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Feature Article

Interfacial Potentials: Measuring the Immeasurable?

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Abstract. The scientific background of measuring and interpreting potentials at interfaces is discussed in a historical setting. Various types of potentials have to be distinguished. Some are measurable, others not. Static and dynamic aspects will be covered and, as applications, the interaction between electric double layers and the slip process in electrokinetics will be considered. In several cases it is expedient to interpret results in terms of charges rather than in terms of potentials.

Keywords. Interfacial potential, surface potential, zeta potential, colloid interaction, electrokinetic slip.

1. INTRODUCTION

- Zum Unterschied von $\Delta\psi$, das wenigstens prinzipiell immer messbar ist, sind Absolutwerte von $\Delta\varphi$ bis heute noch nicht zugänglich¹
- ... the value of the potential of a single electrode is not amenable to direct experimental determination²
- We measured the electro-surface potential electrophoretically³
- The keyword "surface potential" occurred in a recent paper on modern AFM - like techniques⁴
- Surface potentials can be evaluated by second harmonic generation and similar non-linear optical techniques⁵

These five statements all relate to the measuring of surface potentials, but that seems to be the sole binding element between them. For the rest these quotes differ in many respects, even regarding the definitions and even with respect to the basic tenet whether or not these potentials are experimentally accessible at all. It sounds as a cacophony. Do all quotes refer to the same quantity? It is noted that between the oldest and the more recent of these quotes almost a century elapsed. One would wonder if over such a long time span the improvement of the experimental techniques and the development of better defined systems would have contributed so much to our physical insight that quantities that could not be measured long ago are now within reach of our technical achievements. Or, are there certain generic laws of principle precluding that?

The present paper intends to help solving this basic question and considers how our understanding developed historically.

Prior to that it is necessary to agree on the meanings of basic concepts, their terminology and definitions. In trying that, it is realized that in certain scientific circles group-specific nomenclature is used, that does not necessarily match with that of other teams. Some people state that they have studied potentials whereas it appears that they are dealing with something else. One typical illustration is the notion of *pair potential*, routinely encountered in simulation science. This dubbing is a generally adopted habit, which everybody involved in this field appears to understand. Nevertheless, it is basically incorrect because the quantity under discussion is an energy and not a potential. Routinely, interaction potentials are expressed in units of kT or eV , that is in units of *energy* whereas potentials ought to be expressed in *Volts*. Another illustration is that of measuring so-called electrokinetic or zeta potentials (ζ), a daily routine for every colloid scientist. The procedure is straightforward: one measures, say the electrophoretic mobility, of a colloidal particle and interprets it in terms of, say the Helmholtz-Smoluchovski law, which immediately produces ζ in Volts. This looks like a direct potential measurement. However, in reality this is not what happened; an applied electric field can lead to the displacement of free *charges*, not to the displacement of *potentials*. So, in the derivation of the Helmholtz-Smoluchovski equation some conversion of a charge into a potential must have taken place. Not everybody is conscious of that. We shall come back to this in sec. 6.

In the present paper we shall reserve the notion of “potential” to the *electric potential*, expressing it in Volts.

With this in mind, it is realized that, before dealing with the issue of measuring interfacial electric potentials, it is mandatory to agree on terms and definitions. To that end we shall heed the recommendations made over the past decennia by the International Union of Pure and Applied Chemistry (IUPAC). This organization is appreciated for its attempts to recommend internationally accepted rules for definitions of standards and nomenclature. The obvious reason is to “decacaphone” the literature from incorrect statements. Some of its recommendations refer directly to the measurement and interpretation of interfacial potentials.^{2,6-10} and below we have heeded them maximally. In this way it is hoped that at least the text is understandable for a wide readership. This might be particularly useful when addressing the older literature, stemming from before the time that such recommendations were available.

2. EARLY 20TH CENTURY

There are good reasons for starting the historical considerations with the first part of the 20th century. The centuries before that saw the development of rigorous theories for electric fields, some of these resulting in field vector equations like Gauss’ and Stokes’ theorems and general phenomenological laws derived from these, such as Poisson’s law for the relation between charges and potentials and Smoluchovski’s laws for electrophoretic mobilities and streaming potentials. These theories did not address the basic question what the origin is of the spontaneous charging of colloiddally dispersed particles; it was just accepted that (surface) charges were apparently present and that hence the particles would be the seats of an accompanying (surface) potential. The advent of understanding these origins, together with the development of options for their measurements take us to the beginning of the 20th century, and to the central theme of the present study. What was the state of understanding electrified interfaces around ca. 1920?

In that year theory of diffuse double layers was already available, thanks to the pioneering work of Gouy¹¹ and Chapman.¹² Their model is based on the Poisson-Boltzmann (PB) distribution for the countercharge. Underlying the PB theory are two assumptions. In the first place, ions are considered point charges, *i.e.* as volume-less charges. As a result, the theory is *generic*: dependent on the valences of the ions but not on their sizes. The second, mostly tacit, assumption is that the potential occurring in the Poisson equation is the same as that in the Boltzmann equation. This is not necessarily correct: the former is an average potential whereas the latter is a potential of the mean force. This distinction is rather esoteric, and considered in the domain of statistical thermodynamics. If needed we shall return to this issue later; but let it for the moment be accepted that the difference between the two types of potential are negligible when the potentials are low and when the potentials are very high.¹³ Notwithstanding these quantitative limitations, the Gouy-Chapman (GC) theory was an important leap forward because it was one of the first relevant attempts to quantify some surface potential. However, with respect to our main question about the origin and measurability of the interfacial potential, GC theory does not help. The reason was that this theory was developed as an attempt to interpret electrocapillary curves, in the measurement of which the surface potential across a mercury–water interface is simply applied externally. This leaves unanswered why isolate colloidal particles can also carry a charge, let alone what their surface potentials are.

Apart from this central issue in the present context, let us recall another piece of wisdom of the GC model. It predicted the screening of charges to scale with the square root of the electrolyte concentration, a law observed often thereafter, but which was difficult to understand otherwise.

Still another feature of diffuse double layer theory was the prediction of expulsion of electrolyte by a charged diffuse double layer, a phenomenon that was independently measured and called the Donnan effect.¹⁴ The basic phenomenon is the electrostatic expulsion of co-ions, which is a purely electrostatic phenomenon. However, phenomenologically it is observed as the expulsion of *electroneutral* electrolyte by charged surfaces, colloids and polyelectrolytes. The insight that this phenomenon found its basic origin in diffuse double layer theory grew only several decades later.

What was *not* yet known around 1920 included (what is now known as) Stern theory for non-diffuse layers¹⁵ and the Debye-Hückel theory¹⁶ for the activity of strong electrolytes. Nowadays it is common practice to consider as a first approximation the aqueous side of double layers as consisting of two parts, an inner part, or Stern layer and an outer diffuse part, or Gouy layer. The inner part is the seat of ion specificity, meaning that the sizes and non-electric binding Gibbs energies are different between different ionic species. The impact of Stern theory is in recognizing that ions can also adsorb without electric attraction and hence spontaneously create or reduce an electric potential difference. The idea itself of a molecular condenser was familiar around 1920 though, thanks to the work of Helmholtz in the 19th century. Such layers were mostly called Helmholtz double layers and considered as an alternative for diffuse double layers, rather than as an addendum to them. However, around 1920 this essential step in the spontaneous creation of interfacial potentials by specific adsorption in the Stern, or Helmholtz *part* of a double layer was not yet so clear.

3. FREUNDLICH

With this in mind it is historically interesting to read the pertinent literature from that period. A very rich source for obtaining this information is found in the standard books by Herbert Freundlich (1890-1941), one of the most versatile and all-round colloid scientists of that era. He wrote a sequel of books under the main (German) title *Kapillarchemie*, where the subtitle *Eine Darstellung der Chemie der Kolloide und verwandter Gebiete* explained what he understood by the title and subtitle. Nowadays one would call it “Colloid and related

science”. Later, also English translations appeared under the name Capillary Chemistry. For the present purpose we shall now consider the second print of 1922.¹⁷

The problem that Freundlich was facing was matching the interfacial electrochemistry of large flat surfaces and colloidally dispersed systems. Are there common principles in the creation of electric potentials at the surfaces of dispersed particles and macroscopic amounts of surface? It is particularly interesting to read how Freundlich interprets disparate measurements, some even for ill-defined systems. In chapter 6 of that book he starts with comparing measurements on Nernst-type potentials for macroscopic surfaces with those obtained electrokinetically for colloids.¹⁷ At that time it was by no means clear to which extent measured potentials would be identical under identical ambient conditions. Translated into modern symbols, his question was by how much ψ^o (the electric potential at the phase boundary) and the electrokinetic potential ζ differ. At that time for colloids no other independent experimental evidence (like titrations) was available. It was even not yet clear whether there was a difference of principle between transversal and tangential potentials jumps. Of course, potentials being scalars, their absolute values are only determined by the position in the double layer, hence this question can be translated into that of the spatial variation of ψ and ζ along a surface.

