Electronic Supplementary Material (ESI) for Faraday Discussions

SUPPORTING INFORMATION: Exploring the influence of organic species on pre-nucleation clusters of calcium carbonate

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Figures

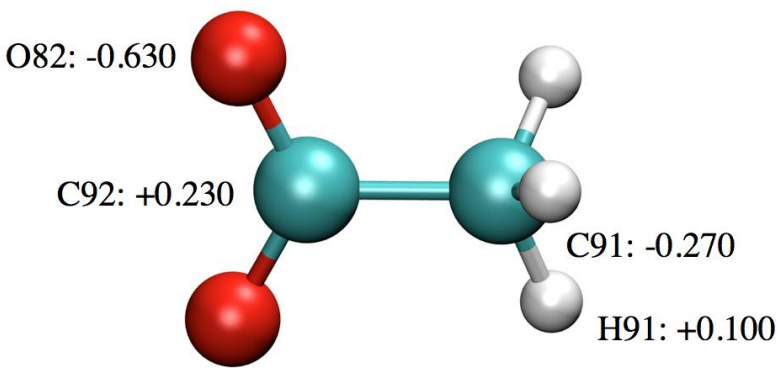


Figure S1 Acetate anion showing atom types and charges (a.u.) used for the conventional force field. Carbon, oxygen and hydrogen are shown in light blue, red and grey, respectively.

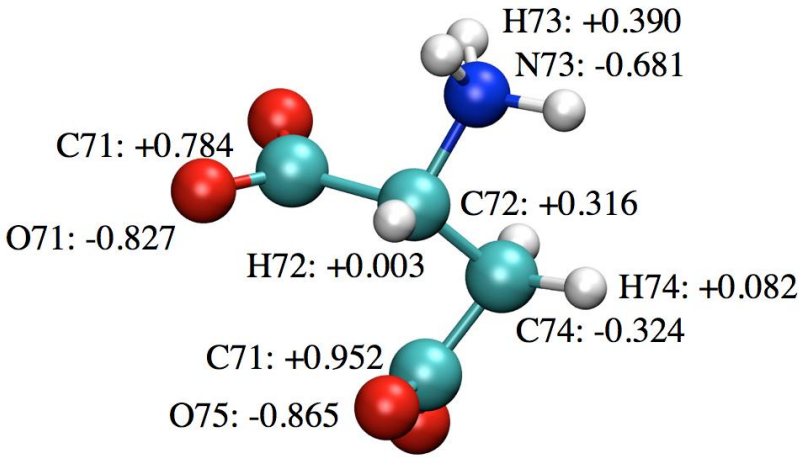
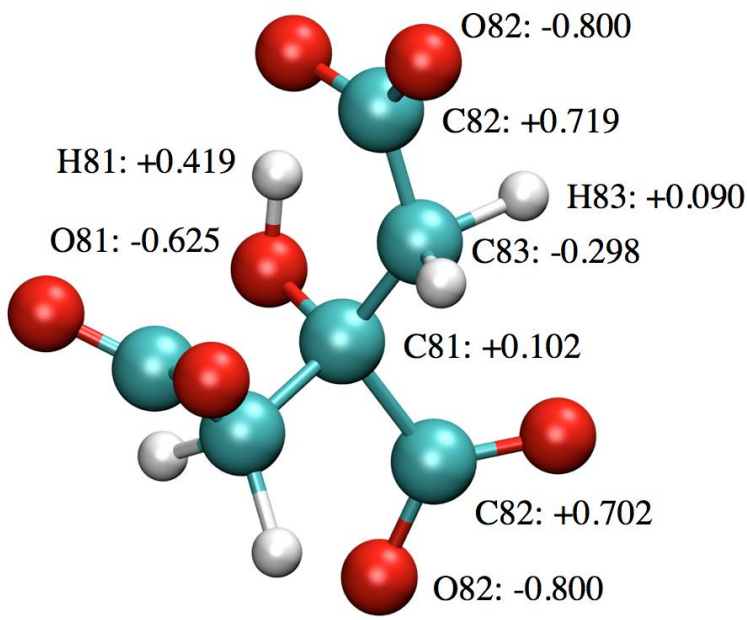


Figure S2 Aspartate anion showing atom types and charges (a.u.) used for the conventional force field. Carbon, oxygen, nitrogen and hydrogen are shown in light blue, red, dark blue and grey, respectively.



