

Spatially-resolved ion mobility on carbonates

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Resolving the molecular origin of macroscopic phenomena remains a current goal in mineral dissolution kinetics. Connecting the contribution of surface topographic features, such as steps, kinks and terraces to macroscopic dissolution rates is a state-of-the-art challenge and is required for development of a quantitative predictive model of carbonate dissolution. Probing this system using a novel polarization force technique will provide such an understanding by enabling direct observation of molecular level phenomena on a carbonate surface.

Trends in the polarization force time response lead to several conclusions regarding the structure of water films and the density and mobility of carbonate surface ions. At RH = 55% the completion of a monolayer of water, the initiation of 3D film growth, and a step increase in the density and the mobility of surface ions is observed for calcite. Results for rhombohedral carbonates (viz. MgCO_3 , FeCO_3 , CaCO_3 , MnCO_3 , and ZnCO_3) show a long relaxation time of the polarization force is connected with rapid dissolution. This finding is rationalized by long lifetimes in terrace positions and hence greater opportunities for detachment of the ion to aqueous solution (i.e., dissolution).

Topographically-constrained observations of the polarization force also provide a valuable new approach. Polarization force images of calcite at RH = 70% reveal a difference in the dielectric character of the water film associated with steps compared to terraces. The source of the step contrast is attributed to changes in the mobility and density of surface ions associated with steps. Extension of this result by mapping changes in the polarization force on calcite dissolution pits should provide a valuable link between ion mobility and rates described within the framework of the kink-kink-annihilation (KKA) model.

Calibration of surface complexation reactions with zeta potentials

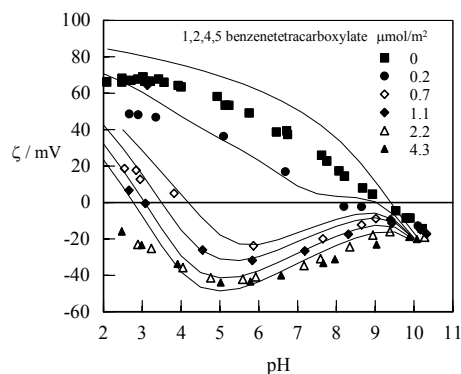
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Knowledge of coordination modes and geometries of surface complexes at metal oxide/water interfaces have become essential in the calibration of thermodynamic models describing molecular-level adsorption reactions. As this information impacts the predicted electric potential profile of the interface, surface potential measurements are invaluable in further calibrating these models.

In this study zeta potentials of goethite ($\alpha\text{-FeOOH}$) suspensions in aqueous media are predicted in the presence of three different benzenecarboxylates. The potentials can be predicted as a function of pH and surface loading even in systems where surfaces are positively-charged but exhibit negative zeta potentials as, for example, the case of pyromellitate (Figure 1).

Figure 1. Electroacoustically-determined zeta potentials of goethite ($23 \text{ m}^2/\text{g}$, 30 g/L) in the presence of 1,2,4,5-benzenetetracarboxylate (pyromellitate) (total concentration in $\mu\text{mol}/\text{m}^2$) ($0.1 \text{ mol dm}^{-3} \text{ NaNO}_3$, 298.15 K).



The performance of different structures of Electric Double Layer models in predicting these data will also be presented as well as the effects of different modelling parameters, such as charge distribution and capacitances.