Comparison of isoelectric points of single-crystal and polycrystalline $\alpha$-Al$_2$O$_3$ and $\alpha$-Fe$_2$O$_3$ surfaces

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ABSTRACT

The surface charging behavior as a function of pH and isoelectric points (IEPs) of single-crystal $\alpha$-Al$_2$O$_3$ (0001) and (1T02) and $\alpha$-Fe$_2$O$_3$ (0001) was determined by streaming potential measurements using an electrokinetic analyzer. The IEPs of $\alpha$-Al$_2$O$_3$ (0001) and (1T02) and $\alpha$-Fe$_2$O$_3$ (0001) were found to be 4.5, 5.1, and 6.5, respectively. These IEP values for oriented single crystals of $\alpha$-Al$_2$O$_3$ are in good agreement with literature values, whereas the new IEP value for $\alpha$-Fe$_2$O$_3$ (0001) is significantly lower than four reported values (IEP = 8–8.5) for single-crystal $\alpha$-Fe$_2$O$_3$ (0001) (Eggleston and Jordan 1998; Zarzycki et al. 2011; Chatman et al. 2013; Lützenkirchen et al. 2013) and significantly higher than one (IEP = 4) recently measured by Lützenkirchen et al. (2015) on a fresh $\alpha$-Fe$_2$O$_3$ (0001) surface. Most of the single-crystal IEP values measured recently are lower than IEP values reported for polycrystalline $\alpha$-Al$_2$O$_3$ and $\alpha$-Fe$_2$O$_3$, which are generally in the pH range of 8 to 10. Calculations of the IEP values based on estimated $K_a$ values of $\alpha$-Fe$_2$O$_3$ and $\alpha$-Al$_2$O$_3$ surfaces in contact with water as a function of defect type and concentration suggest that highly reactive surface defect sites (primarily singly coordinated aquo groups) on the Fe- and Al-oxide powders are possibly a major source of the surface charge differences between polycrystalline samples and their oriented single-crystal counterparts studied here. The results of this study provide a better understanding of the surface charging behavior of Fe and Al-oxides, which is essential for predicting complex processes such as metal-ion sorption occurring at mineral/water interfaces.

Keywords: Isoelectric point (IEP), pH point of zero charge (pH$_{pzc}$), Fe- and Al-oxides, single crystal, polycrystalline, surface, defects

INTRODUCTION

Oxides and oxyhydroxides of iron and aluminum, as well as several other common metals (e.g., Mn), are among the most reactive mineral phases in the natural environment (e.g., Brown et al. 1999; Stipp et al. 2002). Due to their high surface reactivities and large surface areas, these metal-(oxyhydr)oxides often serve as natural sorbents of aqueous metal and metalloid species (e.g., Goldberg et al. 1996; Cornell and Schwertmann 2003) as well as natural organic molecules (e.g., Gu et al. 1996; Nordin et al. 1998) and thus are important in controlling their transport and environmental fate. In addition to their importance in environmental chemistry, synthetic Fe- and Al-(oxyhydr)oxides are manufactured in bulk for use in a wide variety of technological and industrial applications. Synthetic polycrystalline $\alpha$-Al$_2$O$_3$, which are generally in the pH range of 8 to 10. Calculations of the IEP values based on estimated $K_a$ values of $\alpha$-Fe$_2$O$_3$ and $\alpha$-Al$_2$O$_3$ surfaces in contact with water as a function of defect type and concentration suggest that highly reactive surface defect sites (primarily singly coordinated aquo groups) on the Fe- and Al-oxide powders are possibly a major source of the surface charge differences between polycrystalline samples and their oriented single-crystal counterparts studied here. The results of this study provide a better understanding of the surface charging behavior of Fe and Al-oxides, which is essential for predicting complex processes such as metal-ion sorption occurring at mineral/water interfaces.

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