



# IEP as a parameter characterizing the pH-dependent surface charging of materials other than metal oxides

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## ABSTRACT

The numerical values of points of zero charge (PZC, obtained by potentiometric titration) and of isoelectric points (IEP) of various materials reported in the literature have been analyzed. In sets of results reported for the same chemical compound (corresponding to certain chemical formula and crystallographic structure), the IEP are relatively consistent. In contrast, in materials other than metal oxides, the sets of PZC are inconsistent. In view of the inconsistency in the sets of PZC and of the discrepancies between PZC and IEP reported for the same material, it seems that IEP is more suitable than PZC as the unique number characterizing the pH-dependent surface charging of materials other than metal oxides. The present approach is opposite to the usual approach, in which the PZC and IEP are considered as two equally important parameters characterizing the pH-dependent surface charging of materials other than metal oxides.

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## 1. Introduction

Solid/aqueous interfaces undergo pH-dependent surface charging, that is, they tend to be positively charged at low pH, and negatively charged at high pH. The sign and magnitude of the surface charge govern the uptake of ionic species from solution, and the physical properties of dispersions (e.g., their stability against coagulation), and this is why the pH value, at which the net surface charge equals zero is an important parameter characterizing solid surfaces. This parameter is termed  $pH_0$  when specific experimental method (used to determine the zero-point) is not addressed. Otherwise, experimental-method-specific terms, e.g., IEP (isoelectric point obtained by means of electrokinetic measurements) or PZC (point of zero charge obtained by potentiometric titration) will be used. Reliable values of  $pH_0$  for various materials are much desired in colloid chemistry, in materials science, catalysis, geochemistry, soil science, and wastewater management. This study addresses the problem of  $pH_0$  of materials other than metal oxides. This is not a typical review paper, because detailed description of the specimens and of the experimental methods and conditions or literature references to the original studies are not explicitly reported. In contrast, the distributions of  $pH_0$  reported for specific material in existing review papers are discussed, and relations between the  $pH_0$  in groups of similar materials are analyzed.

### 1.1. The surface-charging of metal oxides

The pH-dependent surface charging of metal oxides in aqueous solutions of alkali halides, nitrates(V), and chlorates(VII) up to 0.1 M has been extensively studied, and the results can be summarized as follows.

1. The effect of the nature and concentration of salt on the isoelectric point (IEP) is rather insignificant.
2. The effect of the nature of salt and of the studied concentration range on the common intersection point (CIP) of potentiometric titration curves obtained at various ionic strengths is rather insignificant.
3. The IEP and CIP match for certain specimen, and they are rather insensitive to the experimental conditions (solid-to-liquid ratio, equilibration time, acid titration vs. base titration, etc.). For multiple specimens representing the same chemical compound, the IEP and CIP fall within a narrow pH-range (about 1 pH-unit).

The approach represented by #1–3 dates back to the classical review by Parks [1], which still is the most frequently cited publication reporting the  $pH_0$  of metal oxides. The equality  $pH_0 \approx CIP \approx IEP$  for metal oxides is generally accepted [2–5], it was corroborated by the recent studies, and in spite of the progress in the instrumental technique over the recent half-century, the “recommended” values of  $pH_0$  of metal oxides reported in the recent review [6] are not much different from those reported by Parks [1].

### 1.2. Application of Parks' approach to materials other than metal oxides

Parks' approach became very popular and it is often generalized for materials other than metal oxides. The reviews reporting  $pH_0$  of specific materials [7–10] and of many different materials [11–13] treat PZC and IEP as two equally important parameters characterizing the pH-dependent surface charging. The above reviews explicitly report the  $pH_0$  from literature, and less attention was paid to the

selection of the “recommended” value (the most reliable  $pH_0$  reported for a given chemical compound) or to statistical analysis of the  $pH_0$  from different sources. The present study represents an opposite approach: it is focused on the needs of a reader looking for a “recommended”  $pH_0$  for certain chemical compound.

The availability of the  $pH_0$  of materials other than metal oxides is limited, and many materials are only represented by single literature reference. Thus, the statistical analysis of  $pH_0$  from different sources could be only carried out for a few materials other than metal oxides. Many publications clearly indicate that  $PZC \neq IEP$  for specific materials other than metal oxides [11]. Thus, the approach to the  $pH_0$ , which is generally accepted for metal oxides (Section 1.1) is not suitable for other materials. Obviously a set of two different numbers is not acceptable as a unique parameter characterizing given material.

## 2. Experimental

### 2.1. Electrolyte

The present study is focused on the results obtained in aqueous solutions of alkali halides, nitrates(V), or chlorates(VII) up to 0.1 M, and the results obtained for electrolytes involving multivalent ions are purposely ignored. The inert character of 1–1 electrolytes with respect to metal oxides is well-documented, that is, numerous studies report the  $pH_0$  obtained for a series of 1–1 electrolytes, and indeed, the effect of the nature and concentration of the electrolyte on the  $pH_0$  was insignificant (e.g., [14]). It should be emphasized that the nature of the electrolyte does affect the values of the  $\zeta$ -potential and of the surface charge density away from the  $pH_0$  even for inert electrolytes [11,14]. Thus the  $pH_0$  found in the literature for one inert electrolyte is applicable to another inert electrolyte, but the values of electrokinetic potential or of the surface charge density (at certain ionic strength) are not. The inert character of 1–1 electrolytes with respect to materials other than metal oxides is less well-documented, and in most publications, one electrolyte (e.g., NaCl) was arbitrarily selected, and there is no data available for other electrolytes. There are very few publications reporting sets of potentiometric and/or electrokinetic curves obtained for the same material (other than metal oxide) and a series of different 1–1 electrolytes. Thus, the inert character of dilute solutions of 1–1 electrolytes toward materials other than metal oxides is a hypothesis (based on the studies with metal oxides) rather than an experimental fact. The hypothetical character of this assumption is seldom pronounced, although such an assumption was silently made in most publications reporting the  $pH_0$  of materials other than metal oxides. More concentrated (>0.1 M) solutions of 1–1 electrolytes often show substantial ion-specificity (the electrolytes are not inert) toward metal oxides [15], and they cause experimental difficulties (e.g., in pH-measurements). Similar difficulties are expected with materials other than metal oxides.

Presentation of the  $pH_0$  obtained in solution(s) of certain electrolyte(s) in this paper does not imply that these electrolytes are indeed inert toward specific material.

### 2.2. Temperature

The present study is devoted to the  $pH_0$  at room temperature. Several publications specify the temperature (usually 20 or 25 °C), and many other  $pH_0$  were obtained at an unspecified room temperature, probably about 25 °C. The surface charging of metal oxides is temperature-dependent. A variation in  $T$  by one °C typically induces

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