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INCLUDING CATALYSIS*

Nomenclature, Symbols, Definitions and Measurements for

ELECTRIFIED INTERFACES IN AQUEOUS DISPERSIONS OF SOLIDS

(Recommendations 1991)

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Nomenclature, symbols, definitions and measurements for electrified interfaces in aqueous dispersions of solids (Recommendations 1991)

ABSTRACT

The present document is devoted to electrical double layers on solid particles, dispersed in aqueous solutions. Electrical parameters characterising the double layer are defined and the steps and assumptions that are required to obtain these parameters from experiment are discussed.

1. INTRODUCTION

The motivation of the present contribution stems from the observations that

- (a) the description of interfacial electrochemistry in disperse systems is important for such phenomena as colloid and suspension stability, electrokinetic phenomena, rheology, electrochemical reactions at interfaces, etc.,
- (b) in the literature confusion sometimes arises from the interpretation of measurements, performed to characterise the electrical double layer.

The present recommendation is intended to complement two previous IUPAC recommendations, viz.,

- (a) "*Manual of Symbols and Terminology for Physicochemical Quantities and Units: Appendix II. Definitions, Terminology and Symbols in Colloid and Surface Science, Part I*" (ref. 1)
- (b) "*Interphases in Systems of Conducting Phases*" (ref. 2).

Document (a) treats colloids and suspensions in general but its coverage of interfacial electrochemistry is limited whereas (b) deals with double layers in some detail but pays little or no attention to disperse systems.

2. SCOPE

In the present document attention is paid to colloidal solutions (sols) or suspensions in aqueous solutions, collectively known as *dispersions*.

Although the dispersed matter is referred to as the solid or as "particles", a large part of the following also applies to dispersions of liquids in liquids (emulsions).

Although the discussion here is limited to aqueous systems, many of the ideas and expressions are also applicable to other solvents, particularly polar solvents.

3. BASIC PROBLEMS

As particles cannot be linked directly to an external circuit it is not possible to change their surface charge or potential by application of an external field. In contradistinction to mercury electrodes, (variations of) the surface potential are therefore inoperational, meaning that they cannot be unambiguously measured without making model assumptions. Electrodes can be made of some solids, either electrolytically (e.g. AgI/Ag/Pt electrodes) or by deposition (e.g. iron- or ruthenium oxide on Pt). In that case the material under study can become part of an external circuit but then the electrochemical identity of the dispersed and electrode material cannot be directly proven.

Instead, if the process by which the surfaces of the dispersed particles acquire their charge is known, it is often possible to obtain the total charge on the particle analytically, thereby taking advantage of the usually large interfacial area. Consequently, for disperse systems *the charge is the primary parameter*, rather than the potential.

An entirely different approach involves electrokinetic phenomena. Electrophoresis, electro-osmosis and streaming potentials are the most well known. Under a number of fairly restrictive conditions regarding particle size and shape, surface potential, surface conductivity and electrolyte concentration, equations are available to compute from electrokinetic measurements the *electrokinetic (or zeta) potential* ζ , which can be related to the electrokinetic charge via a model (sec. 5 of this document).

Surface charges and electrokinetic charges are different parameters and should not be confused. If both of them are available, a more detailed picture of the electrical double layer can be obtained.

From adsorption measurements it is impossible to establish surface charges on dispersed particles without making certain assumptions regarding the structure of the electrical double layer. Since, together with the surrounding solution, the particles are electroneutral, model considerations are needed to label certain ionic species as being responsible for the charge on the surface; all other ions then constitute the countercharge by definition.

Henceforth, ions that (by definition) are considered to be responsible for the surface charge are called *surface ions*.

Having measured certain adsorptions or desorptions of electroneutral combinations of ions and having defined the surface ions, it is possible to obtain the total surface charge on all the particles. From this, the average *surface charge density* σ^0 can be calculated provided the specific surface area of the dispersed material is known.

Establishing this area is a problem in itself. One of the difficulties is that conventional procedures to obtain the surface area, such as BET gas adsorption measurements, do not necessarily yield the area involved in electrochemical measurements, because surface ions sometimes accumulate on sites that are different from those onto which gas molecules adsorb and because there may be problems in the drying and re-hydration. Dispersed powders may also be energetically heterogeneous. It is therefore recommended to use more than one method to establish the surface area, preferably one of them based on adsorption from solution and to indicate, which method(s) has (have) been used and which value for the surface area has been chosen.