Given the scarcity of experimental evidence, Freundlich approached this problem by investigating how the addition of certain substances affected ψ^o and ζ . Of the many reported facts involved he states that, following Nernst, oxide and carbon electrodes may be considered as hydrogen or oxygen electrodes. With a bit of surprise he also refers to glass electrodes in the sense that their “potential jumps” with respect to electrolyte solutions behave as if the glass were a swollen gel layer containing a fixed concentration of H^+ and/or OH^- ions. He reports that the ζ potential for this system, in agreement with earlier measurements, is very sensitive to the presence of low concentrations of additives. For example, H^+ ions can reduce ζ without changing its negative sign, whereas $AlCl_3$ and crystal violet do invert the sign of ζ already at concentrations as low as 1-2 and 50 μM , respectively, without having any substantial influence on the Nernst potential, ψ^o . The only effect $AlCl_3$ had on ψ^o was changing the spontaneous acidity of the solution, because it is a weak electrolyte. If this effect was suppressed by carrying out the experiment in an (acetate) buffer, the influence on ψ^o disappeared completely. Freundlich had to conclude that ψ^o and ζ are different quantities. Supposed that ζ would be measurable that would not yet mean that ψ^o would be measurable as well.

His qualitative explanation for this difference is essentially the same as our present idea, namely the existence of a slip plane, or a thin slip range. His argument was that upon tangential shear of the water the forces involved are not strong enough to move the water by shearing it at the solid-liquid border. Rather a thin adhering layer remains *stagnant*. Freundlich also realized that the very fact that electrokinetic phenomena could be observed at all must mean that the double layer must have a certain thickness, supporting the existence of a diffuse part. He quoted Smoluchovski who already in 1914, two years before the publication of Gouy theory, arrived at the same conclusion.¹⁸ Figure 1 sketches these ideas.

Qualitatively, the shapes of the two curves do not differ that much from our present insights. Curve 1 applies to simple double layers, curve 2 for systems with overcharging (as it is nowadays called). The most striking difference with (good) recent pictures is the absence of anything quantitative. There are no ideas about the potential inside the solid, it is not clear why there is a bending point in curve 1 and whether the position of that point coincides with the minimum in curve 2. That minimum ($x = d$) is apparently the distance from the surface where specific adsorption takes place. However, Freundlich identifies the potentials at that distance as ζ -potentials and this suggests that the plane of specific counterion adsorption is assumed to coincide with the boundary between tangentially moving and tangentially

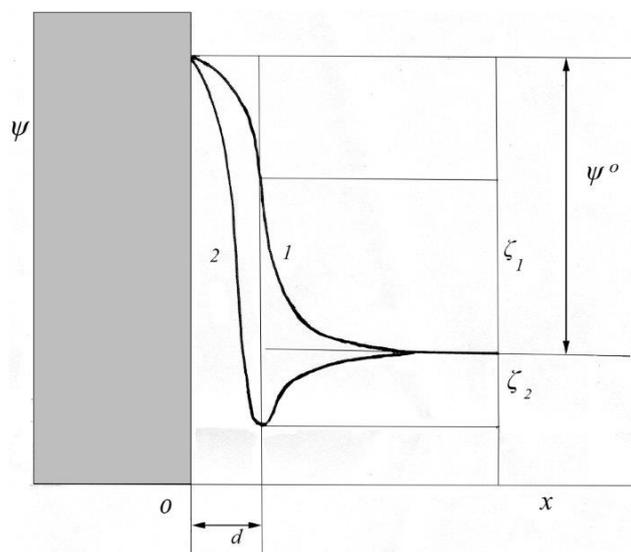


Figure 1. Sketch of the potential distribution $\psi(x)$ in a flat double layer after Smoluchovski (1914) and Freundlich (1922). The border between the solid (hatched) and the liquid is situated at $x = 0$. Discussion in the text.

stagnant water, nowadays called the slip plane. No argument for this is given; at any rate the identity between the two is not obvious: the distance from the solid surface where bound counterions are situated is determined by short range forces and water structure, whereas the position of the slip plane is determined by the tangential motion of many water molecules. There is no *a priori* reason for their identity. We shall return to that in sec. 6.

3.1 Application of Gauss's Law

One feature underlying the sketches of figure 1 that Freundlich did not further elaborate, although its basic physics were perfectly well known to him, was the inference on the various surface charges that can be drawn, using Gauss's vector theorem (also known as Ostrogradski's or Green's theorem). It is a general theorem for a vector field \mathbf{E} in a volume V , bound by a closed area A of arbitrary shape. The space (triple) integral over the divergence of \mathbf{E} equals the surface (double) integral over the inner product $\mathbf{E} \cdot \mathbf{n}$ where \mathbf{n} is the unit vector normal to the surface and directed outward. The mathematics becomes easy if applied to a flat interface, say for a charged sphere with radius $r \rightarrow \infty$. Then $\mathbf{E} \cdot \mathbf{n}$ simply becomes the field strength $E = -d\psi/dx$ normal to the surface. E corresponds to the slope of the curves drawn in Figure 1, integrated over the entire surface A . The triple integral over $\text{div} \cdot \mathbf{E}$ can be written as $\text{div} \cdot (\text{grad} \psi)$, mostly written as $\nabla^2 \psi$ which, according to Poisson's law equals $-\rho/(\epsilon \epsilon_0)$ where ρ is the local space charge density, ϵ is the local relative dielectric permittivity and ϵ_0 is the dielectric permittivity of free space. This triple integral leads to the total charge in the volume V . In our specific case with no space charges in the solid interior, this charge is the surface charge σ multiplied by the area A . Combining all of this leads for one-dimensional situations to the simple expression

$$\frac{d\psi}{dx} = -\frac{\sigma}{\epsilon_0 \epsilon} \quad (1)$$

Eq. (1) is generally valid: at any position in the double layer can we make a cross-section where the part on the left and the part on the right have equal, but opposite charges, given by this equation. For instance, just to the right of the $x = 0$ plane the slope for curve 2 is steeper than that for curve 1, which means that in the second case the surface charge is higher. Phenomenologically this trend is correct: stronger screening leads to higher surface charge at given surface potential. However, curve 2 cannot be correct, because it predicts a maximum in

the countercharge around the slip plane, which is physically unrealistic. Moreover, it would also predict a zero charge coinciding with the slip plane for which also no physical reason can be given. Far from the surface all charges are zero, which is obviously correct.

Although all of this must have been known around 1920, little of such argumentation is encountered in Freundlich's book. In his attempts to get hold of the charging principles he collected many data on the electrokinetic properties of a great variety of systems. Regrettably, in that respect he was not very successful, mainly because he did not have sufficiently well-defined systems at his disposal.

4. LANGE AND KOENIG

About ten years after Freundlich, Lange and Koenig wrote a completely different approach, in which they considered electrical potentials thermodynamically.¹ Not surprisingly, this approach also involved the question of the measurability of surface potentials. The paper is "deutschgründlich" written, with the excuse that they could not present it in even more detail because of lack of space. The Lange-Koenig paper helped the understanding of interfacial potentials in at least two respects: distinguishing between measurable and immeasurable potentials and the introduction of the notion "potential-determining ions".

Their most significant contribution is the insight that there is *in principle* no way for measuring the (electric) potential difference between two adjacent, chemically different phases. Let us by way of paradigm consider the potential of a solid (particle or electrode) with respect to the solution in which it is imbedded. Measuring electric potential differences, say between locations A (the solution) and B (the solid), requires bringing a unit charge from A to B and determining the electric work per unit charge involved. However, when points A and B are located in chemically different condensed phases, the transport of the charge carrier also involves chemical work. For colloids the charge carriers are ions, which have finite sizes and hence they also interact non-electrostatically with their surroundings. The Gibbs energy of that interaction is non-zero even if the phases are uncharged. This chemical contribution cannot unambiguously be separated from the electrical one. Hence, absolute values for the potentials in condensed phases are in principle immeasurable.

It is historically interesting that, in the first quote of the present paper Lange and Koenig take a less absolute stance; they just state that separation is *as yet* not pos-

sible, apparently they believed in technological solutions for all scientific problems. Nowadays the insight is that the impossibility of measuring absolute potentials in condensed phases is intrinsically coupled to the impossibility of measuring thermodynamic potentials of single ionic species. In no way can the energy and entropy of, say a mole of protons be determined because no process can be envisaged to prepare and transport that mole without simultaneously also transporting the same amount of anions. Otherwise stated, potential differences between different condensed phases are *inoperable*. Lange and Koenig realized that.

Given this impossibility, the problem was, and is, how to cope with that in practice. Generally, for such issues two ways are open: avoiding it or subjecting it to penetrating theoretical analyses, two options that are not very handy in daily practice. Lange and Koenig came with two suggestions, the introduction of the notion of *potential-determining (pd) ions* and distinguishing various types of potentials, some measurable, others immeasurable.

4.1 Charge-Determining Ions

As to the former, although absolute potential differences between adjacent condensed phases of different compositions are inoperable, *changes* therein are often accessible, in particular when the material under study can function as an electrode in a Galvanic cell. The simplest example is a cell containing the electrode under study in an electrolyte solution and a reference electrode. The cell potential E_{cell} is in principle measurable and consists of the sum of the sought electrode-solution potential difference $\Delta\psi$ and the reference electrode-solution potential jump $\Delta\psi_{\text{ref}}$. With such a cell one can measure changes in the cell potential as a function of changes in the composition of the solution, like changes of the electrolyte concentration or changes in pH. If the reference electrode is insensitive to those changes, as is the case for a suitable calomel electrode, the change in cell potential comes only on the account of $\Delta\psi$. So, although $\Delta\psi$ is inoperable, $d\Delta\psi$ is relatively well accessible. It was already known to Freundlich that in many systems $d\Delta\psi$ shows Nernst behavior, according to which $d\Delta\psi$ is proportional to the log of certain electrolyte concentrations to the amount of 58 mV per decade of the concentration of that ion. In many cases that electrolyte contains the proton, H^+ and this rule is the basis for applying glass electrodes for the pH measurements. The thermodynamic background of Nernst's law led to the introduction of the notion of potential determining ions by Lange and Koenig.

