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Crystengcomm

Electronic Supporting Information

A potentiometric study of the performance of a commercial copolymer in the precipitation of scale forming minerals

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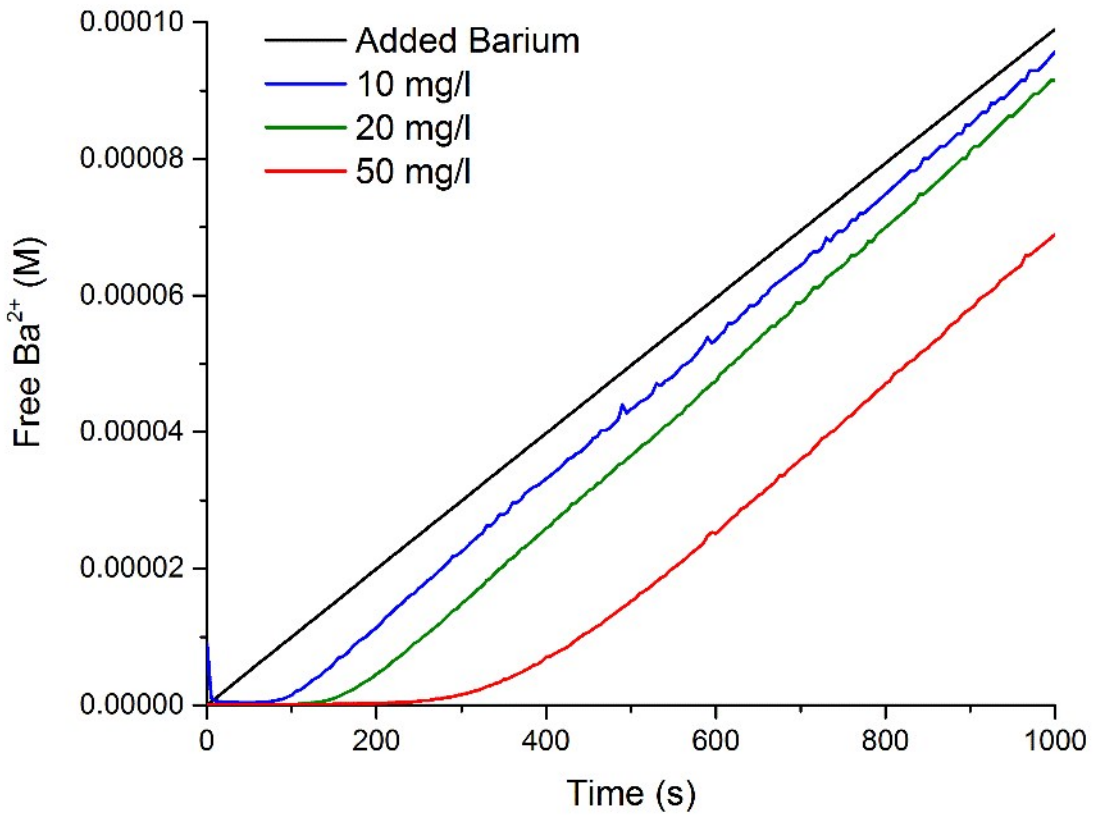
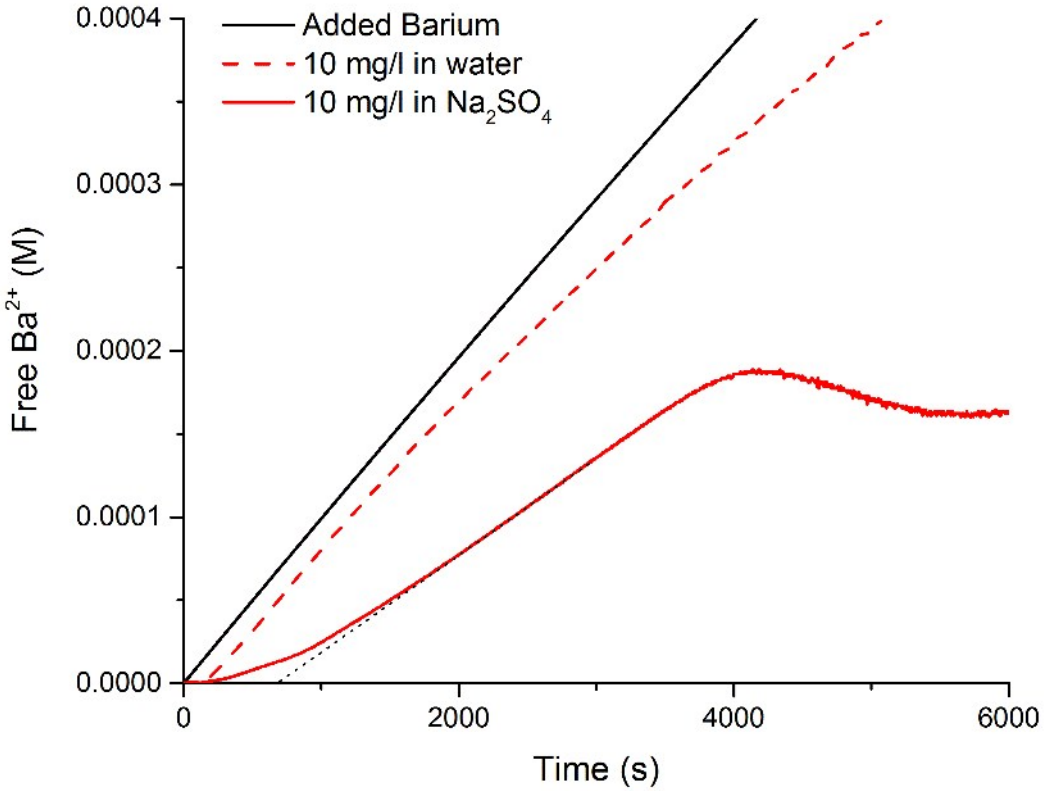
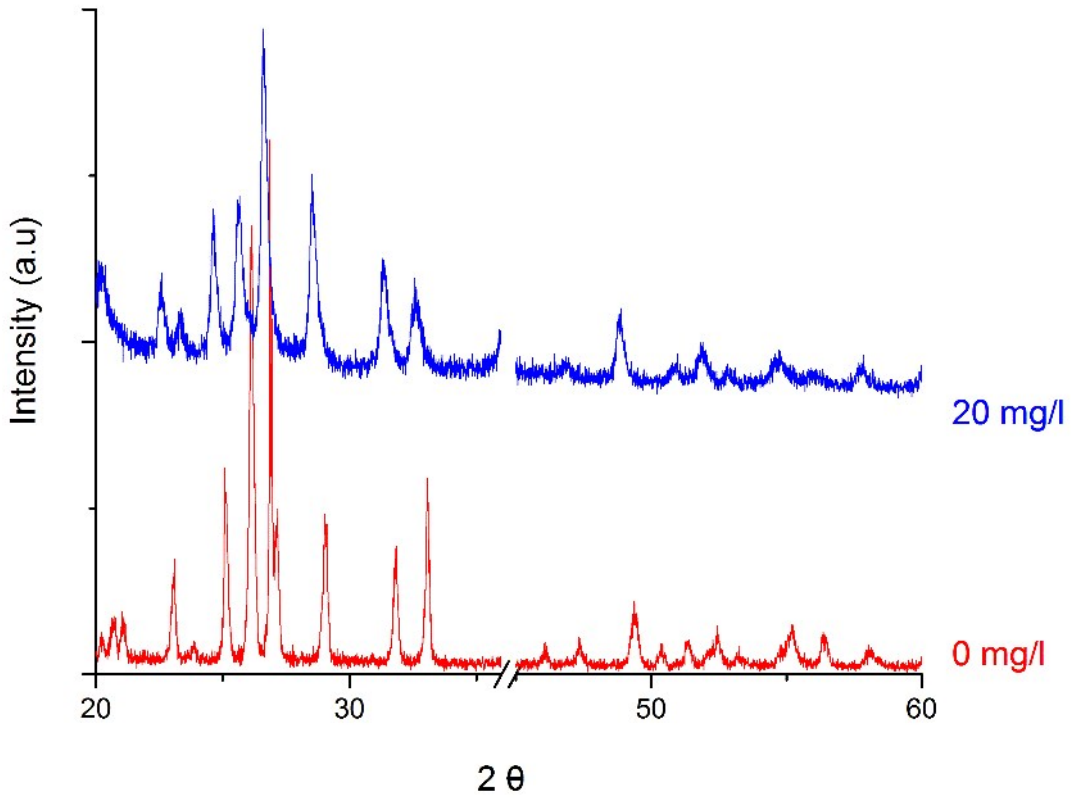


