

The pH dependent surface charging and points of zero charge. VI. Update



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ARTICLE INFO

Article history:

Received 17 January 2014

Accepted 25 February 2014

Available online 12 March 2014

Keywords:

Point of zero charge

Isoelectric point

Surface charge density

Zeta potential

Electrokinetic potential

ABSTRACT

The pristine points of zero charge (PZC) and isoelectric points (IEP) of metal oxides from the recent literature are summarized. This study is an update of the previous compilation (Kosmulski, 2009) [5] and of its previous updates (Kosmulski, 2009, 2011) [6,7]. Only the IEP of materials other than metal oxides are reported, and the PZC of such materials obtained by potentiometric titration and related methods are ignored. IEP of (nominally) CoO, Fe(OH)₂, Gd₂O₃, Ni₂O₃, and Sb₂O₃ have been reported in the recent literature. Those materials have not been studied before.

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Introduction

The pH-dependent surface-charging of solid particles in aqueous solutions of 1–1 electrolytes has been extensively studied. The points of zero charge (PZC) and isoelectric points (IEP) of metal oxides in 0.0001–0.1 M solutions of alkali halides, nitrates(V), or chlorates(VII) are termed pristine PZC/IEP, and they were compiled in the classical paper by Parks [1]. The pristine PZC are independent of the nature of the salt, its concentration and other experimental conditions, thus they characterize the surface-charging behavior over a broad range of experimental conditions. Ions other than alkali metal cations or halide, nitrate(V), or chlorate(VII) anions often adsorb specifically, and induce a shift of PZC and IEP away from the pristine value. The PZC/IEP observed in the presence of specifically adsorbing ions are of limited significance, because they depend on the nature of the salt, its concentration, and other experimental conditions, and they are ignored in the present review. For example, Mehdilo et al. [2] used H₂SO₄ to adjust the pH of dispersions of ilmenite. Their IEPs are not reported in this review, because sulfate anions are known to adsorb specifically on iron compounds, and to induce a shift in their IEP to low pH values.

Several recent publications compile pristine PZC of a specific chemical compound(s) or of certain class of chemical compounds. For example Chorover compiled PZC of soil constituents [3]. In contrast, relatively few publications report PZC of broad ranges of materials. Extensive compilations of pristine PZC of metal oxides and other materials were published by Kosmulski [4,5]. The

classical Parks' review is still more frequently cited as a reference for "recommended" PZC of metal (hydr)oxides than up-to-date reviews as illustrated in Fig. 1. Several recent publications, which cite [1,4,5] are discussed in this compilation. The recent review [5] was updated twice [6,7] and the recent results (2011–2013) and a few older results (overlooked in [5–7]) are compiled in the **Supplementary material in Table 1** (not available in the printed copy of the journal). The significance of the pristine PZC/IEP and their applications were discussed in detail in Ref. [1–7], in many other compilations of PZC/IEP cited therein, and in handbooks of surface and colloid chemistry.

The PZC reported in review papers are especially important for the scientists who do not determine the PZC of their specimens themselves, but who rely on the PZC of similar specimens taken from the literature. In principle the PZC/IEP "recommended" in various reviews are consistent, and the choice of this or another compilation is not crucial. Yet erroneous pristine PZC allegedly based on the review papers are commonplace in the recent literature. For example Sojka et al. [8] used an erroneous value of PZC of niobia (2.8); Usui et al. [9] used erroneous values of PZC of hematite (4.2–6.9) and of goethite (5.9–6.7); and Liu et al. [10] used an erroneous value of PZC of hematite (6.7), taken from old compilations.

The PZC reported in review papers are also useful for the scientists who determined the PZC of their specimens experimentally. The PZC of similar specimens taken from the literature are used to verify the purity of the samples and the correctness of the procedures. Comparison of own results with the literature (original publications or compilations) is commonplace in papers reporting

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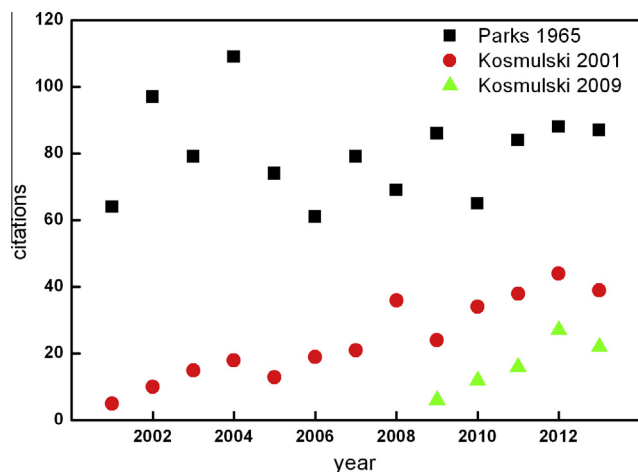


Fig. 1. Citations of selected compilations of PZC/IEP.

