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Aggregation and Sedimentation of Magnetite Nanoparticle Clusters

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Electronic Supplementary Information

Determination of median radius of Fe_3O_4 nanoparticles by TEM

The median diameter for the NaOH-magnetite nanoparticles, obtained by analyzing TEM images using Scion image software of 265 particles, is 10.13 nm. TMAOH-magnetite nanoparticles were smaller compared to NaOH-magnetite having a median diameter of 7.92 nm based on 300 particle counts. These diameters correspond to the radii of 5.0 ± 0.8 nm and 4.0 ± 0.7 nm for NaOH-magnetite and TMAOH-magnetite reported in the manuscript.

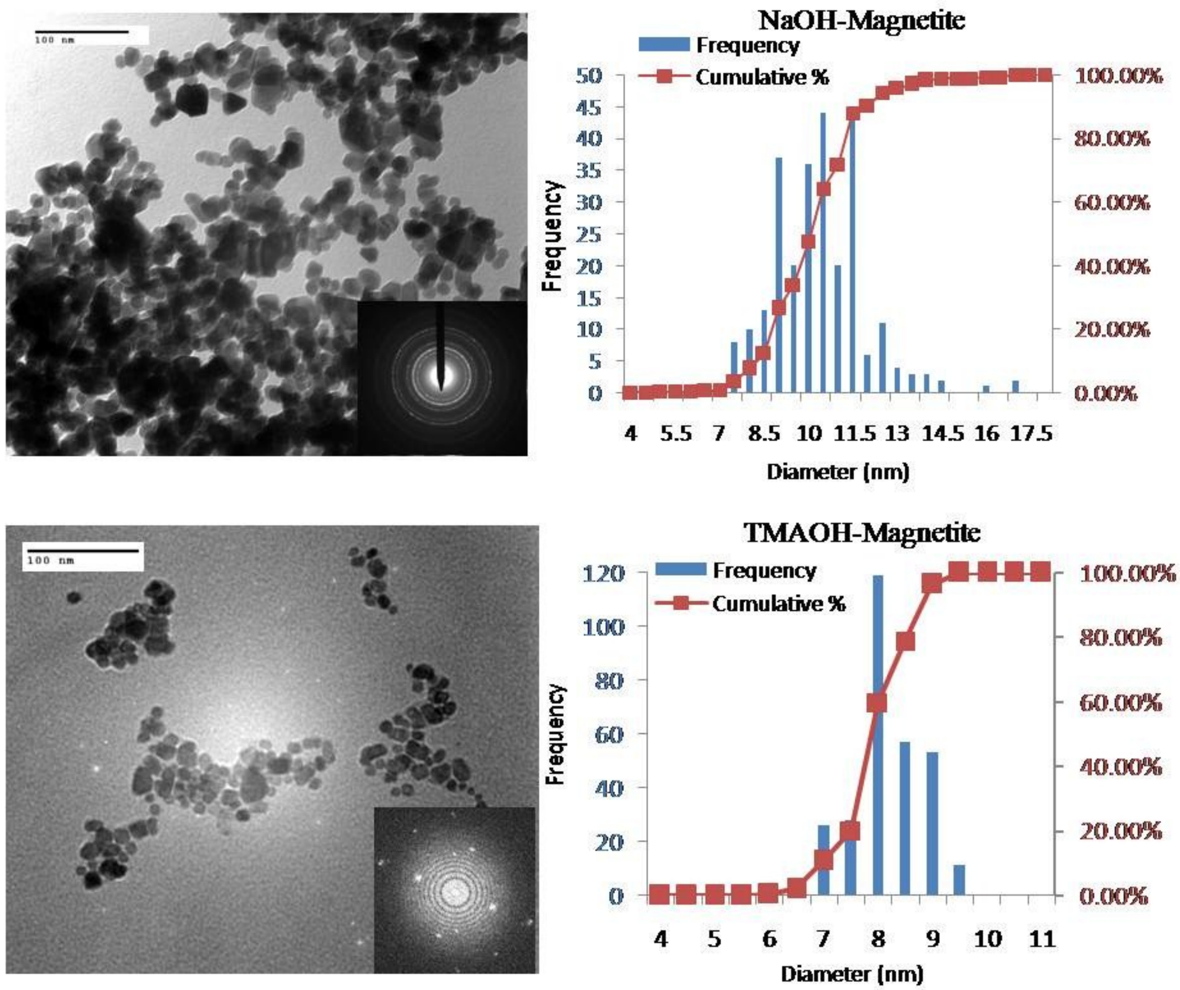

Figure S1 TEM images and distribution analyses of synthesized magnetite nanoparticles