According to Lange and Koenig, potential-determining ions are thought as being present in both of the adjacent phases in sufficient amount as to be thermodynamically significant. Then, an electrochemical potential can be assigned to the activity of the proton in the solution and the solid and their equalization leads to the establishment of the $d\Delta\psi(\text{dpH})$ relation. Mathematically, electrochemical potentials consist of three terms, for pd ion i generally written as $\mu_i^\circ + z_i F\psi + RT \ln a_i$. We are interested in the variation upon changes in a_i . In the solution this leads to $z_i F d\psi(\text{solution}) + RT d\ln a_i$ and in the solid to $z_i F d\psi(\text{solid})$. Equating these two changes in chemical potentials, writing ψ° for $\psi(\text{solid}) - \psi(\text{solution})$, leads to

$$z_i F d\psi^\circ = RT d\ln a_i \quad (2)$$

which predicts $d\psi^\circ/(RT \ln a_i)$ to be constant and equal to $RT/(zF)$ per decade of the activity of z -valent pd ions. At room temperature this amounts to 58 mV/ z per factor 10 in the activity of i , i.e. the observed Nernst behavior.

The above derivation gives some insight into the assumptions that had to be made in order to arrive at Nernst's law. The observed applicability of this law for a given solid-liquid interface is a justification *in retrospect* for the applicability of the model assumptions for that particular system. As to the measurement it has to be added that measuring relative activity changes of single ionic species ($d\ln a_i$) is not possible; only activity changes of neutral electrolytes or electrolyte mixtures are measurable. To overcome this problem in practice, the procedure is working in swamping electrolyte that has the anion in common with the acid that produces the protons to be measured. For example, if the activity of protons must be measured in HCl, the measurement is carried out in swamping KCl, of which the concentration is fixed so that in $d\ln a(\text{H}^+) + d\ln a(\text{Cl}^-)$ the second term vanishes. Calibration is necessary to ensure that this situation is attained. If it is not sufficiently controlled the trend is that lower than 58 mV is found for the Nernst slope. It may be added that "swamping" means "large as compared to the concentration of i ", implying that not necessarily high salt concentrations are needed.

The notion of potential-determining ions has been generally accepted and used for several decades. Nowadays these ions are rather dubbed "charge-determining (cd) ions", just because of the reason that the absolute value of the potential in a chemically different phase cannot be determined, whereas charges can be very well measured. Below we shall adhere to the term "charge-determining".

The conclusion of this part is intuitively sound: Nernst behavior means that upon transport of one ion

from one condensed phase to the adjacent requires an energy of kT per unit charge $z_i e$ and as energy = charge \times potential its quotient is a unit potential $kT/(z_i e) = 58/z$ mV. Ions for which this is in practice measurable are charge-determining ions.

4.2 The χ -potential

As to the fundamental impossibility of determining absolute values of the potential difference Lange and Koenig proposed to distinguish between different types of potentials, each with its own symbol: the Galvani (ϕ), Volta (ψ), real (α) and χ -potentials. Ref. 1 is replete with relationships between these potentials, and with the thermodynamic and electrochemical potentials in solutions. Galvani potentials are the (immeasurable) inner potentials, in our example the potentials in the heart of a colloid particle or electrode with respect to the bulk of the solution. Volta potentials are measured in the solution so close to the outside of the condensed phase that the effect of the nature of that phase is not felt, but close enough to pick up any longer range effect of the electric charge on the phase. By this definition Volta potentials are in principle measurable, but the information they carry is much less interesting than that of Galvani potentials. Real potentials refer to a specific ionic species, say i , and they are combinations of μ_i and the Volta potential. We shall not use this quantity but note that it is identical to the electronic work function for extracting an electron from a metal (or ion from a non-metal) and take it to infinity. Lange and Koenig distinguished between Galvani and Volta potentials through the different symbols ϕ and ψ , respectively. Hence the distinction between $d\phi$ and $d\psi$ in the first quote of this paper.¹ We shall not use this distinction and only use ψ for the electric potential. Where needed, we shall provide enough information on the way in which the non-electric contributions are sequestered.

The last suggestion by Lange and Koenig, was the introduction of the notion of χ -potential, also recommended by IUPAC. We shall call it the *interfacial potential jump*. The potential jump in going from A to B we shall denote as χ^{AB} . In the Lange-Koenig nomenclature $\chi = \phi - \psi$. The quantity χ is immeasurable but has a clear physical meaning: it accounts for the potential jump at the interface between two phases caused by the local polarization of the molecules at the interface, orientation of water dipoles at the interface, polarization of the surface layer of the solid; in short, all contributions to the potential difference between uncharged adjacent phases, that is: at the point of zero charge. The reason why the introduction of χ is so handy, even though it is immeas-

urable, is that all contributions grouped into it are short-range, a few molecular diameters at most, whereas electric double layers have thicknesses of the order of κ^{-1} which can be orders of magnitude larger. For colloids an additional argument is that surfaces are rarely perfectly flat. Roughness of the order of a few molecular layers can rarely be avoided. An additional consideration for using χ is that the properties of diffuse double layers that are relevant for the daily practice of colloid science (say for the interpretation of colloid stability and electrokinetics) can to a large extent be understood by considering the diffuse part only. However, assuming that the surface charge σ^o has been measured, the very relevant and interesting issue is which fraction of the countercharge ($-\sigma^o$) finds itself in the region very close to the surface, that is: in the Stern layer, and which fraction remains for the diffuse part. This is one of the most recurrent question of double layer science anyway, because the Stern layer coincides with the layer determining χ .

One typical illustration of employing this insight is in establishing the point of zero charge (p.z.c.) for amphoteric colloids, that is the point where the total amount of positive charge on the surface is the same as that for negative charge. This is a measurable quantity. For oxides it is a specific value of the pH, to be indicated as pH^o . Tables of pH^o values can be found in the literature.¹⁹ The point is that these points are not identical to the corresponding points of zero potential. The difference between the two zero points is just χ , the elusive unknown.

“Elusive” is a disputable notion. Nowadays χ is a popular topic of investigation because many modern techniques do shed some light on it, if not in the literary sense of optical measurements but also by molecular simulation, statistical mechanics, colloid chemical, and even thermodynamic tools. As to the last one, thermodynamics are phenomenological, hence cannot tell something about molecular organization but do teach us how to obtain surface excess entropies, which in themselves are challenging quantities. For example, for the surface of pure water the surface excess entropy, (that is: the entropy of the layer that is responsible for the χ -potential) has been obtained from the temperature dependence of the surface tension.¹⁹ In this way the difference between the surface energy and the surface tension could be quantified. On the other hand, Guggenheim refused to discuss χ at all because of its immeasurability.^{20,21} However, if one is not from the very onset at war with model assumptions or approximating experiments, some information about the χ potential of water (χ^w) can, and has been, obtained. It stems from different

sides, like making assumptions for single ionic activities for some untypical electrolytes, comparisons between different electrolytes or of ionic Gibbs energies in different media and simulations, jokingly called “experiments”. All these “partial” or approximate analyses led to roughly the same order of magnitude of a few tens of mV positive.¹⁹ The positive sign means that water is positive with respect to water vapor: the negative sides of the superficial water molecules (the oxygens) are on the average pointing outward. Recent studies of the present author seem to indicate that that is also the case for water in contact with condensed apolar media like mercury or silver iodide. The conclusion is that the immeasurability of potential jumps between condensed phases is basically upheld, but that there are interesting attempts of measuring the immeasurable. See also briefly sec. 8.2.

Figure 2 illustrates how Lange and Koenig visualized the χ -potential at the boundary between a condensed phase (left) and an aqueous solution (right). The picture is extremely simplified. As to χ^w the authors are thinking of a monolayer of oriented parallel water dipoles. This is a very unrealistic model because forcing all those molecules into parallel positions is entropically very improbable. In fact, the numbers for χ and ψ^o that the authors substitute by way of illustration are about a factor of 10 higher than we now know and the peak at $x = d$ cannot be that sharp. The figure also contains a diffuse double layer part that in their text is not discussed; apparently they envisage that the creation of a double layer by adsorption of charge-determining ions simply comes additively, a view that is mostly adhered to till today.

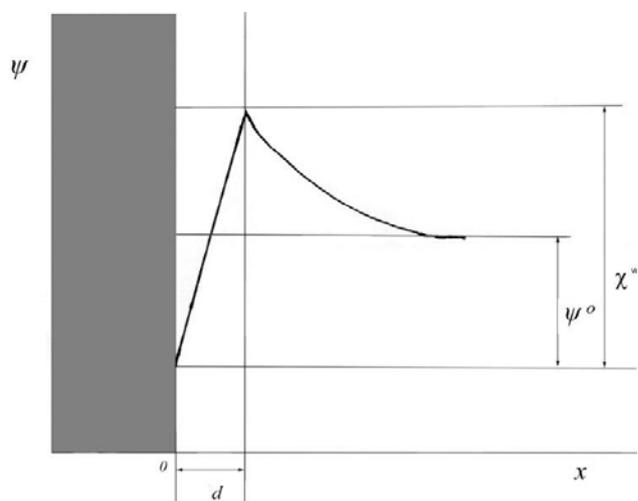


Figure 2. Sketch of the potential jump at a solid-liquid phase boundary as caused by the χ -potential. Modified after ref. 1, their figure 1. Discussion in the text.

