Supporting information for

Ion-Specific Clustering of Metal-Amphiphile Complexes in Rare Earth Separations

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1. Hard-sphere structure factor:

$$S(Q) = \frac{1}{1 - \bar{N}C(Q)}$$

$$x = QD$$

$$\bar{N}C(Q) = -24\phi\left\{\lambda_1\left[\frac{\sin x - x\cos x}{x^3}\right] - 6\phi\lambda_2\left[\frac{x^2\cos x - 2\,x\sin x - 2\cos x + 2}{x^4}\right] - 0.5\phi\lambda_2\left[\frac{x^4\cos x - 4x^3\sin x\ -1\right.\right.$$

$$\lambda_1 = \frac{(1+2\phi)^2}{(1-\phi)^4}$$

$$\lambda_2 = \frac{-\,(1+\,{}^{\phi}/_{2})^2}{(1-\,\phi)^4}$$

D is the hard sphere diameter = 2 * shell radius ($2*R_s$); ϕ is the hard sphere volume fraction.

For more information on the hard sphere fluid structure refer to the textbook by Hansen and McDonald.[1]

2. Structure factor in clustering model

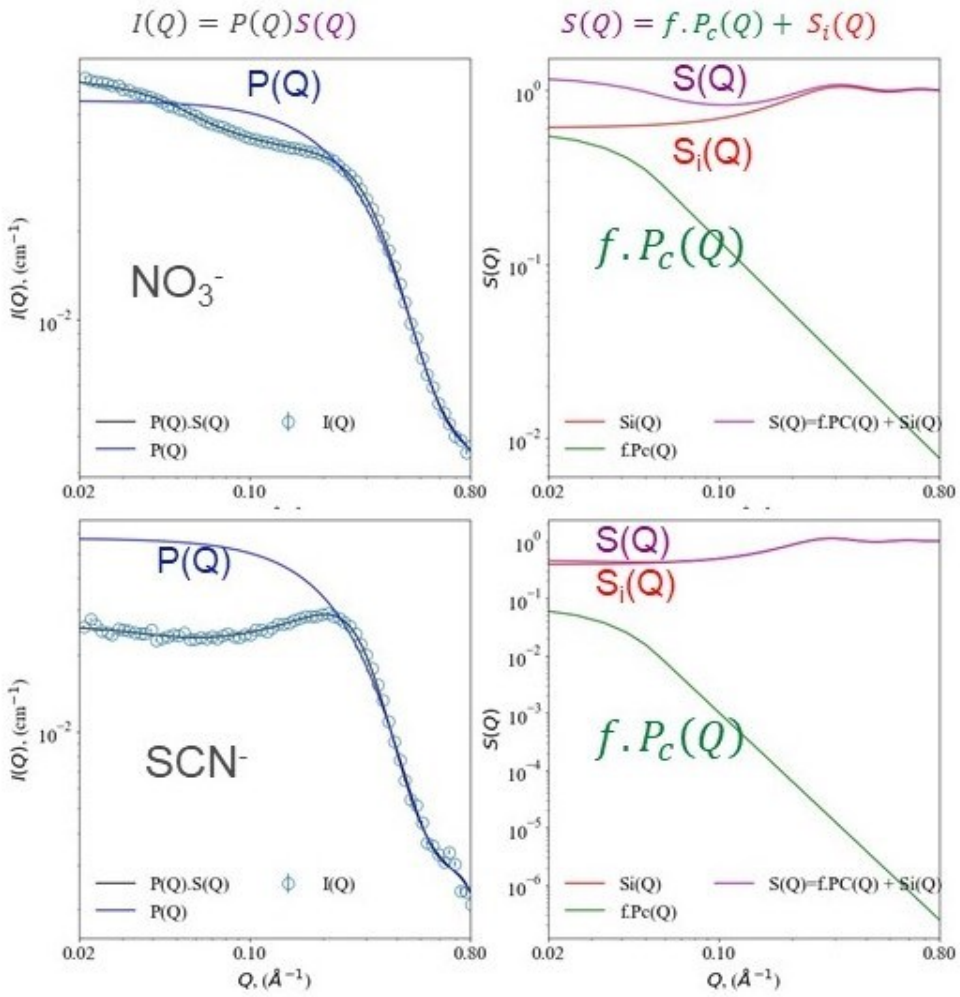

Figure S1. Terms involved in fitting the SAXS data to the cluster model for (a,b) TOMA-NO_3, and (c,d) TOMA-SCN. P(Q) is the form factor of individual reverse micelles, PC(Q) is the scattering from clusters, $S_i(Q)$ is the structure factor within the clusters, and f corresponds to the number of reverse micelles within a cluster.