5

Figure S3 Citrate anion showing atom types and charges (a.u.) used for the conventional force field. Carbon, oxygen and hydrogen are shown in light blue, red and grey, respectively.

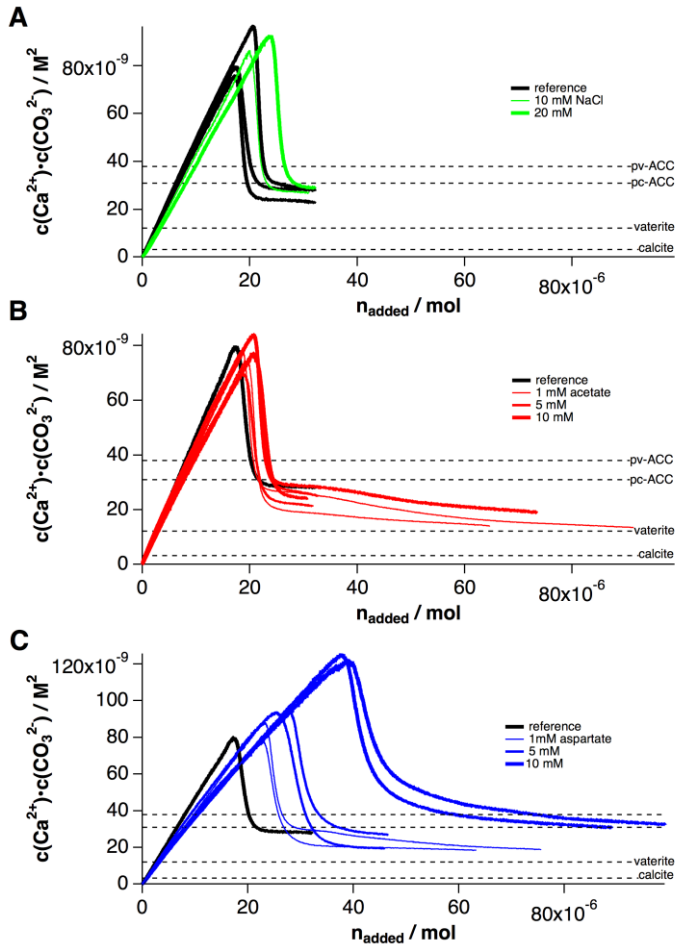


Figure S4. Reproducibility of the titration experiments, as exemplified by the evolution of the free ion product based on two or three independent measurements. A, Reference without any additives (black), together with the data recorded in the presence of sodium chloride (green). B, Different concentrations of acetate (red) as compared to the reference. C, Different concentrations of aspartate (blue) as compared to the reference.