In the last pages of their longish (190 pages) paper Lange and Koenig discuss electrokinetic phenomena, emphasizing the complicated influences on the ζ -potential by various electrolytes. In their figure 75 they place the slip plane at the boundary between the Stern layer and the diffuse part, subsuming the χ -potential in the potential of the solid, which is not further discussed, leaving a variety of issues about double layer potentials and charges for their successors., as we shall do in sec.6).

The conclusion of this section is that essentially the impossibility of measuring the absolute value of the potential difference between adjacent condensed phases of different chemical composition is translated into the problem of evaluating the corresponding χ -potential. For many purposes working with charges rather than with potentials is preferable.

5. SILVER IODIDE, THE LUCKY STRIKE OF THE DUTCH SCHOOL

In the years before World War II one of the major challenges in the domain of interfacial potentials and charges was finding systems for which potentials and/or charges could be assessed, if not measured, *both* for macroscopic surfaces and for colloids. For macroscopic surfaces, in electrochemical cells double layer capacitances could at that time be measured with great precision for mercury electrodes, using Wheatstone bridge techniques. For colloids, stability against coagulation and electrokinetic potentials could be measured for several systems with reasonable confidence. However, from mercury it is virtually impossible to make colloidal sols and for colloids it was impossible to determine the surface potential or surface charge. Otherwise stated, systems for which surface potentials/charges and electrokinetic potentials/charges were both measurable did not (yet) exist. It appeared that silver iodide was an excellent candidate to fill that gap.

Colloidal studies with the AgI system have been carried out over more than a century with a major contribution of the Dutch School of Kruyt, Overbeek and offspring. As a model substance for both interfacial electrochemistry and colloidal studies, AgI has many attractive features. The material is chemically nearly inert, its solubility in water is very low (solubility product about 10^{-16} at room temperature), stable sols (many years without perceptible coagulation) can be made of it and the material is very hydrophobic (contact angles for water droplets around 120°). AgI sols are really hydrophobic sols; their stability is exclusively determined by the interaction of overlapping electric double layers. Changes in

the surface charge of dispersed AgI can be measured by titration with KI or AgNO_3 : changes in ψ° obey Nernst's law, with silver and iodide ions charge-determining, *i.e.* changes in the surface charge σ° can be measured as a function of changes in pAg or pI. This last fact means that $d\sigma^\circ$ as a function of $d\psi^\circ$ is measurable, so that the differential capacitance $C = d\sigma^\circ/d\psi^\circ$ can be established. For mercury, the primary measurable is also the differential capacitance, hence properties of very disparate materials in different states (macroscopic surfaces versus finely dispersed) can be compared with each other, a most rewarding exercise! Studying all of that does not require information on the absolute values of ψ° . Hence, they can be carried out without being thwarted by its principally immeasurability. Given the fact that the point of zero potential cannot be established, one usually refers the point of zero charge for which good experimental methods are available (the common intersection point in Figure 5, see below).

The development of all that insight took several decades and in the following sections some typical achievements in line with the present theme will be considered. For historical reasons it be noted that Kruyt et al. were not the only investigators of the AgI system. For example, older, but more primitive titrations have been carried out by Lange and Berger²² and for AgBr by Lottemoser and Petersen.²³ One of the first, but still rather primitive, titration of AgI with different Ag salts was conducted by De Bruyn.²⁴

5.1 Interaction at Constant Potential or at Constant Charge?

During the Second World War colloid science got a tremendous boost by the publication of the DLVO theory for the stability of hydrophobic colloids.^{25,26} The abbreviation stands for Deryagin, Landau, Verwey and Overbeek. The history is well known: the Russians wrote their paper in 1941 in a Russian journal,²⁵ which because of the war conditions did not make it to the West, whereas the Dutch couple elaborated the theory during the War and then wrote an extensive monography on the matter.²⁶ It was only after the War that it became clear that the two theories were identical as to the main principles stability is determined by a balance of van der Waals attraction and double layer repulsion. The qualitative insight that the stability of hydrophobic colloids had its origin in the interaction between electric double layers was more or less generally accepted in 1940 but the quantifications, some of them by respectable scientists like Levine and Langmuir, were not successful: after all, it is not so obvious to prove that interaction between

two double layers that as a whole are electroneutral are repulsive at any distance between the surfaces. In addition, it must be realized that, say around 1935, the role of attractive van de Waals forces was not yet quantitatively established, so that some investigators even considered electric double layers, that, although electroneutral as a whole, could nevertheless be electrically repulsive over some part of the interaction, but attractive over another range. Now we know that attractive van der Waals forces are quantitatively comparable to electrostatic double layer repulsion forces. However, this part of the story, interesting for its own sake, does not belong to the present theme. Let us state that at the start of the Second World War the main problem was to develop a quantitative theory for the electric double layer repulsion that was strong enough to protect the particles against coagulation by van der Waals attraction. Needless to state that this repulsion is sensitive to the potential - and charge distribution during overlap, which brings us back to the theme of this paper.

A crucial proof of the pudding was to explain the observed extreme sensitivity of the stability of hydrophobic sols to the valence of the counterion (the so-called Schulze-Hardy rule). Both DL and VO were able to do so quantitatively and the two couples arrived at the same law. As to the way of presentation, in particular the motivation of some decisions, the VO book is far more useful than the DL paper: the former gives a careful consideration of all the decisions taken, whereas in DL theory sometimes hand-waving arguments are used. For example, when V and O make a conscientious distinction between double layers at high potential and those at high charge, DL only speak of "strong double layers". In connection with the present theme, we are now dealing with double layers resulting from free ionic charges, which may reside in the diffuse or Stern part; the fact that there exists something like a χ -potential does not (yet) play a role, but may show up later.

As to the elaboration of the electric interaction, DL and VO have in common that both compute the charge and potential distribution between two approaching particles at any distance d using a charging process. In this way, not the energy but the Gibbs energy of interaction is obtained, which also contains the entropic contribution. The interaction Gibbs energy is then found as the isothermal-reversible work to adjust the charge and potential distribution upon increasing the overlap between the two surfaces. In passing, it is a pity that this procedure seems to be forgotten when interaction between more complicated colloids has to be considered, for example upon the interaction of oppositely charged polyelectrolytes, as in the formation of complex coacervates.

Overlap of (diffuse) double layers implies that the two original $\psi(d)$ curves will change. The sum of the two contributions at given distance d is not necessarily additive. For the elaboration of the differential equations describing the potential and charge distributions it is mandatory to know the boundary conditions. Will ψ^o remain constant or will it increase? And what will happen with the concomitant charge σ^o ? Pondering this question, it becomes clear that the problem exceeds that of something purely mathematical: basic physical processes are involved. This becomes immediately clear when eq. (1) is considered. See Figure 3B. Keeping the potential fixed upon the approach of a second double layer of the same charge sign can only be realized by reducing the charge, that is: by desorption of charge-determining ions. This is a *chemical* process. When the double layers are far apart the double layer forms spontaneously; its Gibbs energy of formation is negative. Thus, the origin of the stability has a chemical nature. Case A is the other extreme. Then no ion desorption takes place; upon approach the potential must shoot up and now *electric* work must be done to let the surfaces approach. In reality always repulsion is observed, at any d , but the mechanism can be different. Otherwise stated, equal double layers always repel but not necessarily for

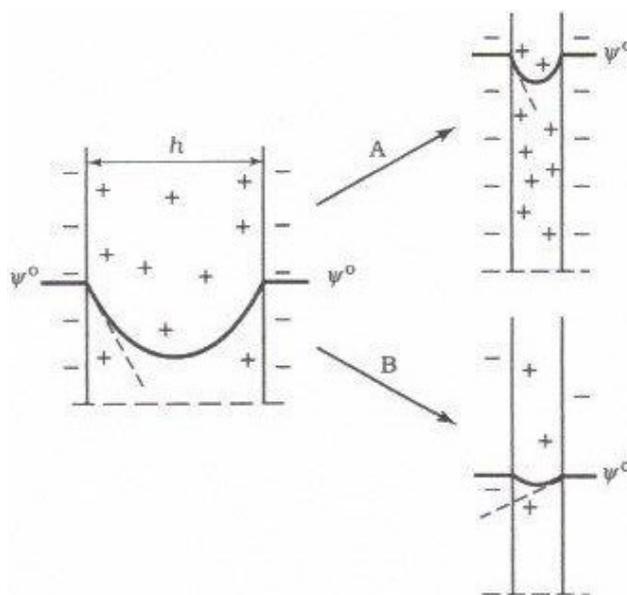


Figure 3. Sketch of the difference between interaction between two diffuse double layers at constant charge (A) and at constant potential (B). In case A, ψ^o increases; the nature of the interaction is electric, whereas in case B, σ^o decreases and the interaction is of a chemical nature. Dashed lines: the slopes, proportional to eq. (1). Reprinted from J. Lyklema, *Fundamentals of Interface and Colloid Science*. Chapter 3: Pair Interactions. 2005. Elsevier, Amsterdam. Copyright © 2005 Elsevier

electrostatic reasons. Case B could well apply to the AgI system, and most of the oxides. Adsorbed Ag^+ ions have to desorb upon approach. Case A is representative for clay minerals for which the charge is more or less fixed because σ^0 is determined by isomorphous substitution of ions inside the solid.

