



## **A new extension of the triple-layer model for selenite and arsenite adsorption to account for the electrostatic consequences of ligand exchange**

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Surface complexation models for the adsorption of anions onto oxide surfaces from electrolyte solutions have evolved from the traditional approach where the charge on the adsorbate is allocated to a single plane at or near the surface (Davis and Kent, 1990) to charge distribution models. In the latter, the charge on the adsorbate is split between the surface plane and a near-surface plane (Hiemstra and van Riemsdijk, 1999) or the net charge on the surface species containing the adsorbate is attributed to a near-surface plane (Villalobos and Leckie, 2001; Arai et al., 2004). The net effect of the charge distribution approaches is a non-traditional electrostatic factor which is quite different to the traditional one resulting in different model predictions of the dependence of adsorption and isoelectric points on pH, ionic strength and surface coverage. As a consequence, it has become possible to fit experimental adsorption and electrokinetic data consistent with available information on the stoichiometry of adsorbed anions derived from X-ray and infrared studies. The key to this success is the non-traditional electrostatic factor associated with charge distribution models.

An alternate way of obtaining non-traditional electrostatic factors for anion adsorption reactions is suggested in the present study. It is recognized here that the electrostatic factor is a property of the reaction under consideration. Traditionally, this factor is formulated by taking account of the charges on the ions involved in the surface reaction (e.g. protons and anions). This is done in order to describe the electrostatic work associated with moving ions to or from a charged surface. However, the movement of dipolar molecules to or from a charged surface is also associated with electrostatic work (Bockris and Reddy, 1970), but is not traditionally included in the electrostatic

factor of surface complexation models. The most important dipolar molecule is water, which is desorbed from surface sites when the adsorption reaction of an anion involves ligand exchange. In the present study, the electrostatic work associated with desorption of water dipoles from the surface has been evaluated in the context of the triple-layer model and applied to anion adsorption when ligand exchange is involved. When ligand exchange is not involved, the traditional electrostatic factors are used.

The magnitude of the electrostatic work per mole of water desorbed during ligand exchange is approximately  $-F(\psi_0 - \psi_\beta)$  joules/mole. Adding this dipole contribution to the electrostatic factor associated with the ions in adsorption reactions produces non-traditional electrostatic factors for the overall adsorption of anions by ligand exchange mechanisms. The application to adsorption data for selenite on goethite (Hayes et al., 1988) resulted in two surface reactions involving non-traditional electrostatic factors. For arsenite on alumina (Arai et al., 2001), one reaction with a non-traditional and one with a traditional electrostatic factor resulted. Both examples involved species consistent with XAFS experiments, as well as the prediction of shifts in isoelectric points consistent with electrophoretic mobility studies (Hansmann and Anderson, 1985; Arai et al., 2001). The dipole extension to the triple-layer model proposed above also results in prediction of the non-traditional electrostatic factors established for arsenate/hematite (Arai et al., 2004) and carbonate/goethite (Villalobos and Leckie, 2001).

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