

# MAGNETOPHORESIS OF POLY(SODIUM 4-STYRENESULFONATE)/Fe<sub>3</sub>O<sub>4</sub> CLUSTERS: THE INFLUENCE OF COLLOIDAL STABILITY

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## MAGNETOPHORESIS OF POLY(SODIUM 4-STYRENESULFONATE)/Fe<sub>3</sub>O<sub>4</sub> CLUSTERS: THE INFLUENCE OF COLLOIDAL STABILITY

by

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- Figure 4.42 Comparison of separation times obtained in the present work 145 to that in literature. (This work: Bare Fe<sub>3</sub>O<sub>4</sub>, + PSS 70K/Fe<sub>3</sub>O<sub>4</sub> clusters; De Las Cuevas *et al.*, 2008:  $\Box$  M 030/40;  $\Delta$  M 020/50)
- Figure 4.43 Schematic diagram showing orientation of magnetic dipole 146 with respect to nearby particles.
- Figure 4.44 Optical micrographs on the earth's magnetic field-induced 148 local structures of (a) bare Fe<sub>3</sub>O<sub>4</sub> and (b) PSS 70K/Fe<sub>3</sub>O<sub>4</sub> clusters dispersed in deionized water solution at concentration *i*. 100 mg/L, *ii*. 1000 mg/L, and *iii*. 10000 mg/L.
- Figure 4.45 Enlarged on portion of figure 4.44b.*iii*. 149
- Figure 4.46 Transformation of the local structures of 10000 mg/L (a) bare 152 Fe<sub>3</sub>O<sub>4</sub> and (b) PSS 70K/Fe<sub>3</sub>O<sub>4</sub> cluster suspensions during the exposure to the external magnet. (Full movies are included in the attached DVD)
- Figure 4.47 TEM images of the PSS  $70K/Fe_3O_4$  clusters dried on TEM 153 grid under the earth's magnetic field (*left*) and the external magnetic field (*right*).
- Figure 4.48 The local structures of 10000 mg/L bare Fe<sub>3</sub>O<sub>4</sub> nanoparticle 154 suspension after the removal of the external magnetic field. (Full movies are included in the attached DVD)
- Figure 4.49 The local structures of 10000 mg/L PSS 70K/Fe<sub>3</sub>O<sub>4</sub> cluster 155 suspension after the removal of the external magnetic field. (Full movies are included in the attached DVD)
- Figure 4.50 Flow diagram showing the possible routes of cluster 157 formation using the proposed electrostatic-mediated assembly technique. The PSS 70K/Fe<sub>3</sub>O<sub>4</sub> clusters drawn at the right, which were formed without salt added to further induce clustering, was used as the control sample.
- Figure 4.51 (a) Average hydrodynamic cluster size of PSS 70K/Fe<sub>3</sub>O<sub>4</sub> 159 clusters prepared without clustering agent (*control*) and with 50 mM of NaCl, CaCl<sub>2</sub>, or AlCl<sub>3</sub> as a clustering agent. (b) Their corresponding intensity-weighted size distributions.

- Figure 4.52 (a) Photographs of conical tubes after used for Fe<sub>3</sub>O<sub>4</sub>/PSS 161 mixing with *i*. NaCl, *ii*. CaCl<sub>2</sub>, and *iii*. AlCl<sub>3</sub> as the clustering agent. (b) Water solubility of PSS in different electrolyte solutions. Markers assigned are NaCl ( $\bullet$ ), CaCl<sub>2</sub> ( $\Box$ ), and AlCl<sub>3</sub> ( $\Delta$ ).
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- Figure 4.54 (a) Photos of PSS  $70K/Fe_3O_4$  clusters suspension prepared 165 through two different strategies. (b) FTIR results on the freeze-dried samples.
- Figure 4.55 (a) Evolution of EPM values of bare  $Fe_3O_4$  at pH ~9.1 in the 166 presence of different CaCl<sub>2</sub> concentrations. (b) Schemes show the interactions between the PSS molecules and the bare  $Fe_3O_4$  surface at pH ~9.1 and the role of CaCl<sub>2</sub> as particlepolymer binder.
- Figure 4.56 (a) Average hydrodynamic cluster size of PSS 70K/Fe<sub>3</sub>O<sub>4</sub> 168 clusters prepared at pH~9.1 using different concentrations of CaCl<sub>2</sub> as clustering agent and particle-polymer binder, and (b) the corresponding intensity-weighted size distribution curves.
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- Figure 4.57 Predicted Fe<sub>3</sub>O<sub>4</sub> cluster formation in alkaline medium in the 171 presence of CaCl<sub>2</sub>.
- Figure 4.58 Average hydrodynamic cluster size of four samples of PSS 172 70K/Fe<sub>3</sub>O<sub>4</sub> clusters monitored by DLS throughout a time course of 12 hours.
- Figure 4.59 Changes of suspension opacity with time for four PSS 174 70K/Fe<sub>3</sub>O<sub>4</sub> cluster samples during the magnetophoresis experiment. Inset shows the remaining sample turbidity after 5 minutes of magnetophoresis.