On closer inspection, the distinction between constant potential and constant charge has a dynamic origin. The critical question is whether or not the adsorbed charge-determining ions have enough time to desorb during particle encounter. Supposed we would be able to shoot the particles very rapidly onto each other, so fast that the adsorbed ions would not have enough time to escape, repulsion would still prevail, but the nature of the repulsion would be different.

Returning to Verwey and Overbeek, they realized all of this but for practical reasons had to make a choice which system to elaborate in detail. Not surprisingly, they had the AgI system in mind. Their decision was to treat purely diffuse double layers interacting at constant potential. Theory for such double layers at large separation was available.^{11,12} Going for diffuse double layers implied ignoring ion specificity and was motivated by the fact that the challenge of explaining the very dramatic ion valence effect on sol stability was generic (as diffuse layers are) whereas the less pronounced ion specific effect (typically in the Stern layer) depends on the nature of the colloidal material. (In passing, Ref. 26 also contains a section on Stern layers). As a consequence, the DLVO model is that of a diffuse double layer with surface potential ψ^0 and surface charge σ^0 . The choice for interaction at constant potential was also made with the AgI system in mind: because of the Nernst behavior: ψ^0 is determined by pAg and as the latter remains constant upon particle interaction, so does the former. Nowadays dynamic arguments support this choice: the time for particle interaction is large compared to the relaxation time of a diffuse double layer. In summary, the theory considers interaction between two (flat) double layers at fixed ψ^0 . In fact, the Russians arrived at the same model, although they did not justify their arguments in so much detail.

In order to apply the theory quantitatively a measure for the stability had to be developed. Nowadays that would go in terms of turbidities, but V and O did not yet have such data at their disposal. The alternative of that time were critical coagulation concentrations (c_c), that are the salt concentrations above which the sol is unstable. At that time, by trial and error a procedure was developed to determine such data with a surprisingly good reproducibility. The procedure involved making series of test tubes containing the sol to which

increasing amounts of the electrolytes were added. Using a smart empirical mixture of what is now called perikinetic and orthokinetic coagulation, sharp boundaries between fully coagulated and fully stable sols could be created. The virtue of this time-consuming method was that the relatively complex phenomenon of aggregation could be translated into only one single number, the critical coagulation concentration c_c , a parameter wanting theoretical interpretation.

5.2 DLVO Stability and the Schulze-Hardy Rule

The DLVO relation between the critical coagulation concentration c_c , and the valence of the (z - z) electrolyte can for the present purpose be written as

$$c_c = \text{const} \cdot \frac{(\tanh zy^0)^4}{A^2 z^6} \quad (3)$$

where the *constant* contains known quantities (like natural constants, temperature, dielectric constants, etc.) and A is the Hamaker constant, a measure of the van der Waals attraction between the particles, not surprisingly in the denominator. The most crucial parameter is the surface potential, for which the dimensionless abbreviation

$$y = \frac{F\psi}{RT}, \quad y^0 = \frac{F\psi^0}{RT}, \quad \text{etc.} \quad (4)$$

is used. For the interpretation of the role of the surface potential the dependency of $\tanh y$ on y is critical. At sufficiently high potentials the hyperbolic tangent is independent of y and equal to unity. Verwey and Overbeek pondered the issue. They wondered whether they should substitute y^0 or the dimensionless electrokinetic potential $y^{\text{ek}} = F\zeta/RT$. One argument for the latter was that for hydrophobic sols often a good correlation between zeta potentials and stability was found. However, the desired data available at that time were not yet sufficiently reproducible and it was not clear where the slip plane was located. Hence they fell back on the well-known surface potential, which at the pAg where the stability measurements had been carried out was several hundreds of mV negative, that is, well into the domain where the \tanh function equals unity. In that case the critical coagulation concentration is independent of the surface potential and inversely proportional to the 6th power of the (counter)ion valency. In passing, as the Russians considered “strong” double layers, they also arrived at the z^6 power.

Establishing this law was the beautiful vindication and quantification of the qualitative Schulze-Hardy rule and it became the justification of DLVO theory, even to the extent that the 6th power was sometimes identified as *the* Schulze-Hardy rule. Verwey and Overbeek tested the inverse 6th power law for critical coagulation concentrations of AgI and other hydrophobic sols. They confirmed the quantitative applicability of the law for the difference between $z = 1$ and $z = 2$, with as a trend a lower power for the difference between $z = 2$ and $z = 3$. This solved one of the main problems of colloid stability at that time. However, it was a pity that for the present issue the result is not useful because the potential does not play a role when it is high enough.

5.3. Hofmeister Series and Stern Layers

Superimposed on the 6th power law of DLVO there is a less dramatic, but certainly quite interesting and not negligible ionic specificity effect. At that time, series of data for different ions of the same valency were called *lyotropic* series. Nowadays, the term *Hofmeister* series is more common. For the critical coagulation concentrations of AgI sols these data were well known. Verwey and Overbeek were familiar with the data by Kruyt and Klompé,²⁷ which were also obtained during the war time. (Marga Klompé was a PhD student of Kruyt; later she became the first female Dutch Minister of education). In the table her results are given for monovalent nitrates.

Table 1. Coagulation concentrations of some (1-1) electrolytes for AgI sols. Data by Kruyt and Klompé (1942).

LiNO ₃	165 mM
NaNO ₃	140 mM
KNO ₃	136 mM
RbNO ₃	126 mM

For alkali ions, the differences in the ion specificities are relatively large, about 30% between Li⁺ and Rb⁺ as the counterion. Other investigators of AgI find somewhat different concentrations but always the same sequence. As a digression, it depends on the nature of the colloid whether the sequence is in the direction of increasing or decreasing ion radius. Otherwise stated, the Hofmeister *sequence* depends on the surface properties of the colloid. In fact, recent studies have confirmed the fact that generally such series are not properties of isolated ions but of pairs. In passing, it is an idiosyncrasy of the AgI system that for HNO₃ $c_c = 137$ mM, similar

to that for the cations mentioned in the table: the proton behaves as an ordinary counterion, in contradistinction to most other systems. For oxides protons are even charge-determining.

Not knowing how to deal with ion specificity, Verwey and Overbeek just took the average value, 142 mM for the monovalent alkali ions. By the same token, for seven bivalent cations they obtained the average of 2.43 mM. The ratio $142/2.43 = 58.4$, is close to $2^6 = 64$. They also tested other colloidal systems, like As₂S₃ and Au sols, and positive sols, like Fe₂O₃ and Al₂O₃ which gave rise to Hofmeister series of anions, and grossly confirmed the z^{-6} dependence. So, the interpretation of stability by overlap of the diffuse layers is almost quantitatively explained. This result is still considered as the most important quantitative success of DLVO theory.

Around 1955, when I started my PhD work with Overbeek I focused on the, then still open Hofmeister trend, trying to exploit the other characteristic propensity of the AgI system, namely that it is possible to measure double layer charges by titration. Do the titration charges also depend on the nature of the (counter) ion? In figure 4 results are presented for three of the four alkali nitrates considered in the table.

The p.z.c. is located at pAg = 5.6. To the left of it the surface is positively charged; there the nitrate is the (common) counterion so that no cationic specificity is observable; to the right, at sufficiently negative charge, Hofmeister effects do show up upon increase of the surface charge in the direction Li⁺ < K⁺ < Rb⁺. It was a satisfying result of this research that the ion specificity found in the stability recurred in that of the double layer. At

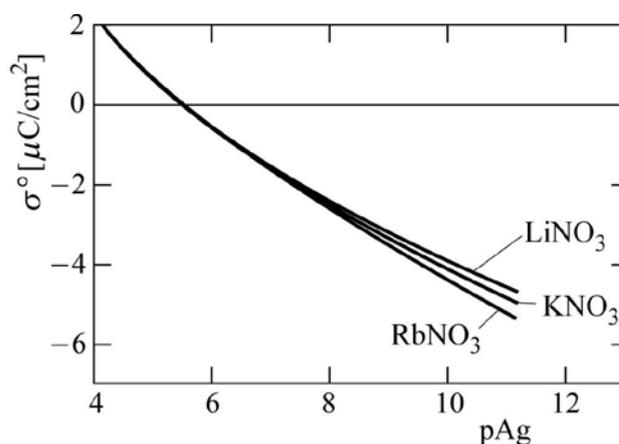


Figure 4. The surface charge on AgI as a function of the pAg in decimolar solutions of the indicated electrolyte, that is the order of magnitude of the c_c . Reproduced from B.H. Bijsterbosch, J. Lyklema, *Adv. Coll. Interface Sci.* **1978**, 9, 147, Copyright 1978, with permission from Elsevier.

the same time it posed a problem in that the direction was unexpected: along the lines of DLVO one would not expect that sols for which the surface charge at given pAg is higher would correspond to less stable sols.

On mercury the same sequence was found in the surface charge but the alkali ion specificity was lower by about a factor of 10^{28} . In fact, had the specificity been so low on AgI, it would have been impossible to measure it at all. Had it been possible to measure the stability of mercury sols, the result as to the Hofmeister effect for alkali ions, would be very dull. This comparison indicates that not only the sequence but also the extent of the specificity depend on the nature of the adsorbent.

