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# The pH-dependent surface charging and points of zero charge
## V. Update

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ABSTRACT

The points of zero charge (PZC) and isoelectric points (IEP) from the recent literature are discussed. This study is an update of the previous compilation [M. Kosmulski, Surface Charging and Points of Zero Charge, CRC, Boca Raton, FL, 2009] and of its previous update [J. Colloid Interface Sci. 337 (2009) 439]. In several recent publications, the terms PZC/IEP have been used outside their usual meaning. Only the PZC/IEP obtained according to the methods recommended by the present author are reported in this paper, and the other results are ignored. PZC/IEP of albite, sepiolite, and sericite, which have not been studied before, became available over the past 2 years.

## 1. Introduction

The pH-dependent charging of various solid surfaces in aqueous solutions of 1–1 electrolytes governs the adsorption of ions, and thus it is of great theoretical and practical interest. The points of zero charge (PZC) and isoelectric points (IEP) observed in 0.0001–0.1 M aqueous solutions of alkali halides, nitrates(V), or chlorates(VII) are termed pristine PZC/IEP (to distinguish them from PZC/IEP observed in the presence of other solutes), and they are used to characterize the materials in materials engineering, catalysis, geochemistry, agriculture, wastewater management, etc. PZC/IEP from the literature have been summarized in numerous reviews. More dilute electrolyte solutions (<0.0001 M) are not suitable for studies of pH-dependent surface charging, because only a very limited pH range can be covered. More concentrated (>0.1 M) solutions of 1–1 electrolytes often show substantial ion specificity (the electrolytes are not inert), and they cause experimental difficulties (e.g., in pH measurements). The classical paper by Parks [1] is the most frequently used reference on pristine PZC. More recent, the most comprehensive compilation of pristine PZC was published by Kosmulski [2]. Due to a high activity in the field, that review was recently updated [3]. Several specialized reviews have been published, limited to certain types of materials, e.g., a recent review on IEP of viruses [4].

The production of new results is still extensive, and the very recent results (2009–2010) and a few older results (overlooked in [2,3]) are compiled in the present paper in Table 1. The reliable and up-to-date compilation of PZC/IEP is especially valuable for those who use the concept of PZC/IEP, but who do not measure their values themselves, and using a value from a random primary source or from an outdated or incomplete review may have adverse effects. For example in a very recent paper [5] IEP of AKP-50 alumina at pH 7.9 is reported, probably based on the literature. This happens to be the lowest IEP ever published for AKP-50, and it is lower by over 1 pH unit than the results reported in other sources. A correlation between IEP and electronegativity discussed in a very recent paper [6] was based on nonexistent results or substantially underestimated IEP, probably taken from a review paper.

### 1.1. Approach to results of insufficient quality

Most studies containing PZC/IEP of insufficient quality (according to the standards defined by the present author [2], and by the others [7]) are simply ignored in the present compilation. The present approach has it pros and cons, and some readers may prefer an exhaustive list of deliberately ignored references, with an explanation why those reference were not used, as it was done, e.g., in the famous book of Dzombak and Morel [8]. A few arguments in favor of the present approach are discussed in this section. First, there is no sharp borderline between "correct" and "incorrect" results. Only a few papers totally conform to the standards settled in this review, and many papers only partially conform to those

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**Table 1**
PZC/IEP compilation: update of [2,3].

