Supporting Information to

Molecular Self-Assembly Versus Surface Restructuring During Calcite Dissolution

Martin Nalbach, Stefanie Klassen, Ralf Bechstein, Angelika Kühnle[*]

Institute of Physical Chemistry, Johannes Gutenberg University Mainz, Duesbergweg 10-14,

55099 Mainz, Germany

Experimental Section

Eriochrome Black T (EBT, ACS reagent, indicator grade), Eriochrome Blue Black B (EBBB, indicator (for complexometry)) and Eriochrome Blue Black R (EBBR, indicator (for complexometry (Al, Fe, Zr))) were purchased from Sigma Aldrich. Eriochrome Black A (EBA) and Eriochrome Red B (ERB) were purchased from TCI Deutschland GmbH. All dye molecules were used in the experiments without further purification.

pH measurements

The pH measurements of the dye solutions prior to the AFM experiments were conducted using a Schott laboratory pH meter (CG 842) equipped with a BlueLine pH-electrode (Schott, 18 pH). The pH-electrode was calibrated weekly utilizing buffer standard solutions with a pH value of 4 and 7 (HANNA instruments, type Hi6004 and Hi6007).

Species distribution calculation

EBT and EBA possessing one sulfonate and two hydroxyl groups each are both triprotic acids. For each protonation / deprotonation step, the acid dissociation constant (K_{ai}) is defined by the quotient of the respective equilibrium concentrations.

$$K_{ai} = \frac{c\left(H_3O^+\right) \cdot c\left(H_{n-i}A^{i-}\right)}{c\left(H_{n-i+1}A^{(i-1)-}\right)} \qquad \text{Eq. (S1)}$$

For EBT and EBA the acid dissociation constants (K_{ai}) for the second and third protonation / deprotonation step are given as follows:[1]

Table S1. Acid dissociation constants for the second and third protonation / deprotonation step of EBT and EBA.

Molecule	-lg K_{a2} = pK_{a2}	-lg K_{a3} = pK_{a3}
EBT	6.30	11.55
EBA	6.20	13.00

Calculation of the carbonate equilibrium species distribution was performed using the relevant protonation / deprotonation equilibrium equations for an *n*-protic acid $\left(H_{n-i+1}A^{(i-1)-}\right)$.[2]

$$H_{n-i+1}A^{(i-1)-}\,(aq) + H_2O \rightleftharpoons H_{n-i}A^{i-}(aq) + H_3O^+(aq) \qquad \text{Eq. (S2)}$$

The total concentration (C) for EBT and EBA is the sum over all protonated / deprotonated species being present in the solution at every pH.

$$C = \sum_{i=0}^{n} c\left(H_{n-i}A^{i-}\,(aq)\right) \qquad \text{Eq. (S3)}$$

Numerical analysis of the resulting system of linear equations enables the precise determination of the equilibrium concentration of all protonated / deprotonated species at a given pH.

$$c\left(H_{n-i+1}A^{(i-1)-}\right) = \frac{c^{n-i}\,(H_3O^+)\cdot C\,(H_nA)\cdot\prod_{j=1}^{i}K_{Sj}}{\sum_{r=0}^{n}\left[c^{n-r}\,(H_3O^+)\cdot\prod_{j=1}^{r}K_{Sj}\right]} \qquad \text{Eq. (S4)}$$

The species distribution of EBT is illustrated in Figure 5a, the species distribution of EBA is illustrated in Figure S1.

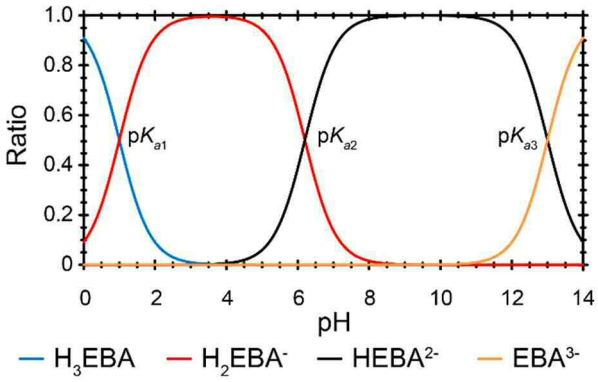

Figure S1. Species distribution of EBA as a function of the pH value.

Azo-hydrazo tautomerization

We note that EBT can undergo an azo-hydrazo tautomerization,[3] resulting in three, four and one different species for the onefold, twofold and threefold deprotonated molecule, respectively. The azo-hydrazo tautomerization of a onefold deprotonated EBT molecule is shown in Figure 5a, the azo-hydrazo tautomerization of a twofold deprotonated EBT molecule is shown in Figure S2.

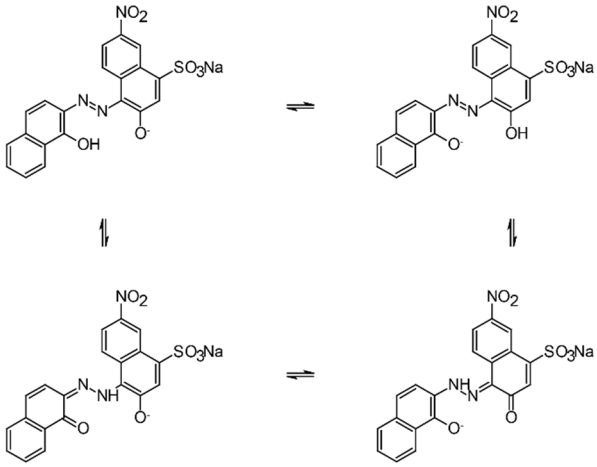

Figure S2. Azo-hydrazo tautomerization of a twofold deprotonated EBT molecule.

References

(1) Schwarzenbach, G.; Biedermann, W., *Helv. Chim. Acta* **1948**, *31*, 678-687.

(2) Bliefert, C., *pH Wert Berechnungen*. ed.; Verlag Chemie: Weinheim, New York, 1978.

(3) Sagaster, H.-R.; Röbisch, G.; Mehlhorn, A., *J. Prakt. Chem.* **1987**, *329*, 1045-1051.