Returning to the AgI case, the seemingly contrasting Hofmeister sequences between c_c and σ° proves that one is dealing with the non-diffuse part of the double layer, that is: with Stern layers. For AgI the non-electrostatic affinity increases in the sequence $\text{Li}^+ < \text{K}^+ < \text{Rb}^+$. Rb^+ ions screen the negative potentials near the surface better than Li^+ ions do, apparently because they adsorb stronger. Consequently, at given ψ° , σ° will become more negative but at the same time more of the countercharge is compensated in the Stern layer so that less charge is left for the diffuse part, which controls interaction, hence the lower c_c values.

The combined action of electric and specific interactions in determining double layer properties is also very well reflected in by overall $\sigma^\circ(\text{pAg})$ curves, given in figure 5. The 10^{-1} curve corresponds to the KNO_3 curve of figure 4. On the r.h.s the surface becomes more negative with increasing salt concentration because of screening of the surface charge by electrolyte. The counterion plays the more important role. A large part has an electrical origin, where, typically for PB theory, the vertical distances between the curves scale as \sqrt{c} . The chemical contributions become visible at higher charges and higher salt concentrations, see also Figure 4. On the left hand side of the point of zero charge the surface is positively charged, this charge becomes even more positive by the addition of electrolyte for the same reason as what happens at the negative side. Only at the point of zero charge there is no charge to screen, hence there is no effect of electrolyte, unless one of the ions adsorbs specifically. In fact, this is the common way of establishing the (pristine) *p.z.c.*, that is the *p.z.c.* in the absence of specific adsorption. For AgI the common intersection point is located at $\text{pAg} = 5.6$ till concentrations of 1 M, where the surface is no longer pristine: a slight shift to the right is observed, indicating specific adsorption of the anion, NO_3^- in this case.

So, the double layer properties of colloidal AgI are well understood, without the need of measuring ψ° . It be

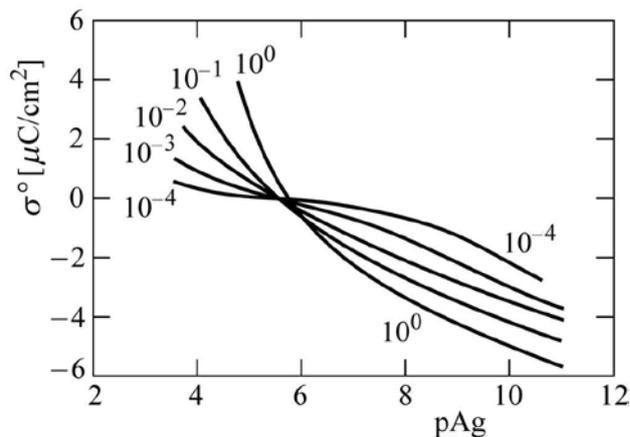


Figure 5. Surface charge as a function of pAg for silver iodide. $T = 25^\circ$. Electrolyte, KNO_3 . The pAg axis may also be read as a ψ° axis with 58 mV per unit of pAg.

repeated that the point of zero charge is not identical to the point of zero potential, which remains immeasurable.

The difference between the pAg of zero potential and that at zero charge is just the χ -potential at the AgI-water interface. When comparing with mercury, the model surface for the electrochemist, it appears that the AgI did become a grown-up counterpart model for which the lesser reproducibility and precision is outweighed by the propensities that double layer charges can be measured because the areas are so large and because the charge-determining ions have been identified.

At this place it is interesting to note that curves like those of figures 4 and 5 have also been measured by the “mercury” method, that is by direct measurement of the differential capacitance of AgI electrodes. The trick is that the adsorption of charge-determining ions is suppressed by working at very high frequencies. The results are very close to those obtained by titration.^{19,29}

This does not yet exhaust the analysis. It is obvious from the above that the DLVO idea of a purely diffuse double layer is untenable. At least a Stern layer has to be added, to account for the fact that even the closest counterions cannot approach the layer where the surface ions are located because of their non-zero volume. That gives rise to a thin charge-free layer close to the surface, the so-called zeroth order Stern layer. It has a (differential) capacitance C_i that is in series with the capacitance C_d of the outer, diffuse part of the double layer. The sum capacitance C is given by

$$\frac{1}{C} = \frac{1}{C_i} + \frac{1}{C_d} \quad (5)$$

The total capacitance is dominated by the lower one of the two. When, in addition to the ion size exclusion, also specific ion adsorption has to be considered, eq. (5) has to be modified. The point is that Figure 5 shows that the double layer is completely diffuse only over a narrow range of very low potentials. The differential capacitance of a purely diffuse double layer depends on ψ^o according to a cosh function, which has a minimum at the p.z.c. For AgI these capacitances are, except for a constant, the slopes of the curves in this figure. Obviously such a minimum is clearly visible only in very dilute solutions around the p.z.c. This conclusion is at variance with the popular statement that one has worked with a “diffuse double layer with Stern corrections”. Nevertheless, as long as no specific adsorption is detectable, the relation between charge and potential for diffuse layers remains valid, except that the diffuse part does not start at the surface but at a short distance from it, corresponding to the thickness of the Stern layer.

Figure 6 illustrates how we look nowadays at the structure of double layers. The distinct subdivision between a diffuse and a non-diffuse part is well-motivated and has many practical advantages, even if we neither know exactly how thick the Stern layers are, nor how much charge they contain. All short-range effects are subsumed in it, so that beyond this layer the layer is purely diffuse, where Gouy-Chapman theory does apply with impunity. Depending on conditions the diffuse part may contain all or only a minor part of the countercharge but even if this is only a low fraction, it nevertheless plays a dominant role in colloid stability and rheology.

Figure 6a is the most simple double layer with a charge-free Stern layer. In this case the diffuse charge σ^d equals minus the surface charge, which is measurable. For a flat double layer (in practice, for $\kappa a \gg 1$) Gouy theory has derived the following useful equation,¹⁹ relating the surface charge to the diffuse potential ψ^d ($y^d = F\psi^d/RT$):

$$\sigma^d = -\sqrt{8\epsilon\epsilon_0 RT} \sinh \frac{zy^d}{2} \quad (6)$$

In the inverse situation, when the charge has been measured, the potential follows from its inverse:

$$y^d = \frac{2}{z} \sinh^{-1} - \frac{\sigma^d}{\sqrt{8\epsilon\epsilon_0 RT}} \quad (7)$$

This equation is often used in electrokinetics, where the charges on moving particles are measured but

where these charges are by force of habit converted into ζ -potentials, (sec. 6).

Figure 6b is characteristic for situations where ion specificity is observed, as in the AgI case of figure 4. The specifically adsorbed charge is called σ^i and the potential at their locus of adsorption is denoted ψ^i . Sometimes the planes where the specifically adsorbed ions reside and the plane from whereon the layer is diffuse are called the “inner and outer Helmholtz layer” (iHp and oHp, respectively). As to our present theme, ψ^i is immeasurable. Eq. (6) remains valid, of course, but only for the diffuse part. Beyond that, its application becomes problematic because from the charge balance $\sigma^o + \sigma^i + \sigma^d = 0$ the diffuse charge σ^d cannot be computed (unless additional data are available, see sec 5.4). In this connection, eq. (6) is often used under conditions where it is not

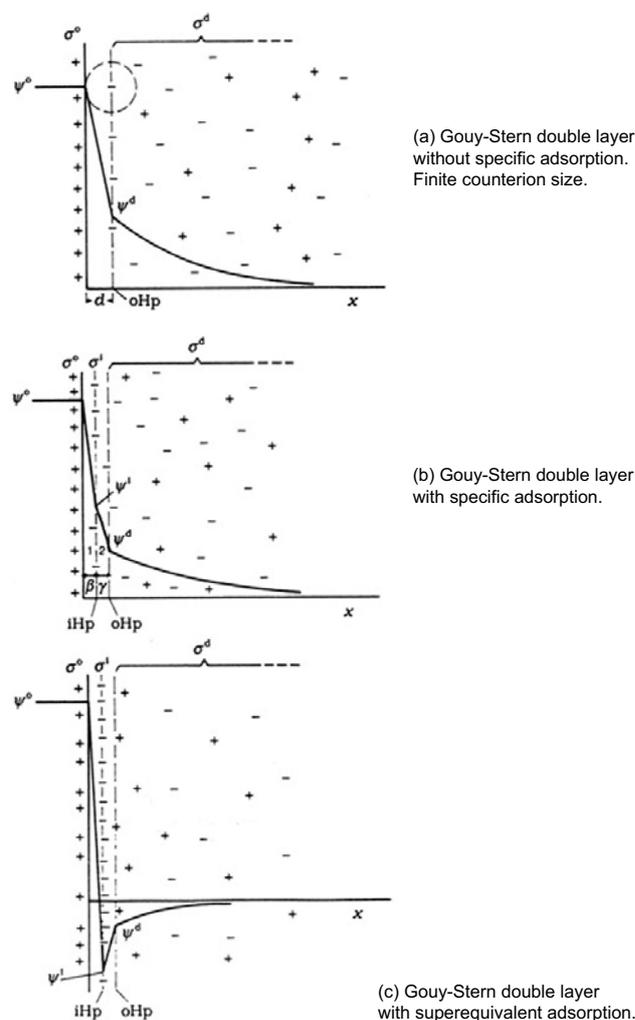


Figure 6. Actual view of Gouy-Stern double layers. Taken from Ref. 19 with permission. Copyright © 1995 Academic Press. Published by Elsevier. Discussion in the text.

allowed. Perpetrators are psychologically lured by the scientific magic and apparent rigor, and by the suggestion that unknown potentials can seemingly, but erroneously be identified. With three unknown potentials and two unknown charges there are six ways of going wrong and only one of them is correct.