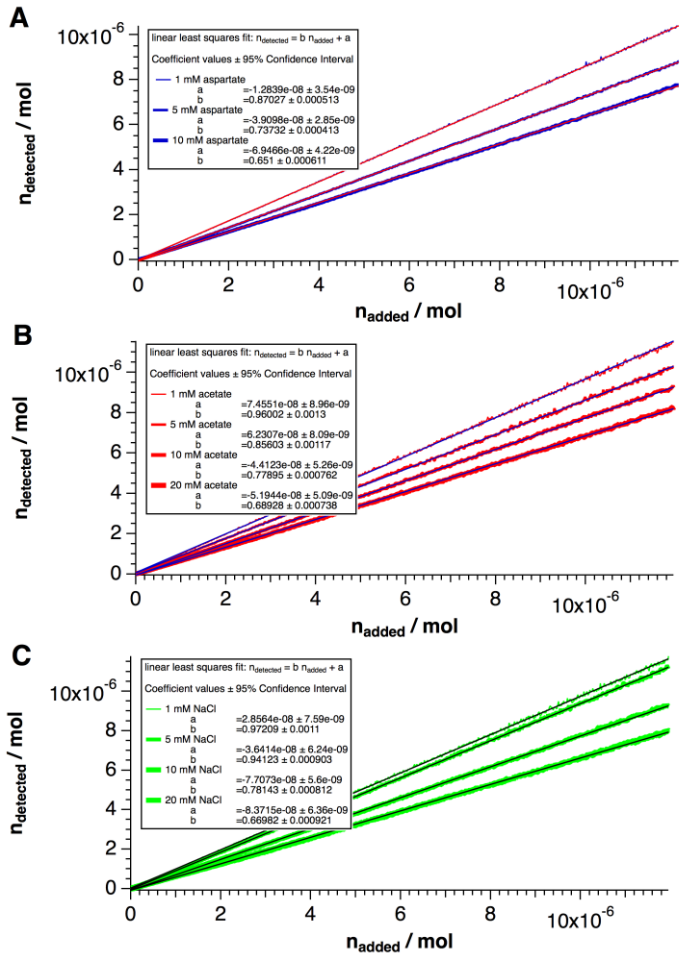


Figure S5. Development of the amount of free calcium detected upon constant addition of calcium chloride into aqueous solutions of (A) L-aspartate, (B) acetate and (C) sodium chloride at different concentrations. In all cases, the obtained curves can be fitted to linear equations as represented by red (A), blue (B) and black lines (C), respectively, with high statistical significance. This shows that, within the investigated range of concentrations, flattening of the slope can largely be ascribed to activity effects (within experimental accuracy). This becomes evident when comparing slope values determined for solutions of aspartate and acetate with those found for sodium chloride at the same ionic strength (cf. Table S4). Calcium-aspartate or calcium-acetate association cannot be detected.

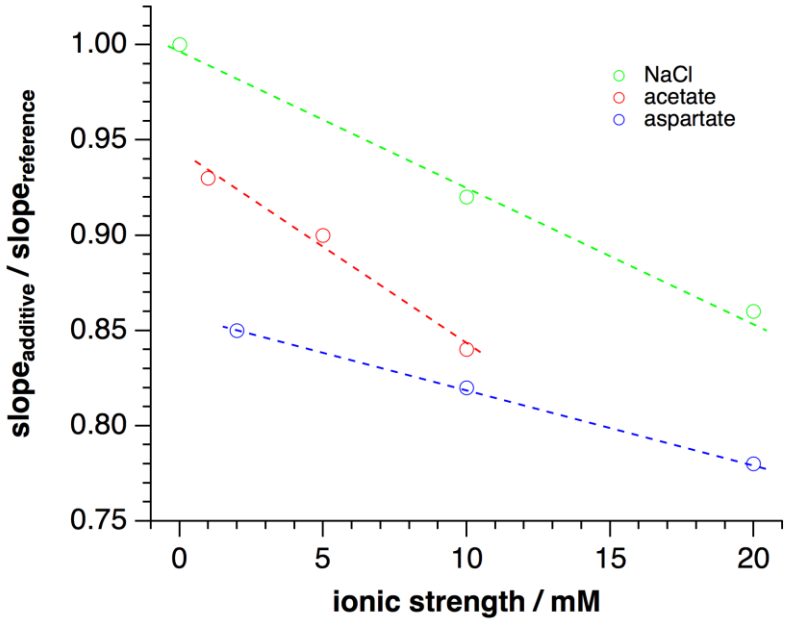


Figure S6. Effect of the different additives on the slope of the increase during the pre-nucleation stage in carbonate buffer. Flattening of the increase in the amount of free calcium (relative to the reference without additives) appears to be enhanced by both acetate and aspartate, as compared to sodium chloride at identical ionic strengths. This may hint at some stabilising influence of the two additives on $CaCO_3$ pre-nucleation clusters, the extent of which seems to increase with the number of carboxylate functions in the additive molecules (as supported by the strong effect found for citrate). On the other hand, we cannot exclude interactions between the additives and the membrane of the ion selective electrode in carbonate buffer, which is however not apparent in pure water (cf. Figure S4).