- Figure 4.60 (a) Photos show magnetophoresis of PSS 70K/Fe<sub>3</sub>O<sub>4</sub> clusters 175 with average hydrodynamic cluster sizes of 196.0 nm and 459 nm, (b) photos show magnetophoresis of bare Fe<sub>3</sub>O<sub>4</sub>.
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- Figure 4.62 Aggregation patterns of PSS 70K/Fe<sub>3</sub>O<sub>4</sub> clusters under 181 various conditions. (a) 1 mM AgNO<sub>3</sub>, pH 4.24 (*inset is the enlarged version*), (b) 3 mM AgNO<sub>3</sub>, pH 4.25, (c) 0.331 mM Cu(NO<sub>3</sub>)<sub>2</sub>, pH 4.24, (d) 0.995 mM Cu(NO<sub>3</sub>)<sub>2</sub>, pH 4.23, (e) 0.164 mM Cr(NO<sub>3</sub>)<sub>3</sub>, pH 3.07, (f) 0.492 mM Cr(NO<sub>3</sub>)<sub>3</sub>, pH 3.00.
- Figure 4.63 Aggregation patterns of PSS 70K/Fe<sub>3</sub>O<sub>4</sub> clusters under 185 various conditions. (a) 0.333 mM CaCl<sub>2</sub>, pH 4.26, (b) 1 mM CaCl<sub>2</sub>, pH 4.27, (c) 0.333 mM MgCl<sub>2</sub>, pH 4.20, (d) 1 mM MgCl<sub>2</sub>, pH 4.21, (e) changes of average hydrodynamic size as a function of time for all cases.
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- Figure 4.65 Optical microscopic images of the mixture of PSS 70K/Fe<sub>3</sub>O<sub>4</sub> 190 clusters and Cu(NO<sub>3</sub>)<sub>2</sub> after (a) 1.30 minutes, (b) 4.30 minutes, (c) 6.04 minutes, (d) 10 minutes of preparation. (e,f) During exposure to external magnetic field and (g,h) after removal of external magnetic field (full movie of this is given in the attached DVD).
- Figure 4.66 (a) Illustration of the experiment conditions. (b) The  $D_{settling}$  193 and the corresponding initial settling rate of the PSS 70K/Fe<sub>3</sub>O<sub>4</sub> clusters under water spiked with Cu<sup>2+</sup> in the presence of different amounts and different types of coexisting DOM species. (Mixture pH for free PSS 70k test: 4.31 ± 0.01; HA test: 4.34 ± 0.06; NaAlg test: 4.42 ± 0.00;

BSA test:  $4.33 \pm 0.02$ ; Gly test:  $4.33 \pm 0.02$ ; Ace test:  $4.04 \pm 0.22$ )

- Figure 4.67 The recorded FTIR spectrum of various DOMs, PSS 196 70K/Fe<sub>3</sub>O<sub>4</sub>-DOM complexes, and PSS 70K/Fe<sub>3</sub>O<sub>4</sub>-Cu<sup>2+</sup>-DOM complexes. DOMs under investigated here include: (a) HA, (b) NaAlg, (c) BSA, (d) Gly, and (e) ACE. The denotation W1 and W4 refer to after one cycle of washing and after four cycles of washing, correspondingly.
- Figure 4.69 Images show the appearance of the mixture of NaAlg and PSS 201 70K/Fe<sub>3</sub>O<sub>4</sub> solution after overnight mixing in the absence and presence of Cu<sup>2+</sup> ions.

### LIST OF ABBREVIATIONS

Ace	Acetic acid
ATR-FTIR	Attenuated total reflectance-Fourier transformed infrared spectroscopy
B&W	Black and white
BET	Brunauer-Emmett-Teller
BSA	Albumin from bovine serum
c.c.c	Critical coagulation concentration
СМС	Carboxylmethyl cellulose
DCB	Divalent cation bridging
DLCA	Diffusion-limited colloid aggregation
DLS	Dynamic light scattering
DLVO	Derjaguin-Landau-Verwey-Overbeek
DOMs	Dissolved organic matters
EPM	Electrophoretic mobility
EQA	Environmental Quality Art
FWHM	Full width at half maximum
Gly	Glycine
НА	Humic acid
HGMS	High gradient magnetic separation
IEP	Isoelectric point
LDV	Laser doppler velocimetry

LGMS	Low gradient magnetic separation
MNPs	Magnetic nanoparticles
Ν	North
NaAlg	Sodium alginate
PAA	Poly(acrylic acid)
PAM	Polyacrylamide
PAP	Polyaspartate
PDI	Polydispersity index
PSS	Poly(sodium 4-styrenesulfonate)
QCM-D	Quartz crystal microbalance with dissipation
RLCA	Reaction-limited colloid aggregation
RNIP	Reactive nanoscale iron particles
S	South
SMCL	Secondary Maximum Contaminant Level
TEM	Transmission electron microscopy
TGA	Thermogravimetric analysis
U.S. EPA	Environmental Protection Agency United States
VSM	Vibrating sample magnetometer
XRD	X-ray diffraction