Conversion between nanoparticle mass concentration and nanoparticle number concentration

1) Start with a magnetite mass concentration of *X* mg/L for nanoparticles with a TEM determined average radius of *Z* nm.
2) Convert to millimolar concentration using the molecular weight of 231.54 mg/mmol:

$$\text{Y mM } Fe_3O_4 = (\text{X mg/L } Fe_3O_4) \div \left(231.54 \frac{\text{mg}}{\text{mmol}}\right)$$

3) The unit cell parameters for magnetite are: a=b=c=0.839 nm. This translates to a unit cell volume of 0.591 nm^3. Each unit cell contains 8 Fe_3O_4 groups.
4) Using the average radius *Z* it is possible to calculate the average volume (*V*) of each nanoparticle:

$$V = \frac{4}{3}\pi Z^3$$

5) Based upon *V* one can calculate *W* number of Fe_3O_4 groups per particle:

$$W \frac{Fe_3O_4 \text{ groups}}{\text{particle}} = \frac{V}{\left(0.591 \frac{nm^3}{\text{unit cell}}\right)\left(8 \frac{Fe_3O_4 \text{ groups}}{\text{unit cell}}\right)}$$

6) Convert from *W* Fe_3O_4 groups to *N* millimoles Fe_3O_4 using Avogadro's Number:

$$N \frac{\text{mmoles } Fe_3O_4}{\text{particle}} = \frac{\left(W \frac{Fe_3O_4 \text{ groups}}{\text{particle}}\right)}{\left(6.022 \times 10^{23} \frac{Fe_3O_4 \text{ groups}}{\text{moles } Fe_3O_4}\right)} \times \left(\frac{1000 \text{ mmol}}{\text{mol}}\right)$$

7) Simply by dividing *Y* by *N* it is possible to calculate the nanoparticle number concentration with units of particles/L.
8) This same series of calculations can be reversed to calculate the mass concentration based upon the number concentration.