4. CHARGING MECHANISMS

In this section the most familiar charging mechanisms will be discussed together with the interpretational steps that have to be made to obtain the surface charge or other charges in the double layer.

4.1 Adsorption of potential-determining (p.d.) ions

According to ref. (1), p.d. ions are defined as those species which by virtue of their equilibrium distribution between the solid and liquid phase (or by their equilibrium with electrons in the solid) determine the difference in Galvani potential between these phases. This definition requires that adsorbed p.d. ions are part of the adsorbent and belong to the category of surface ions. Typical examples are Ag^+ and I^- ions for silver iodide. After adsorption, these ions are indistinguishable from the Ag^+ and I^- ions of the silver iodide itself. It follows from the considerations in sec. 3 that

$$\sigma^0 = F(\Gamma_{\text{Ag}^+} - \Gamma_{\text{I}^-}) \quad [4.1]$$

where F is the Faraday constant and Γ_i the surface excess of i . Equation [4.1] may be regarded as the equation defining the surface charge. Operationally, however, each adsorbing Ag^+ ion is accompanied by, say, a NO_3^- ion in a solution of KNO_3 and each adsorbing I^- ion by, say, a K^+ ion, in the same solution, so that the

operational definition is

$$\sigma^0 = F(\Gamma_{\text{AgNO}_3} - \Gamma_{\text{KI}}) \quad [4.2]$$

where it is understood that NO_3^- and K^+ ions are not surface ions.

Together with the charging of the surface, negative adsorption of indifferent electrolyte (KNO_3) takes place, due to the Donnan effect ($\Gamma_{\text{KNO}_3} < 0$). With this in mind, the various ionic contributions to the charge can be identified as follows

$$\sigma_{\text{Ag}^+}^0 = F\Gamma_{\text{Ag}^+} = F\Gamma_{\text{AgNO}_3} \quad [4.3]$$

$$\sigma_{\text{I}^-}^0 = -F\Gamma_{\text{I}^-} = -F\Gamma_{\text{KI}} \quad [4.4]$$

$$\sigma_{\text{K}^+} = F\Gamma_{\text{K}^+} = F(\Gamma_{\text{KI}} + \Gamma_{\text{KNO}_3}) \quad [4.5]$$

$$\sigma_{\text{NO}_3^-} = -F\Gamma_{\text{NO}_3^-} = -F(\Gamma_{\text{AgNO}_3} + \Gamma_{\text{KNO}_3}) \quad [4.6]$$

The sum of these charges is zero, in agreement with electroneutrality. It is also noted that Γ_{Ag^+} and $\Gamma_{\text{NO}_3^-}$ are different. In the system under consideration, where the charge-determining and constituent ions of the solid are identical, it is very likely that the adsorbed Ag^+ and I^- ions find themselves on the surface or even inside the solid, whereas the NO_3^- and K^+ ions constitute the countercharge. Because of this σ_{Ag^+} and σ_{I^-} have been identified as $\sigma_{\text{Ag}^+}^0$ and $\sigma_{\text{I}^-}^0$, respectively. However, there is no way to establish this unambiguously solely from adsorption measurements.

It must be added that by the conventional methods of measurement (see sec. 6) it is impossible to discriminate between the adsorption of an Ag^+ ion and desorption of an I^- ion. Hence, in eq. [4.1] only the difference between Γ_{Ag^+} and Γ_{I^-} is accessible, not the individual terms.

4.2 Adsorption of other types of surface ions

The AgI model colloid is atypical in the sense that the charge-determining and constituent ion of the solid are identical. For most materials this is not the case, or it is only so over a limited range of the solution composition.

Oxides constitute an important group of model colloids. For them, H^+ and OH^- ions are largely held responsible for the charging of the surface, so that in a solution containing HNO_3 and/or KOH and KNO_3 the operational definition of σ^0 is now given by

$$\sigma^0 = F(\Gamma_{\text{HNO}_3} - \Gamma_{\text{KOH}}) \quad [4.7]$$

It is recommended that the convention that H^+ and OH^- ions are the surface ions be retained. This recommendation is based on experimental (the very strong affinity for the surface of these ions over the entire pH-range and the fact that H^+ ions are natural constituents of many oxide surfaces) and theoretical arguments (surface oxygens or surface hydroxyls are identified as sites for adsorbing or releasing protons).