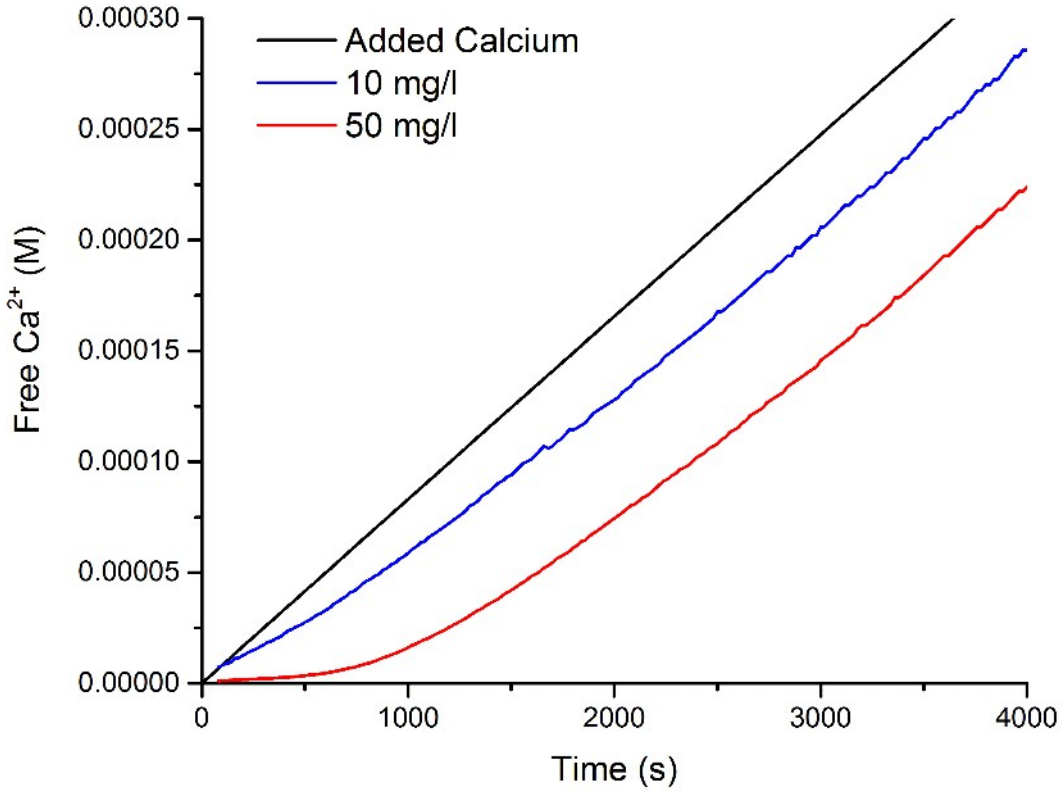
ESI 1. Free-Ba^{2+} evolution in water with different amount of MASP ranging from 0-50 mg/l.



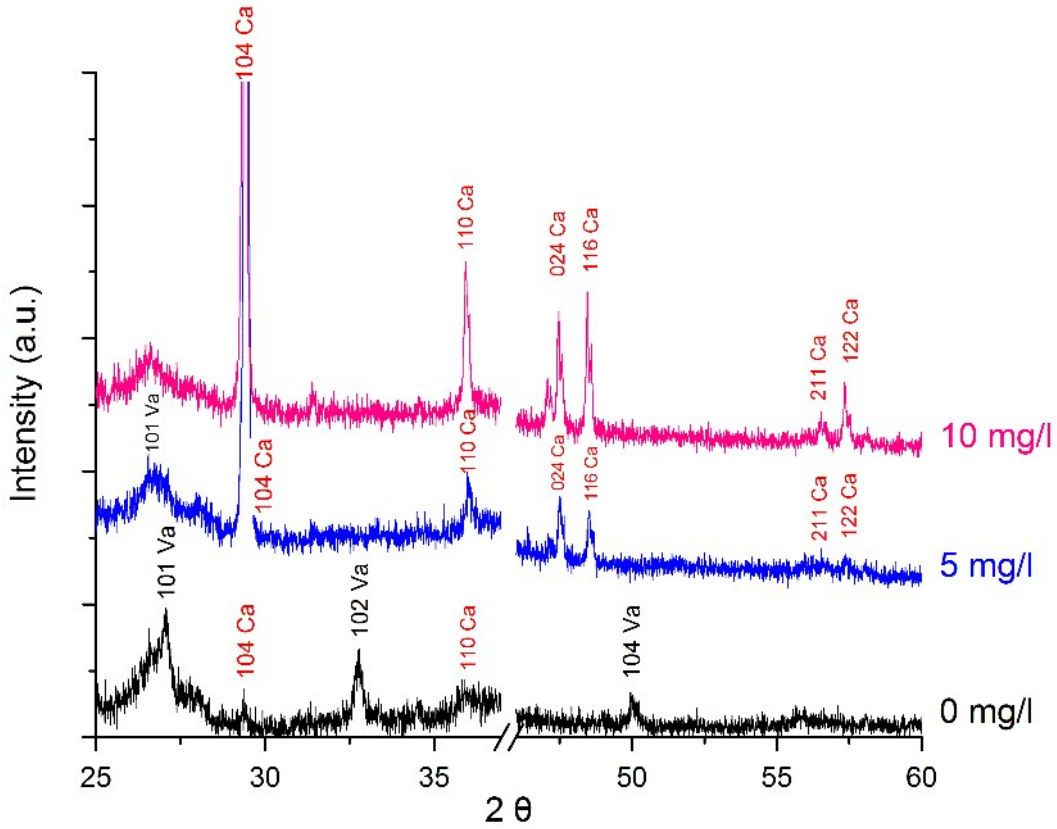
ESI 2. Comparison of the barium binding capacities of MASP (10 mg/l) in water (dotted lines) and in 1 mM sodium sulphate solution (continuous line), the dotted grey line represents the extrapolation of the barium curve. The black line refers to the amount of barium ions added to the vessel.