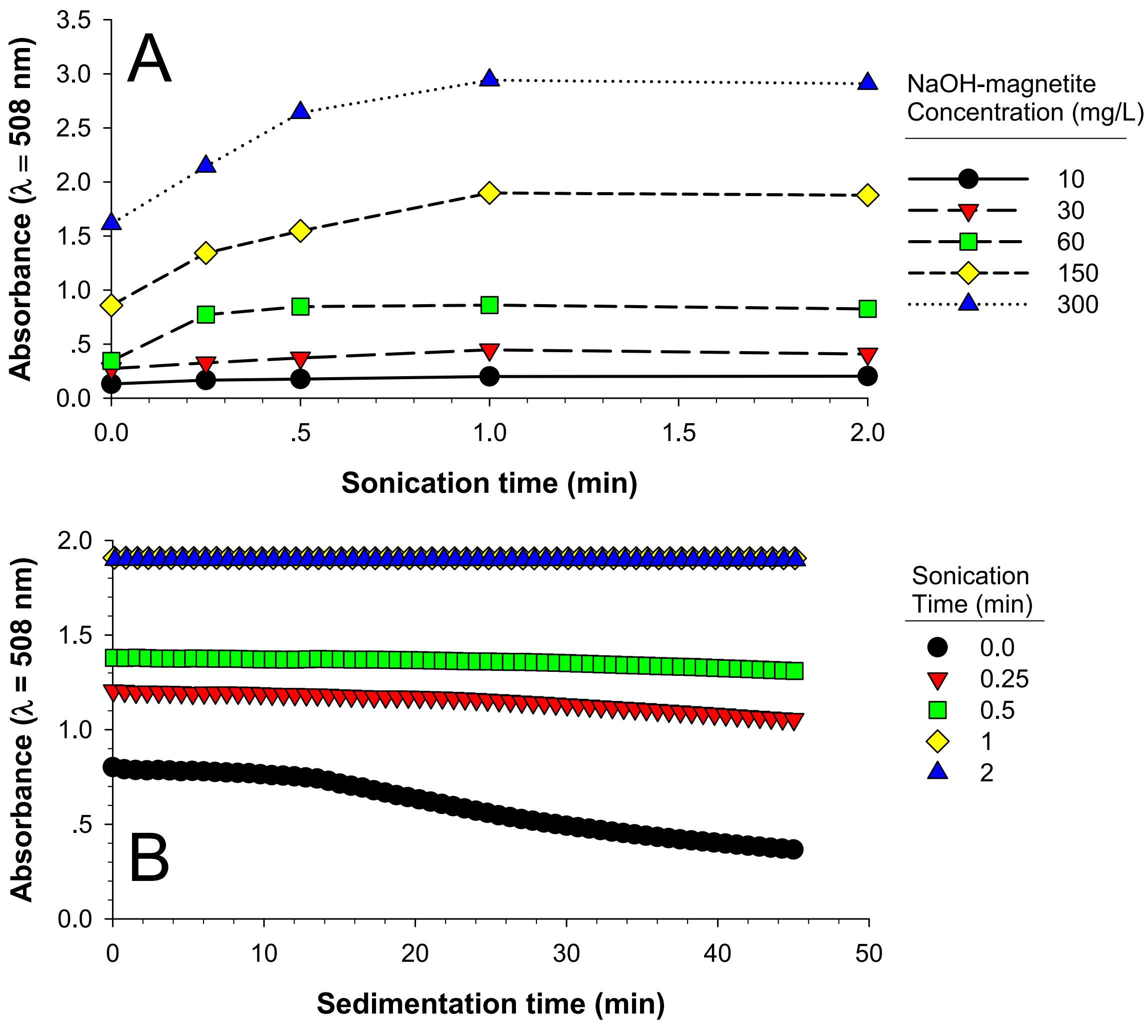

Figure S2 Effect of sonication time on A) the measured absorbance and B) the colloidal stability of NaOH-magnetite. As indicated, the measured absorbance is stable and is maximized at a sonication time of 2 minutes. To provide an extra margin of safety each nanomagnetite suspension was sonicated for 3 minutes prior to use.