By the conventional potentiometric titration technique to determine σ^0 (see sec. 6.1) it is impossible to distinguish between adsorption of an OH^- ion and desorption of a H^+ ion. However, by other techniques (for example spectroscopically) such a discrimination is sometimes possible. By potentiometric titration one is also unable to detect concomitant changes in the hydration of the surface.

The question whether or not H^+ and OH^- ions should or may also be called "potential-determining" for oxides is under dispute. The use of the notion is often linked to whether the surface gives Nernst-response as a function of pH. This type of response has been verified for some oxides. As Galvani potential differences between particles and solutions are derived properties, the term "charge-determining" ions appears to be more appropriate, but at any rate if the term "potential-determining" is used, it should not imply any statement on the response of potential to changes in pH.

4.3 Specific adsorption of other ions

In interfacial electrochemistry, with respect to the countercharge a distinction is usually made between *indifferent* and *specifically adsorbing* ions. Indifferent ions adsorb through Coulomb forces only; hence they are repelled by surfaces of like sign, attracted by surfaces of opposite sign, and do not adsorb on an uncharged surface.

Specifically adsorbing ions possess a "chemical" affinity for the surface in addition to the Coulomb interaction, where "chemical" is a collective adjective, embracing all interactions other than purely Coulombic. Examples: Van der Waals or, hydrophobic bonding, π -electron exchange and complex formation. Specifically adsorbing ions can adsorb on an initially uncharged surface and hence provide it with a charge.

There is no basic difference between specifically adsorbed ions and surface ions as defined in sec. 3. Ions of both categories adsorb by virtue of their chemical affinity to the solid. Hence, there is no operational procedure to establish which ions should be considered as contributing to σ^0 after adsorption. In fact, this has led to confusion in the literature.

For the sake of convenience, in order to avoid confusion and to achieve maximum consistency with customs in electrochemistry (see ref. 2), it is recommended that the use of the notion "surface ions" should be restricted to ions that are constituents of the surface or have a particularly high affinity for the surface or for typical surface sites. The term "specifically adsorbed" then applies to the sorption of all other ions having an affinity to the surface in addition to the purely Coulombic contribution. The distinction is more of a quantitative than qualitative nature. In the light of the above discussions, ions like Cd^{2+} , SO_4^{2-} , dodecylsulfate⁻, cetyltrimethylammonium⁺ belong to the category of specifically adsorbing for oxides. Ions for which there is evidence that they adsorb covalently to a surface should be considered surface ions. An example is HPO_4^{2-} , which under many conditions binds covalently to oxides.

It should always be reported whether or not the ion under consideration is included in the operational definition of σ^0 .

By virtue of their definition, specifically adsorbed charges are not surface charges but *Stern* or *inner layer charges*. Alternatively, it may be said that these charges are adsorbed at the *inner Helmholtz plane* (IHP) defined as the locus of the electrical centres of specifically adsorbed ions. The symbol is σ^1 . Generally, for j specifically adsorbing ions,

$$\sigma^1 = F \sum_j z_j \Gamma_j \quad (\text{sum over specifically adsorbing ions}) \quad [4.8]$$

Here an interpretational step is also involved. Since only neutral entities adsorb or desorb, some assumption has to be made to identify the specifically adsorbing ions (to be included in eq. [4.8]) and the co-adsorbing indifferent ions (not included). The distinction should always be specified.

All remaining ions reside in the *diffuse part* of the double layer, of which the charge σ^d is due to all ions except those constituting σ^0 and σ^1 .

Example. For a solid for which H^+ and OH^- are surface ions, Cd^{2+} is specifically adsorbing and K^+ and NO_3^- are indifferent, we have in a solution to which KOH, HNO_3 and $\text{Cd}(\text{NO}_3)_2$ have been added

$$\sigma^0 = F(\Gamma_{\text{H}^+} - \Gamma_{\text{OH}^-}) = F(\Gamma_{\text{HNO}_3} - \Gamma_{\text{KOH}}) \quad [4.9]$$

$$\sigma^1 = 2F \Gamma_{\text{Cd}^{2+}} = 2F \Gamma_{\text{Cd}(\text{NO}_3)_2} \quad [4.10]$$

$$\sigma^d = F(\Gamma_{\text{K}^+} - \Gamma_{\text{NO}_3^-}) = F(\Gamma_{\text{KOH}} - \Gamma_{\text{HNO}_3} - 2\Gamma_{\text{Cd}(\text{NO}_3)_2}) \quad [4.11]$$

These three equations satisfy the electroneutrality condition

$$\sigma^0 = \sigma^1 = \sigma^d = 0 \quad [4.12]$$

Many cations hydrolyse more strongly in the adsorbed state than in the solution. In such cases, if H^+ and

OH^- are the surface ions, the potentiometrically measured surface charge according to eq. [4.9] includes the OH^- consumed by the complexes.

