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Surface charges and electrokinetic charges: Distinctions and juxtapositionings

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ABSTRACT

Surface charges and electrokinetic charges are very different double layer characteristics. It is mandatory to discriminate between them. If for a given system both of them are known, much relevant double layer information becomes accessible. The present state of this juxtapositioning is reviewed on the basis of real physical measurements with well-defined systems. The added information includes counterion adsorption and stagnant layer conduction. Special attention will be paid to overcharging, including an option for distinguishing between interpretation in terms of specific adsorption and ion correlations.

1. Introduction

The development of electric double layer models and the understanding of electrokinetic phenomena are to a certain extent coupled. Historically these two fields have developed parallel to each other [1]. For example, electrokinetic observations showed that dispersed particles could bear a charge, and in later stages double models appeared necessary to develop advanced theory for electrophoresis [2].

At present, a few methods are available to obtain information on double layer charges and other double layer characteristics. The direct way of measuring the surface charge on dispersed particles is by titration (surface potentials are often ill-defined and difficult to measure). Electrokinetically, the electrokinetic charge can be obtained. Indirect techniques include interaction measurements, for example by using AFM and rheology. The latter types of techniques yield the part of the double layer charge that is responsible for particle interaction. Mostly, this part more or less corresponds to the diffuse part of the double layer. The three charges obtained by these techniques are not necessarily identical, although the literature often does not distinguish them. This is a pity because it causes confusion and precludes the option of obtaining useful insights into the properties of electric double layers. On closer inspection, it appears that real progress in understanding the composition of electric double layers and their behaviour upon tangential motion and interaction requires the *combination*, or rather *juxtapositioning* of double layer and electrokinetic studies, rather than one of these separately. This will be the main thrust of this paper.

2. Electrokinetics and the slip plane

At present, electrokinetics are applied on several levels. Perhaps the most general practical application is finding a measure of the extent to which electrostatic interaction contributes to the stability of dispersions in practical systems. For unknown systems this is often the only way to get some information on the charge of a particle. Handy apparatus are now generally available to measure mobilities or other dynamic properties from which ζ-potentials can be computed. From that, simple equations are available to calculate the electrokinetic charge and to assess the (Gibbs) energy of interaction, using DLVO theory. In order to apply this line of research one does not need much insight into the working principle of the apparatus (although some feeling for the limitations of the software does no harm) and neither does it require much insight into double layer structure. Conversely, such experiments do not provide much substance for advanced double layer insights. In fact, classical equations like that of Helmholtz and Smoluchowski for the electrophoretic mobility

$$u = \frac{\varepsilon\varepsilon_0\zeta}{\eta} \qquad (1)$$

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where u is the electrophoretic mobility, ε the dielectric constant of the solvent, ε_o the dielectric permittivity of free space, and η the viscosity of the solution, can be derived without any information about the properties of double layers. Just the combination of the one-dimensional Navier–Stokes and Poisson equations suffices. In this simple model, from (1) the sole obtainable piece of double layer information is the electrokinetic, or ζ-potential. In this model, the meaning of this quantity follows from the derivation. For the case that a liquid flows tangentially to a solid surface at rest, ζ appears as the potential at a plane beyond which, looking from the solution side, no flow occurs any more. Nowadays this plane is known as the *slip plane*. Long ago it was identified as the surface of the (solid) substrate. Only after independent double layer investigations taught that often ζ is much lower than the surface potential ψ^o and even in some cases had a different sign, did it become clear that electrokinetic charges σ^{ek} and surface charges σ^o are very different entities. The inference is that useful information on structure and flow can be extracted if the two charges are both measured. Otherwise stated, their *juxtapositioning* offers new insights. This takes us to the present theme, namely obtaining more insight into double layer properties, in particular of the inner double layer part.

In order to treat this topic in some depth, our discussion will be restricted to well-defined systems: we mainly consider aqueous dispersions and non-porous surfaces on systems for which both direct measurements of the surface charge (requiring insight into the charge-determining process) and electrokinetic experiments (electrophoresis, streaming potentials, surface conduction, etc.) are feasible. As far as possible we shall start from general experimental evidence on real systems, *i.e.* we shall not consider simulations.