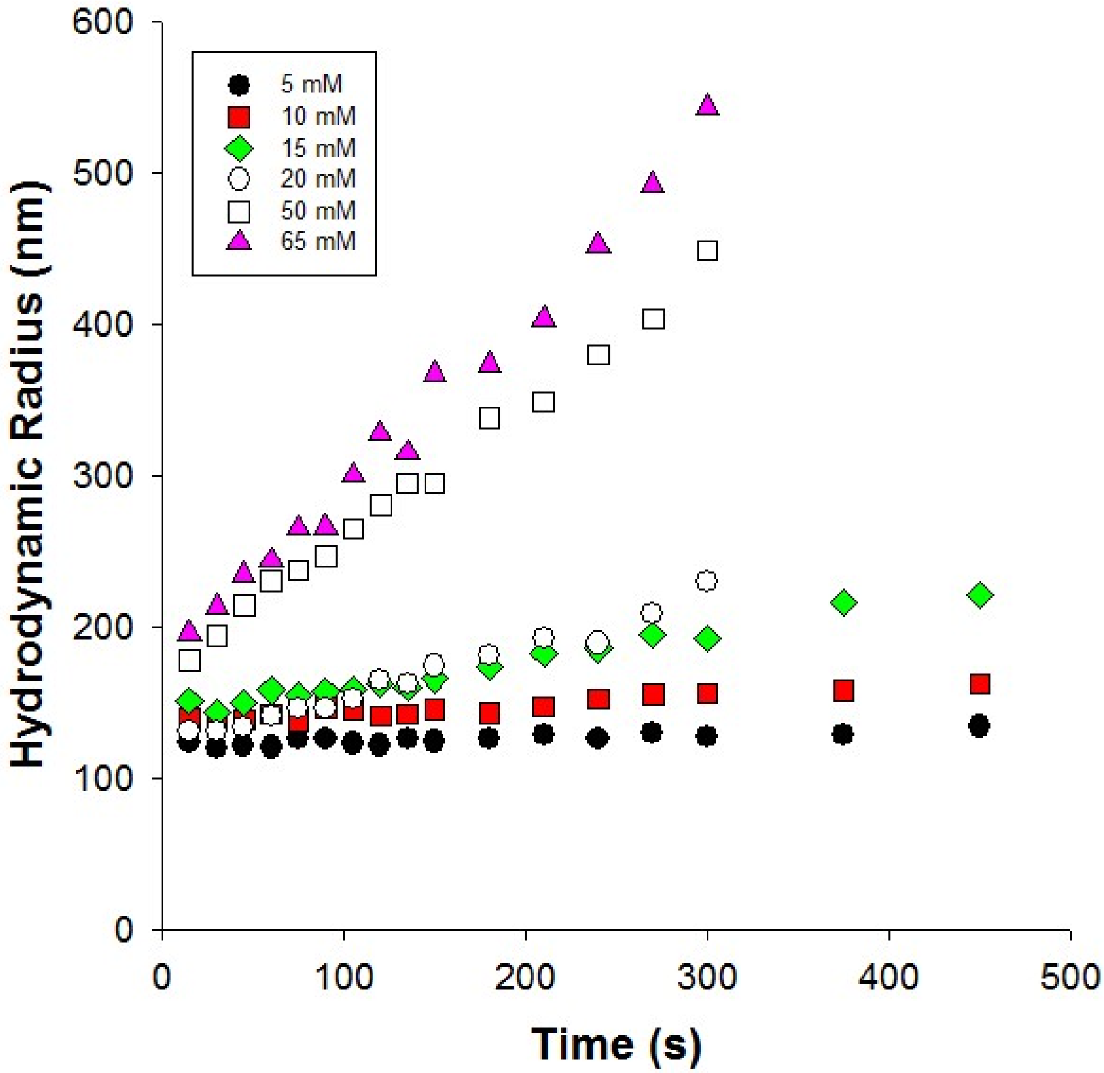

Figure S3. Representative dynamic light scattering (DLS) data. The DLS determined aggregation rate constant is defined as the initial slope. Conditions: 0.864 mM NaOH-magnetite with NaCl added at the given concentrations. pH = 8.0 ± 0.5.