4.4 Dissociation of covalently bound surface groups

Many materials, both natural (proteins, humic acids) and synthetic (lattices, ion exchange resins) carry groups on their surfaces which, on contact with water, dissociate. In this way the surface acquires a charge.

If an ion is released by a surface group it continues to be bound in the thermodynamic sense because of electroneutrality unless it is exchanged against another ion, in which case this other ion becomes bound. Kinetically speaking, the released ion can either be in the Stern- or diffuse layer.

For systems, belonging to this category the surface charge is given by

$$\sigma^0 = F \sum_j z_j \Gamma_j \quad (\text{sum over covalently bound surface ions}) \quad [4.13]$$

In practice, there is no basic difference between this mechanism and the ones discussed under secs. 4.2 and 4.3. For example, oxides brought into an aqueous solution will usually show some dissociation and in order to change the surface charge on proteins an acid/base titration would be needed, after which σ^0 would follow from eq. [4.7].

4.5 Isomorphous substitution

In clay minerals, some isomorphous exchange of polyvalent cations by cations of lower valency occurs. Examples: $\text{Si}^{4+} \rightarrow \text{Al}^{3+}$; $\text{Al}^{3+} \rightarrow \text{Mg}^{2+}$. As a consequence, the clay mineral particle carries an excess negative space charge. This negative space charge density is compensated by adsorption of cations in the diffuse and/or non-diffuse part of the double layer. Often this charge inside the solid cannot be modified over the relatively short periods of time of the actual measurement by changing the solution composition, because diffusion into and within solids is a very slow process at room temperature.

It should be noted that for clay minerals at the edge surfaces of the platelike particles an additional charging mechanism may operate, similar to that on oxides and obeying eq. [4.7]. Therefore, clay platelets are not homogeneously charged. It is beyond the scope of this manual to treat dispersions of particles having such heterogeneous surfaces.

For further information on clay minerals see refs. 3 - 5.

5. ELECTROKINETIC CHARGES

The computation of *electrokinetic* or *zeta potentials* (ζ) from electrophoresis and other electrokinetic phenomena is possible for certain conditions of particle size and shape, ionic strength, etc. See ref. 6 for more information.

If ζ is obtainable, the *electrokinetic charge* σ^{ek} can be computed, using Gouy-Chapman theory.

The procedure involves two assumptions:

- (a) The ζ potential is identified as the potential at a supposed discrete slipping plane, separating the stationary and mobile phases in tangential flow of the liquid with respect to the surface. There is very little direct evidence to support the view of a slipping plane; a slipping layer with a gradual transition of fluidity is more likely. However, for interpretational purposes the simple concept of a step-function in the fluidity is the generally accepted alternative.
- (b) Outside the slipping plane the double layer is purely diffuse, or, in other words, any specific adsorption is assumed to take place in the region between the surface and the slipping plane.

For interpretational purposes the location of the slipping plane must be fixed. In a number of cases, the slipping plane may be identified with the *outer Helmholtz plane* (OHP), defined as the locus of the electrical centres of non-specifically adsorbed ions in their position of closest approach. This identification is based on a detailed comparison of data from different sources (σ^0 , σ^d , σ^{ek} , colloid stability) for a number of well-defined model systems, particularly silver iodide, anionic soap films and micelles. Obviously, this identification is not allowed if, for example due to the presence of adsorbed polymers, the slipping plane is shifted outward.

If the slipping plane and the OHP may be identified,

$$\sigma^{\text{ek}} \approx (\sigma^{\circ} + \sigma^{\text{l}}) = -\sigma^{\text{d}} \quad [5.1]$$

Experience has shown that σ° and σ^{ek} are very different quantities. This follows from the following observations:

- (a) σ^{ek} does not usually exceed a few $\mu\text{C cm}^{-2}$ whereas σ° can amount to several tens or even hundreds of $\mu\text{C cm}^{-2}$.
- (b) σ° and σ^{ek} can have like or unlike signs.