Tables

Table S1 Force field parameters for unreactive force field for acetate in aqueous calcium carbonate solutions. Interaction type is either Buckingham ("buck" with parameters A, ρ and C in eV, Å and eVÅ^6, respectively), Lennard-Jones 12-6 A-B ("A-B" with parameters A and B in eVÅ^{12} and eVÅ^6, respectively) or Lennard-Jones 12-6 in epsilon-sigma form ("lj" with parameters ε and σ in eV and Å, respectively). Atom types are; H2 and O2 for water, Ca for calcium, C4 and O4 for carbonate, C5, O5, O6 and H6 for bicarbonate, C92 and O92 for carboxylate of acetate, and C91 and H91 for the methyl group of acetate.

Atom	Type	Interaction type	A / ε	ρ / B / σ	C
C92	O2	buck	202.2584	0.322725	0.0
O92	O2	buck	7231.4163	0.155	12.09022
O92	H2	buck	418.1692	0.205	0.0
O92	Ca	buck	2564	0.271511	0.0
C91	Ca	buck	1913.2	0.271511	0.0
C92	O5	buck	600	0.3	0.0
C92	O6	buck	600	0.3	0.0
O92	C5	buck	600	0.3	0.0
O92	C4	buck	48.399296	0.57	0.0
C92	O4	buck	67.475158	0.57	0.0
O92	H6	A-B	34	0.0	
C91	O2	lj	0.00566	2.80167	
H91	O2	lj	0.00215	1.9266	
C91	C4	lj	0.00412665	3.47299	
C91	O4	lj	0.00413964	3.25307	
C91	C5	lj	0.00412665	3.47299	
C91	O5	lj	0.00413964	3.25307	
C91	O6	lj	0.00413964	3.25307	
H91	C4	lj	0.00164979	3.15971	
H91	C5	lj	0.00164979	3.15971	
H91	O4	lj	0.00165499	2.93979	
H91	O5	lj	0.00165499	2.93979	
H91	O6	lj	0.00165499	2.93979	

Table S2 Force field parameters for unreactive force field for aspartate in aqueous calcium carbonate solutions. Interaction types are as per Table S1. Atom types are as per Table S1 with the addition of the following for aspartate; C71 for carboxylate carbon, O71 and O75 for carboxylate oxygen nearest and furthest from the NH_3^+ group, respectively, N73 and H73 for the NH_3^+ group, C72 and H72 for the CH group bonded to N, and C74 and H74 for the remaining CH_2 group.

Atom		Interaction type	A / ε	ρ / B / σ	C
C71	O2	buck	530.5	0.317725	0.0
O71	O2	buck	13754.7	0.155	0.0
O71	H2	buck	795.6	0.205	0.0
O75	O2	buck	13754.7	0.155	0.0
O75	H2	buck	795.6	0.205	0.0
N73	Ca	buck	1000	0.2	0.0
N73	Na	buck	500	0.2	0.0
O71	Ca	buck	3365	0.271511	0.0
O75	Ca	buck	3523	0.271511	0.0
H73	O4	buck	914	0.25	0.0
H73	O5	buck	725	0.25	0.0
H73	O6	buck	528	0.25	0.0
C71	O4	buck	600	0.3	0.0
C71	O5	buck	600	0.3	0.0
C71	O6	buck	600	0.3	0.0
H6	O7	12-6	34	0.0	
H6	O7	12-6	34	0.0	
C74	O2	lj	0.00566	3.30167	
H74	O2	lj	0.00215	1.9266	
C72	O2	lj	0.00559558	3.27521	
H72	O2	lj	0.00211976	2.55536	
N73	O2	lj	0.00871909	3.14581	
H73	O2	lj	0.0026497	2.00992	
C71	C4	lj	0.00412665	3.47299	
C71	C5	lj	0.00412665	3.47299	
H72	C4	lj	0.00164979	3.15971	
H72	C5	lj	0.00164979	3.15971	
H72	O4	lj	0.00165499	2.93979	
H72	O5	lj	0.00165499	2.93979	
H72	O6	lj	0.00165499	2.93979	
H74	C4	lj	0.00164979	3.15971	
H74	C5	lj	0.00164979	3.15971	
H74	O4	lj	0.00165499	2.93979	
H74	O5	lj	0.00165499	2.93979	
H74	O6	lj	0.00165499	2.93979	

