, New York (1967), p. 151.
23. S. Trasatti, J.Electroanal.Chem. 28, 257 (1970).
24. J.N. de Wit and J. Lyklema, J.Electroanal.Chem. 41, 259 (1973).
25. D.F. Billett, D.B. Hough and R.H. Ottewill, J.Electroanal.Chem. 74, 107 (1976).
26. B. Vincent, B.H. Bijsterbosch and J. Lyklema, J.Colloid Interface Sci. 37, 171 (1971).
27. J. Kůta and I. Smoler, Coll.Czech.Chem.Commun. 40, 225 (1975).
28. A. de Keizer, Thesis, Agricultural Univ., Wageningen, Neth. (1981).
29. A. de Keizer and J. Lyklema, J.Colloid Interface Sci. 75, 171 (1980).
30. Th.F. Tadros and J. Lyklema, J.Electroanal.Chem. 17, 267 (1968).
31. S.M. Ahmed and D. Maksimov, J.Colloid Interface Sci. 29, 97 (1969)
32. A. Breeuwsma and J. Lyklema, Discuss. Faraday Soc. 52, 324 (1971).
33. H. Freundlich, Z.physik.Chem. 44, 151 (1903).
34. A. Breeuwsma and J. Lyklema, J.Colloid Interface Sci. 43, 437 (1973).
35. F. Dumont and A. Watillon, Discuss. Faraday Soc. 52, 352 (1971).
36. L.H. Allen and E. Matijević, J.Colloid Interface Sci. 31, 287 (1969); 33, 420 (1970).
37. J. Depasse and A. Watillon, J.Colloid Interface Sci. 33, 430 (1970)
38. J. Lyklema, Croat.Chem.Acta 50, 77 (1977).
39. T.W. Healy and L.R. White, Advan.Colloid Interface Sci. 9, 303 (1978).
40. J. Lyklema, J.Electroanal.Chem. 18, 341 (1968).
41. B.V. Kavanagh, A.M. Posner and J.P. Quirk, Faraday Discuss. Chem.Soc. 59, 242 (1975).
42. A.J. van der Linde, unpublished.
43. H.S. Harned and B.B. Owen, The Physical Chemistry of Electrolyte Solutions, Reinhold, New York, and Chapman & Hall, London, 3rd Ed. (1964); compilations at the end of the book.
44. F. Dumont and A. Watillon, priv.commun.
45. T.W. Healy, A. Homola, R.O. James and R.J. Hunter, Faraday Discuss. Chem.Soc. 65, 156 (1978).
46. R.G. Pearson, J.Am.Chem.Soc. 85, 3533 (1963); Science 151, 172 (1966); J.Chem.Educ. 45, 581, 683 (1968).
47. Water at Interfaces, Symp. Puerto Rico, 1976, publ.in Colloid and Interface Science, Vol.I (M. Kerker, R.L. Rowell and A.C. Zettlemoyer, Eds.), Acad.Press, New York-San Francisco-London (1977), p. 231.
48. Proc. IUPAC-IUTAM Symp. on Particle Interactions in Colloidal Dispersions, Canberra, Austr. March 1981, to be published in J.Colloid Interface Sci. and/or Advan.Colloid Interface Sci.
49. D.H. Everett and C.J. Radke, in Adsorption at Interfaces (K.L. Mittal, Ed.), ACS Symp.Series 8, 1 (1975).
50. J.N. Israelachvili and G.E. Adams, J.Chem.Soc. Faraday Trans.I, 74, 975 (1978).
51. R.M. Pashley, J.Colloid Interface Sci. 80, 153 (1981).
52. R.M. Pashley, J.Colloid Interface Sci., subm. (1981).
53. T.W. Healy, Pure Appl. Chem. 52, 1207 (1980).
54. J. Lyklema and H.P. van Leeuwen, J.Colloid Interface Sci., submitted (1981).