Although σ^{ek} is not always a well-established parameter, its measurement provides useful information because

- (a) $\sigma^{\text{ek}} \approx -\sigma^{\text{d}}$; the OHP-potential plays a crucial role in colloid stability and related phenomena such as rheology
- (b) combined measurements of σ° and σ^{ek} allow the computation of the sum of σ^{l} plus any non-specifically adsorbed charge present in the space between surface and slipping plane
- (c) opposing signs for σ° and σ^{ek} are indicative of superequivalent adsorption, that is the situation where σ^{l} and σ° bear different signs and $|\sigma^{\text{l}}| > |\sigma^{\circ}|$.

6. MEASUREMENT OF CHARGES ON PARTICLES

6.1 Measurement of σ°

Taking oxides as the example, σ° is given by eq. [4.7]. The experimental method requires a depletion procedure which can conveniently be carried out by potentiometric acid-base titration. Basically σ° at a certain pH value (pH_1) can be related to $\sigma^{\circ}(\text{pH}_2)$ by titration with HNO_3 or KOH , measuring potentiometrically the amount remaining in solution and finding the amounts adsorbed or desorbed from the material balance. In the same way $\sigma^{\circ}(\text{pH}_3)$ can be related to $\sigma^{\circ}(\text{pH}_2)$ and so on. From a sufficient number of such titration points, a $\sigma^{\circ}(\text{pH})$ curve can be constructed relative to $\sigma^{\circ}(\text{pH}_1)$.

Since KNO_3 is formed during the titration it is desirable to have a fixed background electrolyte concentration that is high enough to minimise total salt concentration changes during the titration.

Titration can also be carried out with electrolytes or with organic additives. In this way it is possible to obtain a set of relative $\sigma^{\circ}(\text{pH})$ curves at varying ionic strength and at varying concentration of organic substances.

In order to render the set of relative $\sigma^{\circ}(\text{pH})$ curves absolute, the point of zero charge (p.z.c.) must be established. This reference point is defined as the pH where $\Gamma_{\text{H}^+} = \Gamma_{\text{OH}^-}$, which is operationally equivalent to $\Gamma_{\text{HNO}_3} = \Gamma_{\text{KOH}}$. However, as these surface excesses cannot be separately measured, there is no operational way of finding the p.z.c. This problem will be dealt with in sec. 7.

In the case of silver iodide, similar titrations yield $\sigma^{\circ}(\text{pAg})$. As in this particular case Nernst behaviour of the interface has been established it is possible to obtain charge-potential curves which, upon differentiation, give the differential capacitance. It may be noted that there is no unambiguous way to establish the absolute value of the Galvani potential difference across the interface; even at the p.z.c. there remains an undetermined contribution to this potential jump due to dipole orientation of solvent molecules and polarisation of the molecules and/or ions in the interfacial region.

Potentiometric titration is also suitable for the determination of the σ° arising from the dissociation of groups bound to the surface. Typical systems amenable to this technique are lattices and proteins. For lattices, conductometric titration can be useful.

Because of the difference in the charge-determining processes on the faces of clay platelets (isomorphous substitution) and the edge surfaces (adsorption or desorption of acids and/or bases), the determination of the charge on clay minerals and its distribution poses a problem which is too specific to justify discussion here.

It may be mentioned that in clay colloid chemistry there are procedures to measure the cation-exchange capacity, defined as the total amount of cationic countercharge¹⁾ that is needed to compensate the negative surface charge and which can be exchanged against an equivalent amount of other cations. The procedure is not exact if used to determine σ^0 , because this quantity is only partly compensated by adsorption of counterions; a fraction is also compensated by negative adsorption of co-ions. However, if σ^0 is very high the negative adsorption contribution is relatively small and may be neglected.

6.2 Measurement of σ^i

Measurement of σ^i is usually carried out analytically. The most appropriate technique depends on the species under consideration and no general rules can be given, although it is noted that the technique should be able to discriminate between specifically bound and indifferent ions.

6.3 Measurement of σ^{ek}

Measurement of σ^{ek} involves interpretation of electrokinetic phenomena which is beyond the scope of this document.

7. THE POINT OF ZERO CHARGE (p.z.c.) and ISOELECTRIC POINT (i.e.p.). INFLUENCE OF SPECIFIC ADSORPTION

7.1 Definition

A surface charge is at its *point of zero charge* (p.z.c.) if $\sigma^0 = 0$. Just as the establishment of σ^0 involves an element of definition, so does the p.z.c. The p.z.c. is a value of the negative logarithm of the activity in bulk of the charge-determining ions. For example; for silver iodide the p.z.c. is a particular value of the pAg or pI (the two are related through the solubility product of silver iodide) and for oxides it is a value of pH (although pOH could also be chosen, the two being related through the dissociation constant of water). The p.z.c. is a characteristic of the nature of the adsorbent and generally it depends on the temperature, the nature and concentration of electrolytes and organic additives.