ESI 3. XRD patterns of barium sulphate precipitates in the presence of 0 mg/l and 20 mg/l of MASP.



ESI 4. Free-Ca^{2+} evolution in water with 10 and 50mg/l of MASP. The black line refers to the amount of barium ions added.



ESI 5. XRD patterns of calcium carbonate precipitates in the presence of 0 mg/l, 5 mg/l and 10 mg/l of MASP.

ESI 6. Application of the Langmuir-adsorption model to experiments performed in the presence of MASP

The Langmuir adsorption model (Equation SI 1) was applied to experiments performed in the presence of MASP in order to quantify the adsorption behaviour:

$$n = \frac{n_{max} * (K_l * c)}{1 + (K_l * c)} \qquad \text{(Equation SI 1)}$$

The amounts of Ca^{2+}(n) or Ba^{2+}(n) bound can be calculated by subtracting the amount of free Ca^{2+} or Ba^{2+} from the amount of Ca^{2+} or Ba^{2+} ions added. The free Ca^{2+} or Ba^{2+} concentration (c) is accessible from the recorded calcium or barium ion potential. The maximum amount of calcium binding sites n_{max} and the Langmuir-coefficient K_L can be calculated by plotting (bound Ca^{2+}(n) or Ba^{2+}(n)) against (bound Ca^{2+}(n) or Ba^{2+}(n)/ free Ca^{2+} or Ba^{2+} concentration (c)). In figure ESI 6.1 can be seen that the maximum amount of calcium/barium binding sites n_{max} increased with MASP concentration. The plot of n_{max} yields to linear graphs in the presence and in the absences of the anions. The number of binding sites in the presence of the two anions increased ca. 65 % and 70% for barium and calcium, respectively.

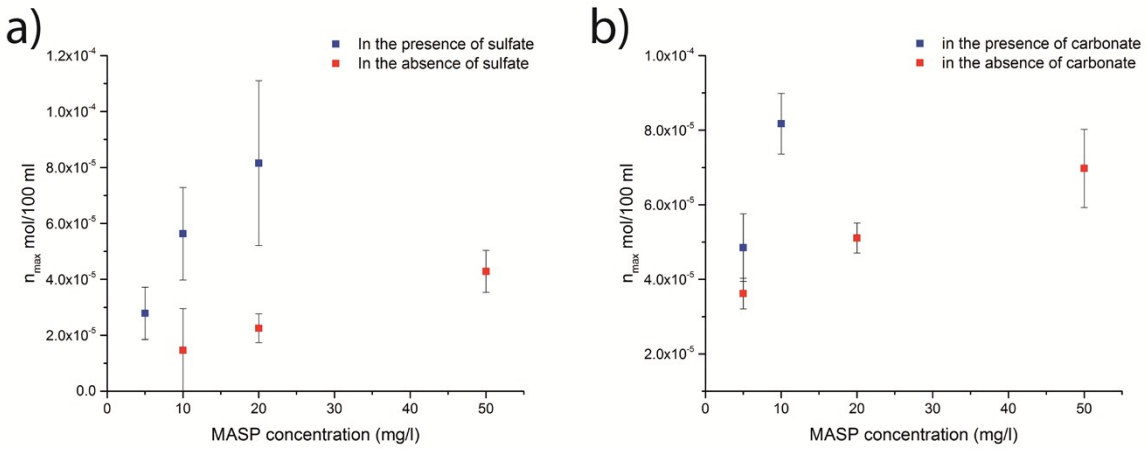


Fig. ESI 6.1: n_{max} values of the Langmuir-equation obtained at different MASP concentrations for a) barium and b) calcium in the presence and in the absence of sulphate and carbonate.