| Section in [2] | Material | Electrolyte | *t*, °C | Method | Instrument | PZC/IEP | Ref. | No. of entries in [2,3] | PZC/IEP in [2,3] |
|---|---|---|---|---|---|---|---|---|---|
| *3.1. Oxides* | | | | | | | | | |
| 3.1.1.1.1 | $Al_2O_3$, AD101-F, from ACE[a] | | | pH | | 8.3* | [14] | | |
| 3.1.1.1.1 | $Al_2O_3$, AO-802 from Admatech, $\alpha$, 99.8% pure | | | iep | Zeta Probe Colloidal Dynamics | 8.5[b] | [15,16] | | |
| 3.1.1.1.1.3 | $Al_2O_3$, $\alpha$, CT300SG, Alcoa, original and NaOH-washed | KOH+HCl | | iep | DT 1200 | 9.5 | [17] | | |
| 3.1.1.1.1.4.1 | $Al_2O_3$, $\alpha$, Aldrich, >99.7%, washed | 0.0005 M NaCl, NaBr, NaI, $NaNO_3$ | 25 | iep | Malvern Zetasizer 3000 HS | 6.7 | [18] | 1 | 6.7 iep |
| 3.1.1.1.1.5 | $Al_2O_3$, $\alpha$, 99.95% pure, from Alfa Aesar | 0.01 M NaCl | 25 | iep | Malvern Nano ZS | 8.2 | [19] | 3 | 9.1 iep |
| 3.1.1.1.1 | $Al_2O_3$, K10 from Alum-Earth Plant[c] | $NaClO_4$ | 20 | pH | | 6.5 | [20,21] | | |
| 3.1.1.1.1 | $Al_2O_3$, $\alpha$, from Antaria | | | iep | ZetaProbe, Colloidal Dynamics | 7.7–8.3 | [22] | | |
| 3.1.1.1.1.21 | $Al_2O_3$, Degussa C, used as obtained | 0.01 M NaCl | 25 | iep | Acoustosizer 2 | 9 | [23] | 48 | 8.9 |
| 3.1.1.1.1.21 | $Al_2O_3$, Degussa C | 0.001–0.1 M $KNO_3$ | 25 | cip | | 8.3 | [24] | 48 | 8.9 |
| 3.1.1.1.1.21 | $Al_2O_3$, Degussa C | 0.005–0.5 M $KNO_3$ | | cip | | 8 | [25] | 48 | 8.9 |
| 3.1.1.1.1.21 | $Al_2O_3$, Degussa C | 0.01 M NaCl | | iep | Zeta-Plus, Brookhaven | 9.2 | [26] | 48 | 8.9 |
| 3.1.1.1.1 | $Al_2O_3$, $\gamma$, from Engelhard | 0.001 M NaCl | 25 | pH | | 8.6* | [27] | | |
| 3.1.1.1.1.29 | $Al_2O_3$, T126 from Girdler, heated at 200 °C for 16 h | 0.001 M KCl | | iep | Zeta Meter 77 | 8.8* | [28] | 3 | 8.8 |
| 3.1.1.1.1 | $Al_2O_3$, $\alpha$, from Interchim, 99.99% pure, NaOH-washed | | | | | 9.1 | [29] | | |
| 3.1.1.1.1 | $Al_2O_3$, sapphire from Kelpin or from MaTeck, 001 plane | 0.001, 0.01 M KCl, NaCl, $NaNO_3$ | | iep | Surpass, Paar | 4[d] | [30] | | |
| 3.1.1.1.1.50.1 | $Al_2O_3$, $\gamma$, from Merck, washed | 0.01 M NaCl | 25 | pH<br>iep | Malvern Zetasizer 3000 | 7.6[e]<br>8 | [31,32] | 5 | 8. 7 |
| 3.1.1.1.1 | $Al_2O_3$, Shanghai Chem. Co. [f] | HCl + NaOH | | iep | Zeta PALS, Brookhaven | 8 | [33] | | |
| 3.1.1.1.1.68 | $Al_2O_3$, Sigma–Aldrich, high purity | 0.01 M KCl | | iep/cip | Zeta-Plus, Brookhaven | 7.9/8.1 | [12] | (1) | 8.6 |
| 3.1.1.1.1.72.2 | $\alpha$-$Al_2O_3$, AKP30, Sumitomo, original/washed | | | iep | Matec ESA 9800, ZetaProbe, Colloidal Dynamics | 9.3*/9.8 | [16] | 21 | 9 |