A surface is at its isoelectric point (i.e.p.) if $\sigma^{ek} = 0$. The isoelectric point can be unequivocally determined even if the computation of ζ from experiment is cumbersome. As is the case with the p.z.c., the i.e.p. is a value of pAg for silver iodide and a value of pH for oxides; it depends on temperature, nature and concentration of any electrolytes and added organic substances present.

In the literature, other types of zero points are also sometimes defined, for instance the point of zero salt effect (p.z.s.e.), which is the point where σ^0 does not depend on the salt concentration (ref. 7) and the point of zero zeta potential (p.z.z.p.) (ref. 8) which is identical to the i.e.p. so that its use is not recommended.

Points of zero charge are non-operational parameters since by the usual analytical technique of determining σ^0 (potentiometric titration) one cannot, for example, discriminate for AgI between adsorption of AgNO₃ and desorption of KI or, for oxides, between adsorption of HNO₃ and desorption of KOH. In eqs. [4.2] and [4.7] only the differences of surface excesses on the r.h.s. can be determined by this technique, but not the constituent terms. It follows that some model assumption has to be made, in order to establish the conditions where $\sigma^0 = 0$, that is, where $\Gamma_{\text{AgNO}_3} = \Gamma_{\text{KI}}$ or $\Gamma_{\text{HNO}_3} = \Gamma_{\text{KOH}}$. This assumption usually comes down to identifying an indifferent electrolyte, in which σ^0 must be zero if it does not change with the electrolyte concentration.

7.2 Determination

In practice, sets of relative $\sigma^0(\text{pH})$ or $\sigma^0(\text{pAg})$ curves are measured at various indifferent electrolyte concentrations c as discussed in sec. 6.1. Such sets of curves often exhibit a common intersection point (c.i.p.) which under ideal conditions (electrolyte fully indifferent, no hysteresis in titration, constant

¹⁾ This countercharge is usually expressed in milli-equivalents per 100 grams of dry clay, but using this unit is discouraged by IUPAC.

surface composition, etc.), is often sharp and is then identified as the p.z.c. The reasoning is as follows. For $\text{pH (or pAg)} > \text{p.z.c.}$, $\sigma^0 < 0$; if c is increased, σ^0 becomes more negative at a given pH or pAg, because there are more cations to screen the surface charge. In electrostatic terms, the double layer capacitance increases. By the same token, for $\text{pH (or pAg)} < \text{p.z.c.}$, σ^0 is positive and becomes more positive upon electrolyte addition because of the increased screening power of the anions. Only if $\sigma^0 = 0$ has the electrolyte no influence; hence $\text{c.i.p.} = \text{p.z.c.}$

Figure 1 gives a sketch of the procedure, as it applies to oxides. If by this procedure the p.z.c. can be established, the relative $\sigma^0(\text{pH})$ or $\sigma^0(\text{pAg})$ curves can be made absolute.

For the method to work, a c.i.p. must be found in the curves and the electrolyte should be indifferent. Regarding the latter, the best way to ascertain the indifference of a particular electrolyte is to see if the p.z.c. and i.e.p. are identical (see below). If electrokinetic data are not available, the indifference of an electrolyte can be indirectly inferred from the fact that the c.i.p. is insensitive to the nature of the electrolyte.

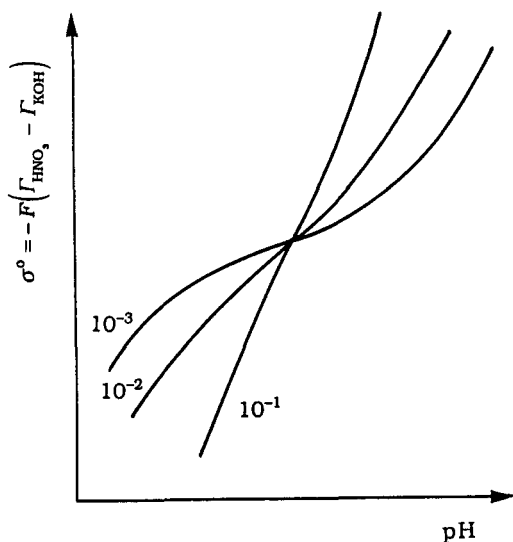


Figure 1. Illustration of the usual procedure of establishing the p.z.c. for oxides. Titrations are carried out at different electrolyte concentrations (in mol dm^{-3}) as indicated at the curves. The relative positions of the curves can be established but not the absolute position of the set of curves. If there is a common intersection point (c.i.p.) and if the electrolyte (KNO_3 in this example) is indifferent, the c.i.p. may be identified as the p.z.c. For silver iodide, the procedure is similar.