Table S3 Force field parameters for unreactive force field for citrate in aqueous calcium carbonate solutions. Interaction types are as per Table S1. Atom types are as per Table S1 with the addition of the following for citrate; O81 and H81 belong to the hydroxyl group, C81 for carbon bonded to the hydroxyl group, C82 and O82 to the carboxylate group, and C83 and H83 to the remaining aliphatic groups.

Citrate		Interaction type	A / ε	ρ / B / σ	C
H81	O2	buck	100	0.425	0.0
C82	O2	buck	316.5784	0.322725	0.0
O82	O2	buck	9159.79	0.155	0.0
O82	H2	buck	529.808	0.205	0.0
C82	O4	buck	67.475158	0.57	0.0
C82	O5	buck	600	0.3	0.0
C82	O6	buck	600	0.3	0.0
O82	C4	buck	48.399296	0.57	0.0
O82	C5	buck	600	0.3	0.0
O81	C4	buck	50.578693	0.57	0.0
O81	C5	buck	600	0.3	0.0
O81	Ca	buck	1898	0.271511	0.0
O82	Ca	buck	2918	0.271511	0.0
O82	H6	12-6	34	0.0	
H81	O4	12-6	34	0.0	
O81	H6	12-6	108	0.0	
H81	O4	12-6	34	0.0	
H81	O5	12-6	34	0.0	
H81	O6	12-6	108	0.0	
C81	O2	lj	0.00566	3.30167	
C83	O2	lj	0.00566	2.50167	
H83	O2	lj	0.00215	1.9266	
O81	O2	lj	0.00674	3.0	
C81	Na	lj	0.009456	3.137	
C81	Ca	lj	0.0299	3.2831	
C81	C4	lj	0.00412665	3.47299	
C81	O4	lj	0.00413964	3.25307	
C81	C5	lj	0.00412665	3.47299	
C81	O5	lj	0.00413964	3.25307	
C81	O6	lj	0.00413964	3.25307	
C83	Na	lj	0.009456	3.137	
C83	Ca	lj	0.0299	3.2831	
C83	C4	lj	0.00412665	3.47299	
C83	O4	lj	0.00413964	3.25307	
C83	C5	lj	0.00412665	3.47299	

Table S4. Increase in the amount of free calcium for additive-containing solutions with (pre-nucleation stage) and without carbonate (Figures S1 and S2). Values are given as the ratio of the slope in the presence of the particular additive to the slope in pure water (*i.e.* the added amount of Ca^{2+}) and the slope in additive-free buffer (i.e. the reference development), respectively.

	Concentration / mM	Ionic strength / mM	Slope ratio (Water)	Slope ratio (Buffer)
Aspartate	1	2	0.87	0.85
	5	10	0.74	0.82
	10	20	0.65	0.78
Acetate	1	1	0.96	0.93
	5	5	0.86	0.90
	10	10	0.78	0.84
	20	20	0.69	n.d.
NaCl	1	1	0.97	n.d.
	5	5	0.94	n.d.
	10	10	0.78	0.92
	20	20	0.67	0.86