Ion specific effects at the calcite(104) – water interface

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In this study the influence of Li^+-, Na^+-, K^+-, Rb^+-, and Cs^+-chloride solutions on the calcite zeta-potential is investigated and surface diffraction data that can be used to relate the observed ion specific effects to the calcite(104) – water interface structure is presented.

Specular and off-specular resonant surface diffraction data are used to locate and quantify Rb^+ ions at the calcite(104) – water interface. In a 0.01 molar RbCl solution equilibrated with atmospheric CO_2 and calcite (pH = 8.2), we observe the main Rb^+ species (~0.17 mono layers (ML)) 3.2 Å above the surface, associated with the second well ordered water layer at the interface, a position that might mark the upper end of a Stern layer at the calcite(104) surface [1]. An unexpected result is that there seems to be inner-sphere adsorbed Rb^+ (< 0.1 ML) closely associated with the surface carbonate groups. Additionally there are outer-sphere Rb^+ species at ~5 and ~11 Å above the surface, likely associated with Rb^+ in the diffuse layer above the calcite surface. In order to test to what extent these results are specific for Rb^+ or whether they can be transferred to the other alkali-metal cations we measured specular surface diffraction data on calcite(104) in contact with equilibrated 0.01 molar alkali chloride solutions across the whole series from Li^+ to Cs^+, and indeed certain trends are observable. The analyses of these data is still ongoing and it is not yet clear if changes are due to the increasing number of electrons in the series Li^+ – Cs^+ or due to actual changes in interface structure.

Streaming potential measurements performed on an Anton Paar SurPASS electrokinetic analyzer show that, if we successively add Ca^{2+} to a solution containing 0.01 mol/L of an alkali metal chloride as background electrolyte at fixed pH (~9), remarkable changes in the behavior of the calcite zetapotential are observed across the series of 0.01 molar alkali chloride solutions: the Ca^{2+} concentration at which zero zetapotential is measured is 0.5 mmol/L in CsCl solution and increases continuously across the series of alkali metals, up to 2.5 mmol/L in LiCl solution. For Ca^{2+} concentrations >5 mmol/L the calcite zetapotential reaches a plateau. The plateau zetapotential value lies at 5 mV in the LiCl system and at 20 mV in the CsCl system. These two effects clearly demonstrate the ion specific effect of the alkali metal cations on the affinity of Ca^{2+} ions to the calcite(104) surface. The calcite zetapotential measured as a function of pH in the absence of added Ca^{2+} is the same in 0.01 molar solutions of all alkali metal chlorides investigated. These results may have important implications e.g. for calcite growth-, adsorption-, or surface complexation models.

[1] Heberling et al. (2011) *Journal of Colloid and Interface Science* **354**, 843-857.