K_L values are not significantly affected by MASP concentration, and in most cases differences are within experimental error (figure ESI 6.2). Interestingly, the K_L-value, which is a measure of the binding affinity, is lower in the absence of sulphate and, to a lesser extent, carbonate (figure ESI 6.2).

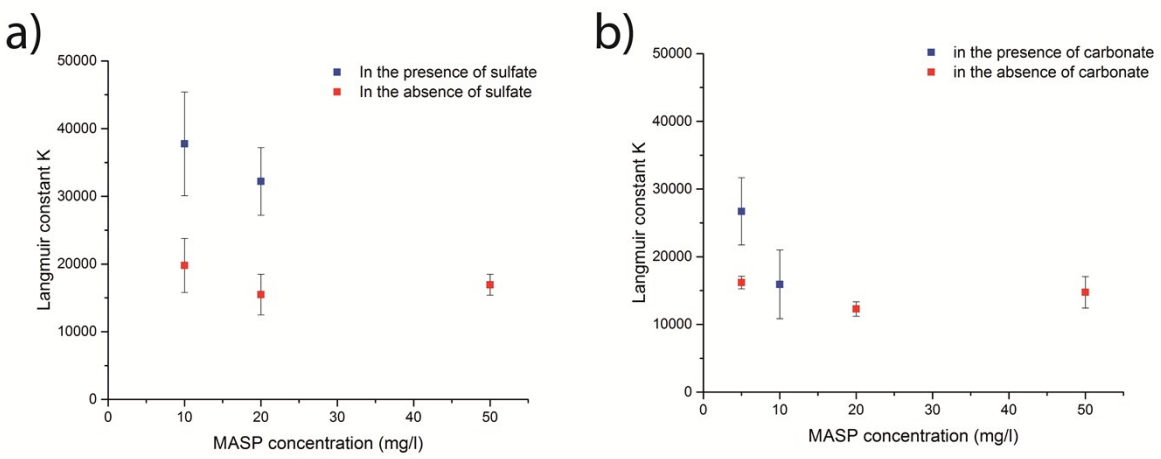


Fig. ESI 6.2: K values of the Langmuir constant obtained at different MASP concentrations for a) barium and b) calcium in the presence and in the absence of sulphate and carbonate.

ESI 7. Application of the multiple binding equilibrium

A simplified multiple binding equilibrium[2] (Equation SI 1 and SI 2) was applied in order to assess the stability of $BaSO_4$ and $CaCO_3$ prenucleation associate formation. With this aim, the linear part of the pre-nucleation regime was analyzed.

$$\vartheta = 1 + \frac{n_{free}({SO_4}^{2-})}{n_{bound}(Ba^{2+})} = \frac{1}{x} + \frac{1}{x * K} * \frac{1}{c_{free}(Ba^{2+})}$$

(Equation SI 2)

$$\vartheta = 1 + \frac{n_{free}({CO_3}^{2-})}{n_{bound}(Ca^{2+})} = \frac{1}{x} + \frac{1}{x * K} * \frac{1}{c_{free}(Ca^{2+})}$$

(Equation SI 3)

Assuming that barium and calcium are bound 1:1 to sulphate and carbonate respectively, we can simplify the equations above taking into account that $n_{free}\ SO_4^{2-} = (SO_4^{2-})_0 - \text{bound}\ (Ba^{2+})$ and $n_{free}\ CO_3^{2-} = (CO_3^{2-})_0 - \text{bound}\ Ca^{2+}$; x and K values can be then calculated by plotting:

$$\frac{({SO_4}^{2-})_0}{Added\ (Ba^{2+}) - free\ (Ba^{2+})} = \frac{1}{x} + \frac{1}{x * K} * \frac{1}{cfree\ Ba^{2+}}$$

