Consistent treatment of 'denticity' in surface complexation models

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Spectroscopic studies and atomistic simulations of (hydr)oxide surfaces, which show that some aqueous cations bind to two or four surface oxygen atoms, have increased interest in multi-dentate surface complexation models (SCMs) [1-3]. However, it remains unclear how the (fitted) values of intrinsic equilibrium constants K_M^{int} (referenced to infinite dilution) for δ-dentate M surface-binding reactions ($\delta > 1$) depend on the choice of concentration scale. In existing SCM codes, a surface complex may be treated in scales of either: molarity/molality ([]); site coverage fraction (θ); surface mole fraction (x); molecular surface density (Γ, in mol·m^{-2}); or relative density Γ/Γ_o (o, where $\Gamma_o = 2 \cdot 10^{-5}$ mol·m^{-2} is the reference adsorbed density [4]). Our aim was to investigate, for 'denticities' $1 \le \delta \le 4$, how to convert the $K^{int,\delta}$ values fitted for a given titration data set (the same solid concentration c_S, specific surface area A_S, and monolayer site density Γ_C) between different concentration scales.

For single-site monodentate surface binding reactions, K_M^{int} expressed in all concentration scales ([], θ, x, Γ, o) reduce to the same value $K_M^{\text{int},1}$. For the binding with $\delta \ge 2$, conversion factors from $^x K_M^{\text{int},\delta}$ to $^\theta K_M^{\text{int},\delta}$ are about δ. From $^{[]}K_M^{\text{int},\delta}$ to any other scale, they involve $(c_S A_S \Gamma_C)^{\delta-1}$ which is ca. 10^{-5} for $\delta = 2$ or 10^{-15} for $\delta = 4$ at typical $c_S = 1$ g·dm^{-3}, $A_S = 10$ m^{2}g^{-1}, and $\Gamma_C = 10^{-6}$ mol·m^{-2}. Conversions of K^{int} from [], θ and x scales into the Γ scale involve $(\Gamma_C)^{1-\delta}$, which has a value ranging from 10^5 to 10^{18} at $10^{-6} < \Gamma_C < 10^{-5}$ mol·m^{-2}. The K^{int} conversions from [], θ and x to the o scale include $(\Gamma_o/\Gamma_C)^{\delta-1}$ which vanishes if $\Gamma_C = \Gamma_o$ (then $^o K_M^{\text{int},\delta} = {}^x K_M^{\text{int},\delta}$).

Our findings show that the use of published $K_M^{int,\delta}$ ($\delta \ge 2$) in SCMs may lead to erroneous results, if concentration scales are not precisely defined both in the original fitting and in the subsequent application. At trace ion concentrations, using formally monodentate surface species would be safe especially on 'strong' sites, for which the density is typically adjusted to reproduce multi-site isotherms. Our results from comparative fitting of $K_M^{int,\delta}$ with SCM codes using different scales show the magnitudes of 'denticity effects'; we discuss ways to correct for these effects in re-using, comparing or correlating values of $K_M^{int,\delta}$. In a further thermodynamic treatment, e.g. deriving the entropy effect of the adsorption reaction from $K_M^{int,\delta}$ fitted for different temperatures, the constants must first be made dimensionless and independent of δ and Γ_C by converting them into the (o) scale.

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Geochemistry of lavas from Barren Island volcano, Andaman Sea

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Barren Island (BI) (12.29°N, 93.85°E) of Andaman and Nicobar Islands, India is the only subaerial active volcano of the Andaman Subduction Zone, and is one of the northernmost volcanoes of the Indonesian Arc. Located on the Burmese plate, which overrides the Indian plate, this stratovolcano is believed to have emanated from the ocean floor during the Pleistocene [1-2]. It has had historic subaerial eruptions during 1787-1832 and has been active since 1991 [1-2].

Study of the Nd-Sr isotopic, trace element and major element characteristics of lava, scoria and ash from the volcano provides insights into the nature of the magma chamber, and the mantle source. Major element analyses of these samples reveal that most volcanics are less to moderately evolved basalts or basaltic andesites (Mg# = 43.5-68.1) of subalkalic nature (SiO_2 = 47-57 wt%, Na_2O+K_2O < 5.1 wt%,). The high alumina content of a majority of samples (Al_2O_3 > 20 wt %) possibly hints at dissolution of xenocrystic plagioclase, derived from plutonic rocks present in the magma chamber [1]. Alternatively, this could indicate a shallow mantle source for these volcanics.

Primitive mantle normalized trace element patterns of BI samples indicate that these lavas represent typical subduction zone magmas. They show large relative Nb, Ta and Ti depletions and strong relative enrichments in K and Pb, with lesser enrichment of Sr. $^{87}Sr/^{86}Sr$ of BI lavas vary from 0.70379 to 0.70415, and $^{143}Nd/^{144}Nd$ range from 0.512861 (ε_{Nd} = 4.4) to 0.512992 (ε_{Nd} = 6.9). These data suggest that the BI lavas are derived from a large ion lithophile element (LILE) depleted source, and that the mantle source is marginally enriched in LILE compared to the Indian-Mid Oceanic Ridge Basalts (I-MORB). Our results suggest that BI magmas are the most primitive in comparison to that of all other volcanoes of the Indonesian Arc [3]. Mixing calculations suggest that the material contribution from the Indian plate slab to the BI magmas is < 10%. This conclusion is also supported by low Th/Ce ratios (< 0.12) of the lavas.

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