Experience has shown that in solutions containing ions that can adsorb specifically, the c.i.p. and the p.z.c. do not coincide. If the cation adsorbs specifically, the c.i.p. is shifted to the left (positive) side of the p.z.c. (that is: to lower pH for oxides or to lower pAg for silver halides, etc.); if the anion adsorbs specifically, it is shifted to the right (negative) side (that is: to higher pH or pAg). The difference between the c.i.p. and the p.z.c. is larger the stronger the specific adsorption and, therefore, the difference between these two values is a measure of the affinity of the specifically adsorbing ion for the surface. It may be noted in passing that in the fortuitous case that the cation and anion of the electrolyte exhibit exactly identical chemical affinity for the particle surface, p.z.c. and c.i.p. coincide again (pseudo-indifferent behaviour).

7.3 Thermodynamic interpretation

The thermodynamical basis of the interpretation is as follows.

Taking oxides again as the example, with σ^0 defined in eq. [4.9], at each intersection point between two curves taken at different electrolyte activity a_{\pm} .

$$\beta = \left(\frac{\partial \text{pH}}{\partial \ln a_{\pm}} \right)_{T, \sigma^0} = 0 \quad [7.1]$$

The parameter β is known as the *Estin-Markov coefficient*, after ref. 9 where the corresponding quantity for

the electrical double layer on mercury has been introduced. The c.i.p. is sharp if the situation characterised by $\beta = 0$ is independent of a_{\pm} . For β it can be shown (ref. 10) that

$$\beta = -\frac{1}{|z_+|} - \frac{|z_+| + |z_-|}{|z_+||z_-|} \left(\frac{\partial \sigma_-}{\partial \sigma^0} \right)_{a_{\pm}} = \frac{1}{|z_-|} + \frac{|z_+| + |z_-|}{|z_+||z_-|} \left(\frac{\partial \sigma_+}{\partial \sigma^0} \right)_{a_{\pm}} \quad [7.2]$$

where z_+ and z_- are the valencies of the cation and anion of the electrolyte, respectively, and σ_+ and σ_- stand for the contributions of these cations and anions, to the charge in the double layer, respectively. For instance, with KNO_3 as the indifferent electrolyte, $\sigma_+ = F\Gamma_{\text{K}^+} = F(\Gamma_{\text{KOH}} + \Gamma_{\text{KNO}_3})$ and $\sigma_- = -F\Gamma_{\text{NO}_3^-} = -F(\Gamma_{\text{HNO}_3} + \Gamma_{\text{KNO}_3})$.

The quantities σ_+ and σ_- , also known as the *ionic components of charge* are measurable, except for a constant. If there is an intersection point, in a (1-1) electrolyte

$$\left(\frac{\partial \sigma_-}{\partial \sigma^0} \right)_{a_{\pm}, \beta=0} = \left(\frac{\partial \sigma_+}{\partial \sigma^0} \right)_{a_{\pm}, \beta=0} = -0.5 \quad [7.3]$$

In a (2-1) electrolyte

$$\left(\frac{\partial \sigma_-}{\partial \sigma^0} \right)_{a_{\pm}, \beta=0} = -\frac{1}{3} \quad \left(\frac{\partial \sigma_+}{\partial \sigma^0} \right)_{a_{\pm}, \beta=0} = -\frac{2}{3} \quad [7.4]$$

and similarly in solutions of other types of electrolytes. On the basis of these expressions, at each intersection point there is equal differential contribution of the ions of the electrolyte to the compensation of σ^0 , apart from a valence factor. If there is a c.i.p. this equal differential compensation is invariant with electrolyte concentration and solely characterised by the nature of the particular oxide-electrolyte system.