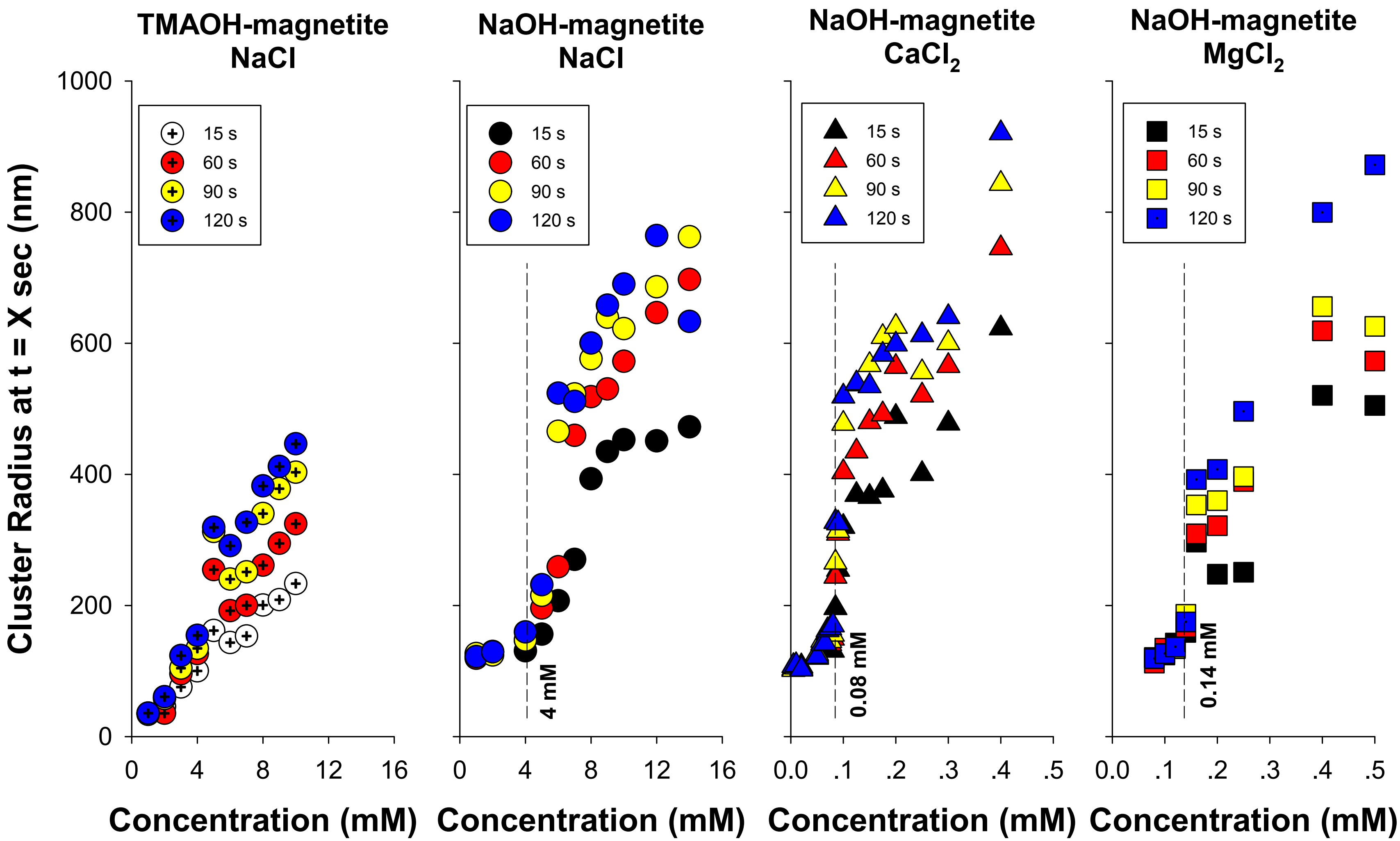

Figure S4. Measured cluster radius at t=15, 60, 90, and 120 s following salt addition. As indicated by the dotted lines for NaOH-magnetite, 4 mM of NaCl, 0.08 mM $CaCl_2$, and 0.14 mM $MgCl_2$ were required to initiate substantive cluster growth.