(Equation SI 4)

$$\frac{(CO_3{}^{2-})_0}{Added\ (Ca^{2+}) - free\ (Ca^{2+})} = \frac{1}{x} + \frac{1}{x * K} * \frac{1}{cfree\ Ca^{2+}}$$

(Equation SI 5)

Where $(SO_4^{2-})_0$ and $(CO_3^{2-})_0$ are the total amount of sulphate and carbonate at the beginning of the experiments. These initial amounts of $(SO_4^{2-})_0$ and (CO_3^{2-}) were calculate with the speciation code PHREEQC[3]. The macroscopic equilibrium constant and the Gibbs free energy constant for the formation of stable pre-nucleation clusters are accessible from x and K values.

$$Ba^{2+}{}_{aq} + SO^{2-}{}_{4\ aq} \rightleftharpoons BaSO_{4cluster,aq} \qquad \text{(Equation SI 5)}$$

$$\frac{c\ (BaSO_{4cluster,aq})}{c\left(Ba^{2+}{}_{aq}\right) * c(SO^{2-}{}_{4\ aq})} = K' = x * K$$

$$Ca^{2+}{}_{aq} + CO^{2-}{}_{3\ aq} \rightleftharpoons CaCO_{3cluster,aq} \qquad \text{(Equation SI 6)}$$

$$\frac{c\ (CaCO_{3cluster,aq})}{c\left(Ca^{2+}{}_{aq}\right) * c(CO^{2-}{}_{3\ aq})} = K'$$

$$-RTln(K') = \Delta_R G_{ion\ pair}{}^{x} \qquad \text{(Equation SI 7)}$$

The calculation of the microscopic equilibrium constant K and the averaged, dynamic coordination number of a single sulphate/carbonate x enables the determination of the macroscopic equilibrium constant for the formation of stable pre-nucleation associates K'. Figure ESI 7 shows the values of the Gibbs free energy constant with different amounts of MASP for $BaSO_4$ and $CaCO_3$ prenucleation associates. It can be seen that for the case of barium sulphate, the differences in ΔG between the control run and the experiments in the present of MASP are within experimental error. In the case of calcium carbonate prenucleation species (figure ESI 7), it can be seen that increasing MASP concentration yields to slightly more stable values of the Gibbs free energy.

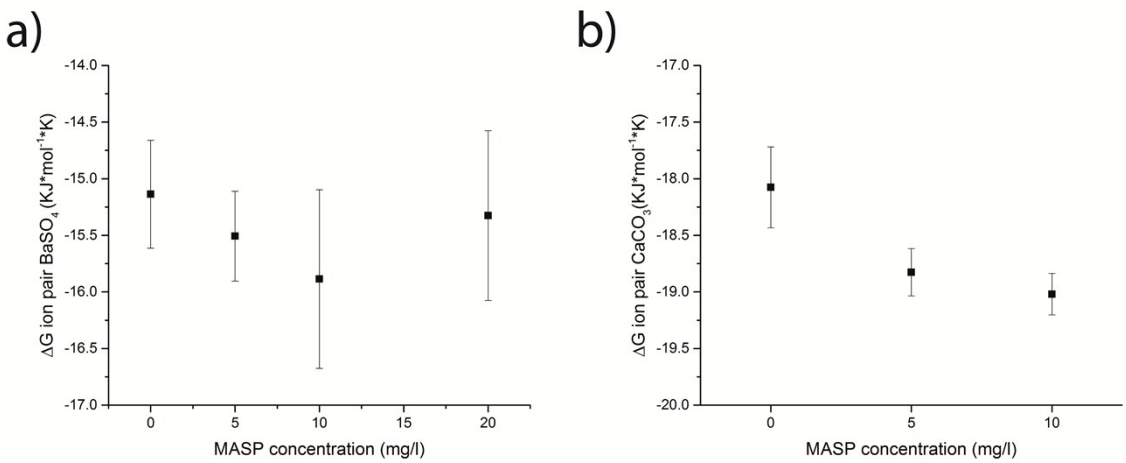


Fig. ESI 7. Gibbs standard energy for the formation of a) barium/sulphate and b) calcium/carbonate ion pairs in prenucleation associates. Gibbs standard energy relates to the binding strength in clusters. Gibbs free energy constant of ion pair formation for a) $BaSO_4$ and b) $CaCO_3$ in the presence of different amounts of MASP.

References

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3 D. L. Parkhurst, C. A. J. Appelo, U.S. Geological Survey Water-Resources Investigation Report, 1999.