No thermodynamic argument can be given to identify a c.i.p. with a p.z.c., but model considerations can be invoked. Based on a purely diffuse double layer picture, that is, applying Poisson-Boltzmann statistics, it is possible to derive eqs. [7.3], [7.4], etc. for the low potential limit (ref. 11). This means that, in the absence of specific adsorption, a p.z.c. is a c.i.p. However, in the presence of specific adsorption this is not generally true, as experiments have shown. The observation that, for example in the case of specific adsorption of a cation, a c.i.p. is observed for $\sigma^0 > 0$ must perhaps be interpreted as follows: after the chemical attraction of this cation has been exactly compensated by a counteracting repulsion due to the positive potential, any additionally added electrolyte behaves as if it were fully indifferent.

Experience has shown that alkali metal ions and "simple" anions like F^- , Cl^- and NO_3^- are often indifferent, although there are exceptions. Examples: Li^+ adsorbs specifically on haematite ($\alpha\text{-Fe}_2\text{O}_3$), Cl^- on ruthenium oxide, NO_3^- shows weak specific adsorption on silver iodide and F^- adsorbs specifically on Al_2O_3 .

Table 1. Direction of shifts of p.z.c. and i.e.p.^{a)}

Electrolyte	contains specifically adsorbing cation	indifferent	contains specifically adsorbing anion
p.z.c.	+	0	-
i.e.p.	-	0	+

a) A plus (+) sign means: shift towards lower pH or pAg that is, to the side where $\sigma^0 > 0$. A minus (-) sign means shifts in the other direction.

Determination of the i.e.p. involves measurements of the ζ potential. For those electrokinetic procedures requiring stable sols, such as electrophoresis, it is not possible to obtain ζ exactly at the i.e.p. because the sol coagulates. In such cases the i.e.p. can be found by interpolation between data to the negative and to the positive side of the i.e.p.

Just as σ^o and σ^{ek} are different double-layer characteristics, so are the p.z.c. and the i.e.p. Only in the absence of specific adsorption may the two be equated, because in that case $\sigma^l = 0$, so that $\sigma^o = 0$, hence $\sigma^o = -\sigma^d = \sigma^{ek}$ (eq. [5.1]). Such an identity is the best criterion for the absence of specific adsorption.

If the concentration of an electrolyte containing a specifically adsorbing ion is increased, the p.z.c. and i.e.p. shift in opposite directions as indicated in table 1.

The physical background is as follows. If a cation adsorbs specifically (in the Stern layer), this phenomenon will:

1. promote the adsorption of negative surface ions. To equate this adsorption with that of positive surface ions, in order to reach the p.z.c. again, the concentration of the latter in the solution must be enhanced, i.e. pH or pAg should decrease.
2. render the particle *together with its Stern layer* (that is: the electrokinetically active unit) more positive; to return to the point where this total charge is zero, that is, to re-establish the i.e.p., the adsorption of negative surface ions should be promoted by increasing pH or pAg.

Similar reasoning applies to the case of specific anion adsorption.

The difference between p.z.c. and i.e.p. is a second measure of the extent of specific adsorption.

The so-called "reversal of charge" in colloid science is often inferred from the change in sign of ζ upon specific adsorption. It follows from the above discussion that this reversal applies to σ^{ek} and not to the surface charge, σ^o . To avoid confusion it is therefore recommended to discriminate, where appropriate, between "reversal of surface charge" and "reversal of electrokinetic charge".

8. CONCLUDING REMARK

Unlike the situation with polarised electrodes (ref. 2) the potential does not play a significant role in this document because it is a derived quantity that can only be obtained from the charge, using some double-layer model. Only in exceptional cases (in particular when the solid under consideration can be made into an electrode or when its identity with an otherwise prepared electrode of the same material can be ascertained) can the surface potential be established with respect to a chosen reference.

LIST OF SYMBOLS AND ABBREVIATIONS

σ_-	charge density in the solution side of a double layer due to anions	$C\ m^{-2}$
σ_+	charge density in the solution side of a double layer due to cations	$C\ m^{-2}$
σ^d	charge density in diffuse part of double layer	$C\ m^{-2}$
c.i.p.	common intersection point	
σ^{ek}	electrokinetic charge density	$C\ m^{-2}$
ζ	electrokinetic potential	V
β	Esin-Markov coefficient	
σ^l	inner layer (or Stern) charge density	$C\ m^{-2}$
IHP	inner Helmholtz plane	
i.e.p.	isoelectric point	
OHP	outer Helmholtz plane	
p.z.c.	point of zero charge	
σ^o	surface charge density	$C\ m^{-2}$
Γ_i	surface excess (or surface concentration) of i	$mol\ m^{-2}$

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