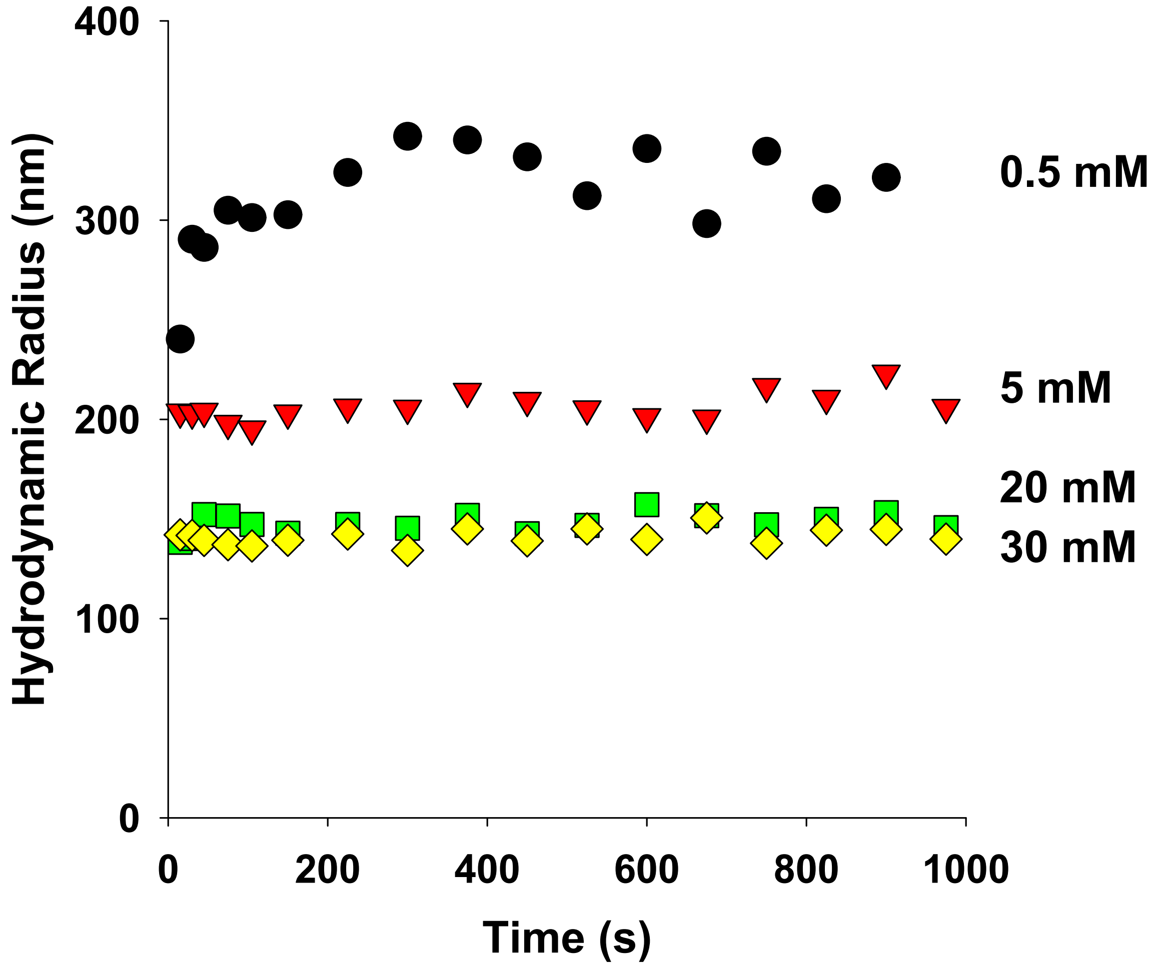

Figure S5. Measured cluster size as a function of time for different initial concentrations of Fe^{II}. In each case the starting magnetite concentration was fixed at a concentration of 2.73 mg/L.

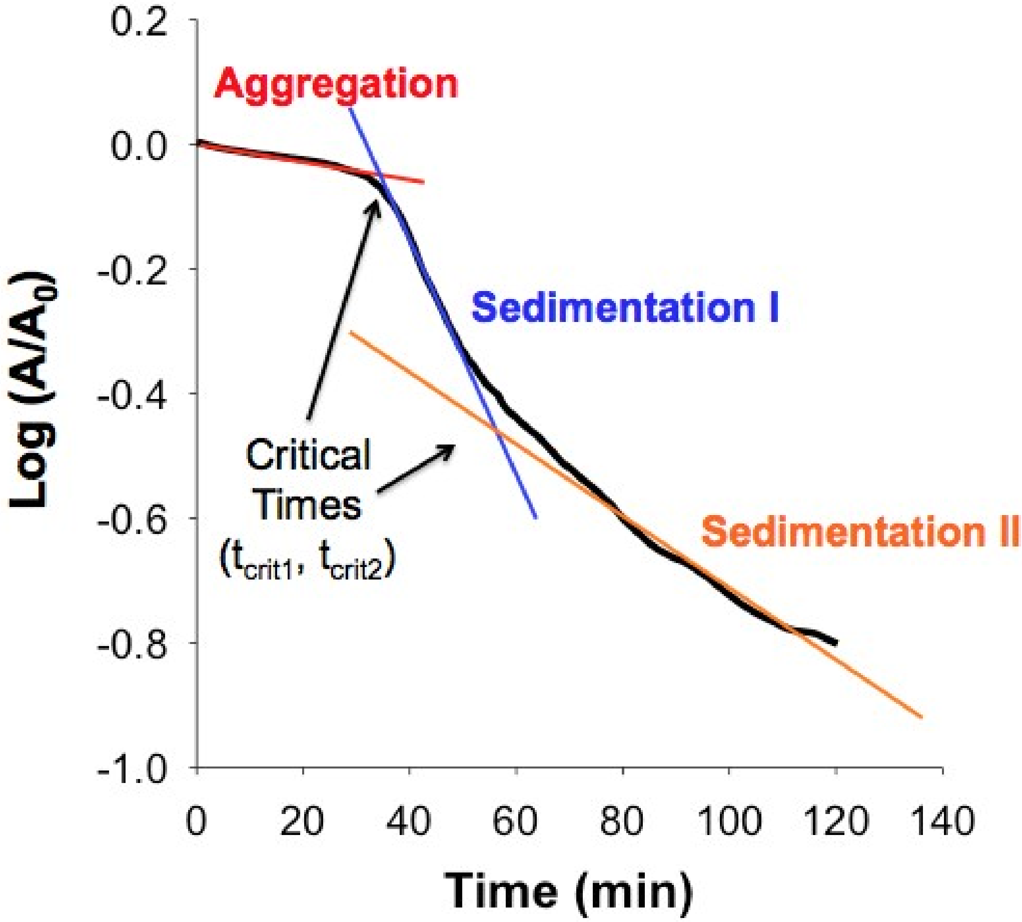

Figure S6. Schematic illustration of the demarcated regions within a sedimentation curve. The slopes for each zone correspond to the measured rate constants tabulated in Table S1.

Table S1 Aggregation and sedimentation rate constants obtained by analysis of sedimentation curves. The definitions for each parameter are shown graphically in Figure S5. The rate constant errors reflect the 95% confidence interval of the slope.