Turning to Figure 6c, this is a sketch of the potential distribution in cases where the double layer contains more countercharge in the Stern layer than needed to compensate the surface charge. This phenomenon is commonly called overcharging. Several theories have been proposed to explain it. For the AgI case, and probably much more generally, overcharging occurs for counterions of higher valency if they hydrolyse in the adsorbed state. The hydrolyzed complexes have a strong chemical affinity to the surface. That this is the right mechanism can be proven by systematically investigating the pH dependence of the charge inversion.³⁰ So, it is a chemical, rather than electrical phenomenon.

5.4 DLVO Theory Revisited

It is obvious from the previous sections that the premises of DLVO theory, notwithstanding its successes, have to be reconsidered. The main correction is that only part of the counterlayer is diffuse and that the potential of the diffuse layer is not ψ^o but ψ^d . The latter potential is quite a bit lower than the former and depends on the nature of the counterion. Let us consider these points systematically.

Is ψ^d measurable? There is no argument against measurability of the nature as we invoked when explaining why ψ^o is immeasurable, because the location of the potential ψ^d is in the same solution as the reference. On the other hand, ψ^d is a model parameter; it is based on a number of assumptions. The most relevant is that of having replaced some gradual functions by step distributions, say the extent to which the dielectric permittivity changes with distance. So, in practice quantification is rather a matter of doing independent experiments that give information on the charge of the diffuse part of the double layer only and then subtracting that from the total (titration) charge to find how much is left for the inner layer. Electrophoresis is one of these (a double layer with only a Stern layer as the counterlayer will not move in an electric field), to which we shall come back in sec. 6. Electrokinetic potentials are difficult to measure for systems on the verge of instability, but the order of magnitude is at least a factor of ten lower than the ca. 400 mV assumed for ψ^o in DLVO theory. This means that in (3) it is no longer allowed to replace the hyperbolic tangent by its high potential limit (unity), rather $\tanh y$ must rather be replaced by the first term of its

series expansion, $\tanh y \approx y$. Consequently for the coagulation concentration we obtain instead of (3),

$$c_c = \text{const} \frac{(\psi^d)^4}{A^2 z^2} \quad (8)$$

So, for low diffuse double layer potentials ψ^d can be obtained from stability measurements. The inference is that the interpretation of the Schulze-Hardy rule is more complicated than expected by DLVO. An exact z^{-6} power would require ψ^d to scale as z^{-4} . More pertinent to the present theme is the finding that ψ^d depends on the nature of the counterion in the Stern layer, hence the Hofmeister effect is automatically incorporated. It is a small step to consider again charges instead of potentials, by moving further and use (6) to compute σ^d , subtract that from σ^o (from titration) to find the Stern charge σ^i . In many situations the charge in the diffuse part is only a minor fraction of the total. In those cases one does not have to estimate σ^d very accurately but still find for σ^i an acceptably correct value. Applying the Frumkin-Fowler-Guggenheim adsorption isotherm equation (a modified Langmuir isotherm) it is even possible to estimate the specific ionic Gibbs energy of adsorption of the alkali cations on silver iodide.³¹ The ranges are 2.3 - 3.6 kT , 2.5 - 4 kT and 2.9 - 4.2 kT for Li^+ , K^+ and Rb^+ , respectively. (The uncertainty margins are mainly caused by the uncertainties in the assessment of ψ^i). That is about as far as we can get with classical means for a well-studied model system. Similar exercises have also been carried out for other systems, like oxides.

The general message is that for a proper handling of interfacial potentials measuring absolute values for the surface potentials are not needed and that there are advantages in considering charges instead.

Introduction of a Stern layer has also an important advantage when considering the interaction dynamics. Recall that, according to DLVO theory, interaction at constant (surface) potential required discharging of the particles upon encounter. For negatively charged AgI sols that would mean desorption of adsorbed I^- ions and transporting them through the narrowing gap between the approaching surfaces toward the open space further away. This does not look like a simple and fast process. On the other hand, if there are two Stern layers between the surfaces, discharging can be rapidly realized by the formation of ion pairs between surface charges and the close-by counterions.

This, somewhat extended, review of the AgI work illustrates how far one can get nowadays with the simple Gouy-Stern picture without worrying about the immeas-

urability of ψ° . It is questionable whether more advanced models would work better because of the inherent imperfections of solids such as the reproducibility of the interface, and the homogeneity of the surface charge distribution.

6. ELECTROKINETIC POTENTIALS.

Having dealt in some detail with the (im)measurability of various static potentials it is appropriate to also consider the domain of electrokinetic, or zeta (ζ) potentials. The main reason for that decision is their outstanding practical relevance for colloid stability and hence for much industrial process control. As over the years the instrumentation has become quite sophisticated, measuring them is nowadays more or less routine, but instead now the interpretation is the issue. In particular the question is how electrokinetic potentials match into the static pictures of figure 6? Anticipating the discussion, we shall show that in many practical cases identifying the slip plane with the (oHp) plane where the diffuse part of the double layer starts appears to be a very acceptable approximation. This identification has no scientific background, but it adds to the accessibility of ψ^d .

Electrokinetic potentials are very different from static potentials. They do not relate to equilibrium situations but to stationary state processes, involving tangential shear parallel to the surface. It leads to slip between a thin liquid layer, close to the surface, that remains stagnant and a mobile layer in which charge transport takes place. The shearing motion creates a potential difference between the tangentially mobile and the tangentially stagnant parts of the liquid. Phenomenologically it looks as if the fluidity of the liquid decreases rapidly with distance from the (solid) surface, but for lack of simple theory about this, the fluidity profile is usually replaced by a step function with a slip plane, where the fluidity increases jump wise from zero to its bulk value. The double layer potential at the slip plane is identified as ζ .

Of the many electrokinetic phenomena we shall emphasize electrophoresis, perhaps the most familiar illustration, and indeed suitable to discuss how ζ -potentials fit into the picture. For a more extended review see Ref. 32. Many equations have been derived for converting electrophoretic mobilities into ζ -potentials, depending on the nature, size and shapes of the particles and their conductivities. Here, we shall consider two limiting cases: spherical, non-conducting particles for high and low κa . The equation for converting the electrophoretic mobility u into a zeta potential depends on κa where κ is the reciprocal Debye length and a the radi-

us of the (spherical) particle. For the $\kappa a \gg 1$ limit the Helmholtz-Smoluchovski relation is

$$u = \frac{\epsilon_0 \epsilon \zeta}{\eta} \quad (\kappa a \gg 1) \quad (9)$$

whereas for $\kappa a \ll 1$ the Hückel-Onsager equation applies, which reads

$$u = \frac{2\epsilon_0 \epsilon \zeta}{3\eta} \quad (\kappa a \ll 1) \quad (10)$$

Equation (9) is characteristic for dilute sols of small particles whereas (10) rather represents macroscopically flat surfaces, where the flow takes mainly place parallel to the surface. Equations also exist for intermediate κa cases. We shall not worry here about these and neither about surface roughness problems, although these are very relevant for daily practice.

Equations (9) and (10) are straightforward: a mobility is measured and the ζ -potential follows directly, by force of habit. This procedure looks as a direct measurement of a potential. However, as stated in sec. 1, things are not as they like. Rather a charge is measured, which is converted into a potential. For example, in the derivation of (10) this step involves the writing of the total charge Q as $4\pi a \epsilon_0 \epsilon \zeta$. This is a decent equation of electrostatics where ζ stands for the potential at the surface of a charged sphere with radius a . However, electrostatics does not consider something like a slip plane or stagnant layer; hence the border between the moving particle and the stationary fluid is taken to be identical to the borderline between the solid and liquid, demanding that ζ and ψ° coincide. A colloid scientist would therefore rather say that a is the particle radius, inclusive the stagnant layer. A similar argument can be presented for the derivation of (9). In this case the Poisson equation is used, which relates the space charge density to the second derivative of the potential, similar as in the derivation of (1).

For all electrokinetic phenomena the question is what determines the existence of a slip plane. By what factors is it determined? It is imaginable that some of the fluid molecules, in close or immediate contact with the surface could remain somewhat adhered to that surface, and it could also be imagined that upon increasing distance from the surface the fluidity would gradually increase with increasing distance. As stated, the basic electrokinetic assumption is that for practical purposes the gradual transition from stagnant to mobile may be

replaced by a step function. Such a step function was also assumed for the double layer potential to introduce ψ^d . Given the very different origins for assuming a step function in the potential and in the fluidity there is no *a priori* reason for assuming the outer Helmholtz plane and the slip plane to be identical. Or, for that matter, assuming ψ^d and ζ to be identical. Nevertheless, experience has shown that often the two are so close that they are experimentally indistinguishable.

Perhaps the most cogent argument for identifying the oHp and the slip plane is in the very meaning of the slip plane: it separates the electrokinetically active charges from those inactive. The former category coincides with the diffuse parts of the double layer, the latter with the Stern part, just as is the case for the oHp. Ions in the Stern layer are not electrokinetically active (a particle with a Stern layer around it will not move in an electric field), although the ions there are not immobile (they do contribute to the surface conductivity). So, the oHp and the slip plane have in common that for both the outer side is the diffuse part of the double layer. Hence, for both can we apply equations (6) and (7) to relate charge and potential of the diffuse part.