| 3.1.1.1.1.72 | $\alpha$-$Al_2O_3$, AKP-HP40, Sumitomo | | | iep | Zetasizer III Malvern | 9 | [34] | | |
| 3.1.1.1.1.84 | Commercial $\gamma$-$Al_2O_3$ from unknown source[g] | 0.001 M KCl | | iep | Zeta Meter 77 | 8* | [35] | | |
| 3.1.1.4.1.1.1 | Gibbsite, S11 from Alcoa | 0.015 M NaCl | | iep | Zeta Meter 3.0 | 9.1 | [36] | | |
| 3.1.1.4.1.2.1.4 | Synthetic gibbsite[h] | 0.01–0.5 M $KNO_3$ | 25 | cip | | 10.1 | [37] | 7 | 10 |
| 3.1.1.4.1.2 | Synthetic gibbsite[i] | 0.01 M KCl | 25 | iep | Coulter Delsa 440 | 5.7 | [38] | | |
| 3.1.6.1.2 | Synthetic $CeO_2$ | | | iep | electrophoresis | 8.5 | [39] | | |
| 3.1.6.1.2 | Synthetic cerianite, $CeO_2$ | | | iep | Brookhaven Zeta PALS | 8.1 | [40] | | |
| 3.1.8.4.1 | $Cr(OH)_3$[j] | 0.0001–0.01 M $KClO_4$ | | iep | Laser Zee Meter 501 | 8.4 | [41] | 2 | 7.8;8.4 iep |
| 3.1.9.2.1.1 | CuO from Aldrich | | | iep | Otsuka | 8.5[k] | [42,43] | 2 | 8.5;9.2 iep |
| 3.1.9.4.4 | $Cu(OH)_2$[l] | 0.01 M $KNO_3$ | | iep | Malvern Nano ZS | 10 | [44] | 2 | 8.5;10.3 iep |
| 3.1.12.2.1 | Magnetite from Prolabo | 0.001–0.1 M NaCl | | cip | | 6.7* | [45] | | |
| 3.1.12.2.2.1.3 | Synthetic magnetite[m] | | 25 | iep | Malvern Zetasizer 3000 HS | 5.6 | [46] | 4 | 6.7 iep |
| –”– | –“– | 0.002 M $NaNO_3$ | 25 | iep | Malvern Zetasizer 2000 | 6.5 | [47] | –”– | –“– |
| 3.1.12.2.2.1.3 | Synthetic magnetite[n] | | 25 | iep | Zeta PALS, Brookhaven | 6.5 text<br>5.5 Fig. 1 | [48] | 4 | 6.7 iep |
| 3.1.12.2.2 | Synthetic magnetite, prepared under nitrogen | 0–0.5 M $NaNO_3$ | | cip | | 8.2 | [49] | | |
| 3.1.12.2.4 | Magnetite, natural, from Ward’s | 0.005, 0.01 M NaCl | | iep | Coulter Delsa 440SX/ Zeta Probe,Colloidal Dynamics | 3.8/3.8 | [50] | | |
| 3.1.12.2.5 | Magnetite, 105 $m^2/g$ | 0.001–0.1 M NaCl | | cip | | 8 | [25] | | |
| 3.1.12.3.1.1.2 | Maghemite from Alfa Aesar, 40 $m^2/g$ | 0.001 M NaCl | | iep | Malvern Zetasizer 3000 HSA | 6.9 | [51] | 1 | 7.7 iep |
| 3.1.12.3.1.2.5 | Synthetic maghemite[o] | | | iep | Malvern Zetasizer 2000 | 7.5 | [52] | | |
| 3.1.12.3.1.2.5 | Synthetic maghemite, from $FeCl_2$ and $FeCl_3$ | 0.1 M $NaNO_3$ | 25 | pH | | 6.5 | [53] | 3 | 6.6 |
| 3.1.12.3.1.2 | Synthetic maghemite[p] | | | iep | Malvern Zetasizer Nano ZS | 6.1 | [54] | | |
| 3.1.12.3.1.2 | Synthetic maghemite[q] | 0.001 M KCl | | iep | Zeta PALS, Brookhaven | 6.4 | [55] | | |
| 3.1.12.2.2 | Hematite from Alfa Aesar | 0.001 M NaCl | | iep | Zeta Probe, Colloidal Dynamics | 8.9 | [56] | 2 | 6.5, 9, iep |