Radius (nm)	NaCl (mM)	Magnetite (mM)	t_{crit1} (min)	t_{crit2} (min)	k_{agg} (min^{-1})	k_{sed1} (min^{-1})	k_{sed2} (min^{-1})
NaOH Magnetite							
5	10	0.22	149	N.A.	3.0 (± 0.02) x 10^{-4}	2.3 (± 0.07) x 10^{-3}	N.A.
		0.32	112	159	3.7 (± 0.02) x 10^{-4}	7.1 (± 0.05) x 10^{-3}	3.5 (± 0.05) x 10^{-3}
		0.43	87	150	5.5 (± 0.05) x 10^{-4}	7.3 (± 0.06) x 10^{-3}	3.1 (± 0.03) x 10^{-3}
		0.65	65	85	1.4 (± 0.01) x 10^{-3}	1.6 (± 0.04) x 10^{-2}	5.0 (± 0.03) x 10^{-3}
		0.86	38	50	1.4 (± 0.01) x 10^{-3}	2.2 (± 0.02) x 10^{-2}	6.7 (± 0.02) x 10^{-3}
		1.30	22	34	2.7 (± 0.03) x 10^{-3}	2.2 (± 0.01) x 10^{-2}	4.0 (± 0.01) x 10^{-3}
		1.73	20	28	2.8 (± 0.09) x 10^{-3}	2.9 (± 0.09) x 10^{-2}	8.6 (± 0.06) x 10^{-3}
		2.16	12.5	20	4.9 (± 0.3) x 10^{-3}	3.1 (± 0.6) x 10^{-2}	6.0 (± 0.07) x 10^{-3}
	20	0.32	108	164	3.3 (± 0.03) x 10^{-4}	8.1 (± 0.09) x 10^{-3}	2.0 (± 0.08) x 10^{-3}
		0.43	78	115	4.9 (± 0.06) x 10^{-4}	1.0 (± 0.02) x 10^{-2}	2.3 (± 0.04) x 10^{-3}
		0.65	67	107	1.3 (± 0.01) x 10^{-3}	1.1 (± 0.01) x 10^{-2}	4.1 (± 0.04) x 10^{-3}
		0.86	30	58	1.3 (± 0.01) x 10^{-3}	1.5 (± 0.03) x 10^{-2}	6.3 (± 0.02) x 10^{-3}
		1.30	24	46	2.2 (± 0.02) x 10^{-3}	2.3 (± 0.02) x 10^{-2}	5.3 (± 0.01) x 10^{-3}
		1.73	11	28	3.6 (± 0.13) x 10^{-3}	3.5 (± 0.16) x 10^{-2}	8.9 (± 0.09) x 10^{-3}
		2.16	9	22	4.8 (± 0.19) x 10^{-3}	3.2 (± 0.17) x 10^{-2}	6.1 (± 0.07) x 10^{-3}
	30	0.32	100	117	4.0 (± 0.02) x 10^{-4}	1.5 (0.03) x 10^{-2}	2.6 (± 0.02) x 10^{-3}
		0.43	70	117	6.3 (± 0.08) x 10^{-4}	1.5 (± 0.02) x 10^{-2}	2.9 (± 0.04) x 10^{-3}
		0.65	54	90	5.8 (± 0.04) x 10^{-4}	1.4 (± 0.03) x 10^{-2}	2.2 (± 0.02) x 10^{-3}
		0.86	13	27	3.4 (± 0.14) x 10^{-3}	1.9 (± 0.02) x 10^{-2}	7.5 (± 0.04) x 10^{-3}
		1.30	13	24	3.8 (± 0.18) x 10^{-3}	3.3 (± 0.06) x 10^{-2}	6.7 (± 0.07) x 10^{-3}
TMAOH Magnetite							
4	10	0.22	81	123	7.3 (0.01) x 10^{-4}	8.8 (± 0.05) x 10^{-3}	3.9 (± 0.05) x 10^{-4}
		0.43	34	53	8.0 (0.04) x 10^{-4}	1.8 (± 0.03) x 10^{-2}	2.6 (± 0.05) x 10^{-3}
		0.86	19	45	1.0 (0.03) x 10^{-3}	2.6 (± 0.5) x 10^{-2}	3.5 (± 0.07) x 10^{-3}
		1.30	14	28	2.3 (0.02) x 10^{-3}	4.0 (± 0.07) x 10^{-2}	5.2 (± 0.06) x 10^{-3}