In order to better understand the slip process, in Figure 7 for some amphoteric model systems the electrokinetic and surface charge are plotted. These are all experimental data, the only difference with more classical measurements is that charges are plotted instead of potentials. This makes the role of the position of the slip plane better visible.

The skewed straight line ($\sigma^{\text{ek}} = \sigma^{\circ}$) would apply if the thickness of the stagnant layer would be zero (slip plane coincides with solid-liquid boundary), or if the diffuse layer is so extended that no measurable amounts

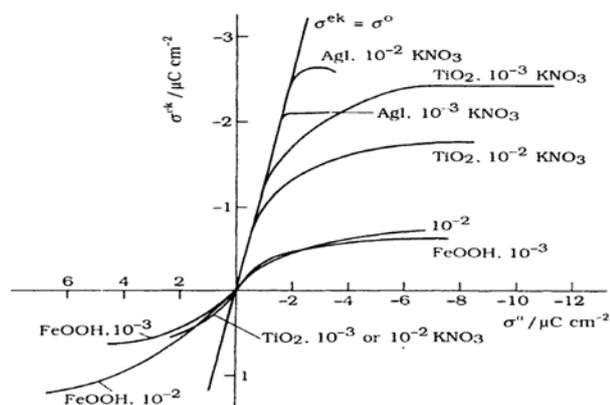


Figure 7. Comparison between electrokinetic (σ^{ek}) and surface charges (σ°) for a number of amphoteric model colloids. Taken from Ref. 32 with permission. Copyright © 1995 Academic Press. Published by Elsevier.

of charge are detectable between the surface and the slip plane. This limit is always reached for very low surface charge, say about $1 \mu\text{C cm}^{-2}$. But when the surface charge becomes a bit higher, the electrokinetic charge always falls far below that of the surface charge, meaning that a relatively large fraction of the countercharge resides within the stagnant layer. Electrokinetic charges are not very high. About $2.5 \mu\text{C cm}^{-2}$ appears the maximum that can be reached, independent of the nature of the surface. This charge can be compared with the surface charge which can become 10 times as high, especially for oxide surfaces. So, only a minor fraction of the counterlayer is electrokinetically active. The same may be stated about the fraction of the countercharge that is accounted for by the diffuse parts of the double layer. Also in this respect there is a definite analogy between the diffuse part and the electrokinetically active double layer part.

A second striking point is that the influence of indifferent electrolyte is not as strong as when the data would have been presented in terms of potentials. For iron oxide the 10^{-2} and 10^{-3} curves even coincide. It would be interesting if more data of this kind would become available to generalize this observation.

Given the present query about the nature of the slip process this figure contains some interesting pieces of information. Consider first the situation with the iron oxide (FeOOH), which is typical in that it is rather symmetrical with respect to the point of zero charge. This important observation means that the stagnant layer is the same to the right (surface negative) as to the left (surface positive) of the point of zero charge; it does not depend on the *sign* of the charge. Stagnant layers must also be present around the zero point of charge, even though there we cannot electrokinetically measure them. We conclude that the formation of macroscopically stagnant layers is a *hydrodynamic* phenomenon; it does not have an electrical origin and the double layer is there only to measure and quantify its existence. For rutile (TiO₂) the situation is less symmetrical but here the presence of a stagnant layer on the uncharged surface is beyond discussion.

Stagnant layers are not very different between hydrophilic and hydrophobic surfaces: compare the hydrophobic AgI with the hydrophilic oxides. This observation means that attraction between water in the first adjacent rows and the surface does not lead to thicker stagnant layers. Neither is there a thin empty layer between the AgI surface and the first adjacent bulk water along which the liquid could slide away (of course, sliding might occur if the interfacial layer would contain microscopic air bubbles).

The collected inference on the slip process is that stagnancy results from the mutual *repulsion* between adjacent fluid molecules. This repulsion gives rise to a layer-like ordering in the fluid: the density distribution exhibits a few maxima and minima, petering out rapidly with distance. As this mutual stacking of the water molecules holds for all liquids in contact with solid surfaces the phenomenon is general. One must therefore expect that also for non-aqueous systems such a process with slip occurs.

The general conclusion is that the observations made are sufficiently relevant to look for additional information on well-defined systems

7. POTENTIAL DANGER?

In May 2014 a conference on electrokinetic phenomena took place in Gent (Belgium). At that occasion a problem surfaced with the measurement of electrokinetic potentials. As this issue has its ramifications it deserves paying attention. The problem had to do with the sophistication of instrumentation that went so far that the very truth was huddled in uncertainties about the software.

At the beginning of electrokinetic investigations, say about a century ago, measuring electrophoretic mobilities was very laborious. Stable sols had to be made, thin homogeneous glass tubes blown, arrangements made to view the motion of individual particles ultramicroscopically, and exhausting velocity measurements carried out on different levels inside the capillary. Inconvenient as such measurements were, they had at least the advantage that the individual behaviour of the particles could be directly observed. With time novel techniques were developed and marketed; in the first place those based on laser-Doppler techniques. More recently very powerful instrumentation was developed on the basis of modern techniques that could, hand-waivingly summarized as electroacoustics.³² Very sophisticated instruments based on these principles are now commercially available. They allow fast electrokinetic and rheological studies of concentrated systems in a variety of media. Industrial labs are willing to pay prices of the order of 10^5 € apiece. The challenge is that the road from primary data to the desired end product is long and replete with problems. The ways in which these problems are solved depend on the different providers and is so deeply hidden in the software that the average user will not notice them.

During the conference mentioned above, a discussion developed when measurements of the electrolyte concentration dependency of silica sols in alcohol, meas-

ured by two electroacoustic apparatus of differing provenance, did give different results for the zeta potentials.³³ (The difference was smaller if electrokinetic charges were considered instead of potentials). The roots of this difference must be attributed to differences in the software and in the assumptions made in developing it. At the time of the meeting representatives of both industries were present but they were not available to explain how their software worked on grounds of propriety arguments.

Although the dispute did not assume Faustian dimensions it is mandatory to remain alert on the possibility that such issues may develop more easily than with less sophisticated apparatus. Anticipating and dealing with them involves also an ethical aspect.

8. STILL OTHER POTENTIALS

Or should we say “still other ways to measure (interfacial) potentials”? More recently, increasingly sophisticated techniques have been developed for “measuring” surface potentials and more will become available. Do these attribute really new insights or do they just reflect a repetition of techniques already considered? We shall briefly discuss two of those developments, anticipated in two of the quotes with which we started this discussion.^{4,5}

8.1 Surface Potentials from AFM and Related Techniques

To this category belong the several techniques by which properties of a surface are measured by probing it with a probe, measuring the force of interaction as a function of distance and position. When the force that the probe experiences as a function of distance obeys classical laws of colloid interaction (say, an exponential decay with distance) extrapolation to zero distance yields a “surface potential”. However, this is not our (immeasurable) ψ^o but ψ^d because the exponential decay only applies to the interaction of diffuse double layers. So, the immeasurability is not affected although measuring ψ^d has its virtues.

8.2 Surface Potentials from Non-Linear Optics

This is a new development with a physical basis, which offers promised additional information on measuring interfacial potentials. The techniques involve modern developments of surface spectroscopy and go under acronyms like SHG (second harmonic generation), and

SFG (sum frequency generation).³⁴⁻³⁶ For our present purpose the challenging new element is that molecules can be studied that are located under non-centrosymmetry conditions, implying that in a two-phase system molecules at the interface are selectively measurable, in fact through their molecular susceptibilities. Charges at the interface lead to an additional dipole contribution, which is measurable and can be analyzed to produce an interfacial potential. Which potential?

It is obvious that, as far as our present theme concerns, the added value refers to the Stern part of the double layer, not to the diffuse part. This is immediately seen in figure 6, where the high field strengths (slopes of the curves) are almost exclusively in the Stern part. In fact, the habit of dividing the counterlayer in a diffuse and a non-diffuse part tacitly presumed ideality, and hence centrosymmetry, of all ions in the diffuse part. More arguments can be given, such as the fact that the charges in the Stern part (figure 7) are too low for dielectric saturation. All of that is a happy coincidence because the Stern part is much less understood than the, relatively dull, diffuse part.

In practice, so far only very few elaborations have been given leading to values of a potential, be it ψ^o or ψ^i or still something else. These elaborations are somewhat suspicious because they contain hyperbolic functions, typical for the diffuse part only. The conclusion is that here is a field awaiting systematic elaboration from a team containing physicists and colloid scientists.

9. CONCLUSIONS

The issue of surface potential measurement is considered in a historical context. The absolute value of the potential difference between two condensed phases is and remains principally immeasurable. Changes in it as a function of the composition of one of the phases are sometimes accessible, with Nernst's law as a typical illustration. Immeasurability does not mean that no theories can be made for them. Many of these attempts belong to the domain of model approaches to assess interfacial potential jumps χ . Avoiding these immeasurabilities, a variety of other interfacial potentials have been introduced. These are discussed with a critical evaluation of the steps and assumptions to be made in order to assess them. Several interfacial systems are more transparently analyzed if interpreted in terms of charges rather than of potential. It is recommended to change the notion of "potential-determining ions" into "charge-determining ions".

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