PZC/IEP measurements. However, several recent studies reported rather unusual pristine IEP of common metal oxides, e.g., 6 for alumina [11] and 4.2 for Fe_2O_3 [12], without a reference to the existing literature on similar specimens. This is not clear whether the authors realized that their IEP were very different from the IEP of similar specimens reported by the others.

The present review reports selected results from the literature. The pristine PZC and IEP are summarized in [Supplementary Table 1](#) (not available in the printed copy of the journal). Erroneous or less credible results were deliberately neglected. Also the PZC/IEP reported in the original papers were verified when the original data (ζ potential or surface charge density σ_0 as a function of pH) were available.

Several publications report ζ potential or σ_0 measured in multi-component dispersions (dispersions containing various types of colloidal particles). The σ_0 in multi-component dispersions is additive, that is, the information about the composition of dispersion and the charging behavior of individual components makes it possible to predict the charging behavior of multi-component dispersions. In contrast there is no simple relationship between the apparent ζ potential observed in a mixture of various minerals and the composition of that mixture. Erroneous allegations in this respect are published now and then even in top-quality scientific journals, e.g., Eq. (2) in [13]. Kosmulski [14] studied the ζ potentials in dispersions containing two types of colloidal particles. The background subtraction procedure made it possible to calculate the ζ potential of individual types of colloidal particles in two-component dispersions. However, such a background subtraction procedure is only valid in the absence of heterocoagulation. The present review is focused on the PZC/IEP obtained in one-component dispersions, and the PZC/IEP allegedly obtained in multi-component dispersions (e.g., soils and rocks) were deliberately ignored.

Structure of Table 1

The structure of [Supplementary Table 1](#) (not available in the printed copy of the journal) follows the same principles as Table 1 in Refs. [6,7]. The materials are organized into 13 categories according to their chemical composition. Within each category the materials are sorted by their chemical formula. Multiple specimens corresponding to the same (idealized) formula are sorted into the following categories: commercial, synthetic, and natural materials. The commercial specimens are characterized by their manufacturer and/or trade name. The synthetic materials are characterized by the recipe. The natural materials are characterized by

geographical locations (mine, region, country). The formula and concentration (concentration range) of the electrolyte(s), temperature, method, and instrument used in the surface charging measurements are reported in separate columns of [Supplementary Table 1](#) (not available in the printed copy of the journal). Empty boxes denote that the information was not available or not applicable.

Methods

Experimental

The terminology of experimental methods used in the literature is not consistent. Very often the same method is described by various names or the same name is used for different methods. The following terminology, adapted from previous compilations [4–7] is used in [Supplementary Table 1](#) (not available in the printed copy of the journal):

- cip (common intersection point of potentiometric titration curves obtained at three or more ionic strengths)
- intersection (intersection point of potentiometric titration curves obtained at two ionic strengths)
- iep (isoelectric point obtained by electrokinetic or electroacoustic measurements)
- salt titration (salt addition): addition of inert electrolyte (powder or concentrated solution) induces a shift in the pH of dispersion toward the pristine PZC. The pH value, at which salt addition does not induce any shift in the pH is equivalent to CIP.
- pH (natural pH of dispersions, e.g., obtained by mass titration). Such results were deliberately ignored in most materials. Silica (for which cip is not observed) is an exception.

Moreover in a few papers reporting PZC of less common materials, the description of the method was not precise enough, and the “method” in [Supplementary Table 1](#) (not available in the printed copy of the journal) is followed by “?”. On top of measurements carried out by standard methods, a few publications present less common solutions. Corbett et al. [15] proposed a technique to measure the ζ potential of macroscopic specimens. They observed the velocity of tracer particles between two flat parallel electrodes as the function of the distance from the studied surface (in the range 0.1–1 mm), which was perpendicular to those electrodes. The new method has an advantage of using small specimens of solid and small volumes of liquid as compared to standard electroosmotic or streaming potential measurements, and it inherits most disadvantages of those methods (difficulties in the pH measurement, sensitivity to traces of impurities).

Jordan et al. [16] obtained a hematite layer by atomic layer deposition and report a PZC of that layer at pH 5.5, derived from second harmonic generation (SHG) studies. Their PZC is substantially lower than the PZC/IEP usually reported for hematite powders. Sung et al. [17] studied an α -alumina single crystal, and report a PZC of (1–102) plane, derived from sum frequency vibrational spectroscopy (3230 cm^{-1} band) at pH 6.7. Their PZC is substantially lower than the PZC/IEP usually reported for alumina powders. Similar discrepancies (e.g., SHG vs. electrophoresis) are well-documented in the older literature. SHG is not considered a standard method in the present study, but a few PZC obtained by SHG are reported in [Supplementary Table 1](#) (not available in the printed copy of the journal).

There is a substantial difference between the present approach and that in Refs. [4–7], namely the PZC obtained by means of titration at one ionic strength (which in fact are natural pH values of dispersions) for materials other than metal oxides were ignored

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