On the Temperature Dependence of Intrinsic Surface Protonation Equilibrium Constants: An Extension of the Revised Music Model

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The revised MUltiSIte Complexation (MUSIC) Model (Hiemstra et al., 1996) is the most thoroughly developed approach currently available that explicitly considers the protonation behaviour of the various types of surface hydroxyl groups known to exist on mineral surfaces. As such, a principal advantage of the MUSIC Model over the more traditional 2 pK description of surface protonation is that it is possible to more directly reconcile bulk macroscopic measurements such as surface charge and adsorption pH edge data with *in situ* spectroscopic information concerning actual adsorption structures, as well as with quantum and molecular dynamics simulations of these structures. We have extended the revised MUSIC Model to temperatures other than 25ºC to help rationalize the adsorption data we have been collecting for various metal oxides including rutile and magnetite to 300ºC. A critical component of this approach was to incorporate an empirical correction factor that accounts for the observed decrease in cation hydration number with increasing temperature. In any case, this extension of the revised MUSIC Model matches our experimentally determined point of zero net proton charge pH (pHznpc) values for rutile to within 0.06 pH units between 25 and 250ºC (Machesky et al.,

1998). Moreover, combining the MUSIC Model derived surface protonation constants with a three-plane description of electrical double layer structure results in a good fit to our experimental surface protonation data for all conditions investigated (25 to 250C, and 0.03 to 1.0 m NaCl or tetramethylammonium chloride media). In addition, the temperature corrected MUSIC Model has provided a consistent framework that has helped us rationalize adsorption data for metal oxides that are less well behaved than rutile, including magnetite (Wesolowski et al., 2000). Consequently, this approach should be useful in other instances where it is necessary to describe and or predict the adsorption behaviour of metal oxide surfaces over a wide temperature range.

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