The interpretation of ζ-potentials as potentials at a slip plane is widely accepted, as is evidenced by Hunters monography [3], a recent treatise on electrokinetics [4] and the IUPAC codification of symbols in electrokinetics [5]. However, for the present purpose it is necessary to revisit the issue. To start with, even the name provokes dispute. From the (macroscopic) fluid dynamics point of view, *i.e.* from the solution side of the solid surface, the plane is rather a no-slip plane, because it is the plane beyond which tangential viscous flow stops. On the other hand, from the particle side the plane is viewed as indicating the separation between the thin layer of liquid remaining adhered to the solid surface upon tangential flow and the fully fluid bulk; hence it is the location beyond which slip starts. Here we shall continue to use this "colloidal" interpretation. According to this definition, fluid between the surface and the slip plane is considered *stagnant* or "within the slip plane" and that on the other side, which is fully fluid is called "beyond" the slip plane. For our discussion, the interpretation and location of this plane is crucial because important phenomena like surface conduction and specific adsorption can in principle take place either within or beyond the slip plane or at both sides of it. Having stated that, at issue is its interpretation on a molecular scale.

This issue has been addressed recently [6]. The most relevant conclusions, based on experiments with a number of well-defined systems, are the following:

(1) The slip plane is an abstraction of reality: the fluidity of the adjacent liquid or, for that matter, its viscosity, does not jump abruptly from the bulk value to zero (for the fluidity) or infinite (for the viscosity) but changes over a narrow range. It is hard to define the fluidity on a molecular scale, but the step function at the slip plane is located at such a position as to yield the same macroscopic fluid flux as in the real system;

(2) Stagnant layers occur at any type of surface; both on hydrophilic and hydrophobic surfaces;

(3) Stagnancy is dominated by the adjacent water (the only liquid for which reliable information is available). Ionic mole fractions in that layer are so low that the presence of ions has only a negligible effect on the averaged stacking of water molecules;

(4) Stagnant layers are also present on uncharged surfaces, *i.e.* at the point of zero charge. However, this presence cannot be detected electrokinetically;

(5) Generally, fluids adjacent to hard walls tend to exhibit layer-like stacking, with maxima and minima in the density distribution profiles. It was postulated that the location of the slip plane is coupled to this layerwise stacking. Assuming this to be true, the implication is that stagnant layers also do occur in media of low dielectric permittivity (although their presence cannot be detected electrokinetically because of the slow potential-distance decay) but are absent at fluid–fluid interfaces (where measurements are virtually impossible because of the problem of stabilizing such interfaces without surfactants);

(6) For large κa surfaces electrokinetic charge densities are obtainable via the Gouy–Chapman equation:

$$\sigma^{ek} = \sqrt{8\varepsilon_0\varepsilon cRT}\,\sinh\left(\frac{zF\zeta}{2RT}\right) \tag{2}$$

where the symbols have their usual meanings [7]. They rarely exceed values of a few μC/cm^2, although the surface charge can be higher by several factors of 10. So there is an additional factor preventing σ^{ek} from growing. It has been suggested that this additional factor is the viscoelectric effect, that is the increase of viscosity of a fluid as the result of an imposed electric field [8]. Whatever the interpretation, electrokinetic charges are only a fraction of the surface charges and should not be interpreted as such.

In summary, the notion of a slip plane is a well-established working hypothesis, although its actual location is hard to define. One can only state that the thickness of the stagnant layer corresponds to the distance over which the influence of a solid wall on the density distribution of adjacent water has petered out, that is, over a few water molecules.

3. Gouy–Stern double layers

Most electric double layers are well described in terms of the Gouy–Stern (GS) model [7]. General experience has indicated that purely diffuse double layers are exceptional. Only at very low surface potentials and low electrolyte concentrations can the diffuse model account for all properties. Beyond that range specific ionic effects, in particular finite ionic volumes and non-electrostatic interactions (with each other and with the surface) have to be also accounted for. GS theory takes these "corrections" into account in only the first few molecular layers on the surface. The result is that the potential decay over the counterlayer consists of an inner and an outer part. The inner part contains all the specific ionic effects and looks like a molecular condensor, or two molecular condensors in series, depending on the sophistication of the model. A sketch is presented in Fig. 1. More details can be found in the literature [7–9]. The potential decay over the inner layer is rather steep and depends on specific ionic properties. If the approximation holds that all deviations from ideality can be collected in the Stern layer, the outer part is automatically generic and purely diffuse. In fact, the application of Eq. (2) is based on this idea. At issue is now how thick the Stern layer is.

With respect to their strengths and ranges, ionic interactions with a surface vary greatly. The strongest ones involve chemisorption with Gibbs energies of several tens of a kT. This can only take place when the ions are so close to the surface that electron exchange can occur. Weaker, but very general are interactions involving complex formation or some kind of change in hydration. The last category is collectively denoted as "water structure-induced" and involves Gibbs energies of the order of a few kT.