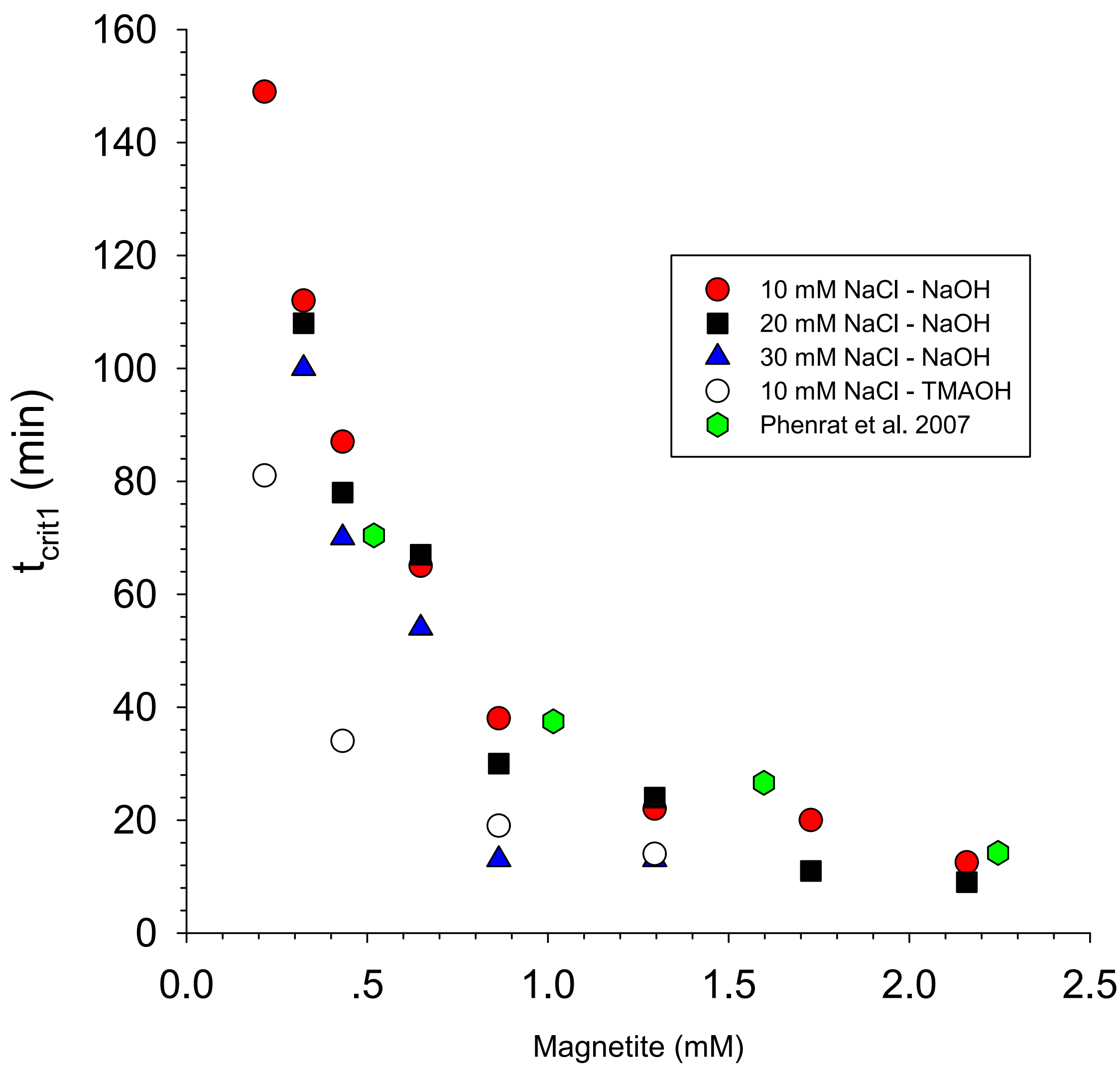

Figure S7. First critical time, t_{crit1}, as a function of the magnetite mass concentration in suspensions containing 10-30 mM NaCl. As shown, t_{crit1} is consistently lower for TMAOH-magnetite than for NaOH-magnetite at a comparable salt concentration. For comparative purposes the t_{crit1} values determined by Phenrat at al. (**2007,** *ES&T, Vol. 41*, pp. 284-290) are included. Their results were obtained using commercially available magnetite.