Table S1. Parameters obtained from fitting the clustering model to the SAXS data for the organic phase obtained after extraction of varying concentrations of lanthanum or lutetium with TOMA-NO_3 or TOMA-SCN from 3 M of corresponding background salt solutions. Rc and Rs are core and shell radii respectively. ρ_c and ρ_s are core and shell electron densities. ϕ_{HS} is the apparent hard

sphere volume fraction. f+1 is the average number of aggregates per cluster, R_g is the radius of gyration of the cluster, and d is the Porod exponent corresponding to the scattering from the cluster.

Ln	Background	[Ln], M	R_c (Å)	R_s (Å)	ρ_c (e/Å^3)	ρ_s (e/Å^3)	ϕ_{HS}	f	R_g (Å)	d
None	NO_3^-	0	3.4±0.1	9.4±0.1	0.71±0.05	0.30±0.01	0.068±0.002	0.7	25.8±0.4	1.1±0.1
La	NO_3^-	0.002	3.2±0.1	9.2±0.1	0.79±0.06	0.31±0.01	0.066±0.002	0.6	24.5±0.4	1.4±0.1
La	NO_3^-	0.02	3.1±0.1	9.0±0.1	0.99±0.09	0.31±0.01	0.070±0.002	0.7	23.7±0.3	1.3±0.1
La	NO_3^-	0.1	3.1±0.1	9.3±0.1	1.30±0.14	0.32±0.01	0.075±0.002	1.2	22.6±0.2	1.1±0.1
La	NO_3^-	0.2	3.1±0.1	9.2±0.1	1.20±0.11	0.32±0.01	0.069±0.002	1.4	22.5±0.2	1.0±0.1
Lu	NO_3^-	0.002	3.1±0.2	9.3±0.1	0.83±0.09	0.30±0.01	0.069±0.002	0.6	24.5±0.4	1.2±0.1
Lu	NO_3^-	0.02	3.1±0.1	9.4±0.1	0.88±0.07	0.30±0.01	0.070±0.002	0.7	24.3±0.4	1.1±0.1
Lu	NO_3^-	0.1	3.1±0.1	9.2±0.1	0.89±0.08	0.31±0.01	0.067±0.002	0.7	24.1±0.4	1.2±0.1
Lu	NO_3^-	0.2	3.1±0.1	9.5±0.1	0.98±0.08	0.30±0.01	0.065±0.002	0.7	23.9±0.4	1.2±0.1
None	SCN^-	0	3.4±0.1	10.0±0.1	0.74±0.01	030±0.01	0.129±0.001	0.0	*	*
La	SCN^-	0.002	3.1±0.1	10.1±0.1	0.83±0.01	0.31±0.01	0.092±0.001	0.2	*	*
La	SCN^-	0.02	3.1±0.1	9.9±0.1	0.87±0.02	0.31±0.01	0.123±0.001	0.2	*	*
La	SCN^-	0.1	3.2±0.1	10.2±0.1	0.91±0.02	0.31±0.01	0.157±0.001	0.0	*	*
La	SCN^-	0.2	3.3±0.1	10.1±0.1	0.99±0.02	0.31±0.01	0.159±0.001	0.0	*	*
Lu	SCN^-	0.002	3.1±0.1	10.5±0.1	0.94±0.02	0.30±0.01	0.085±0.003	0.4	*	*
Lu	SCN^-	0.02	3.1±0.1	9.3±0.1	0.96±0.03	0.30±0.01	0.109±0.005	1.8	20.5±0.4	1.0±0.1
Lu	SCN^-	0.1	3.1±0.1	9.3±0.1	1.26±0.09	0.29±0.01	0.064±0.010	4.0	20.8±0.4	1.3±0.1
Lu	SCN^-	0.2	3.1±0.1	9.4±0.2	1.23±0.14	0.29±0.01	0.064±0.011	4.2	20.3±0.4	1.1±0.1

Table S2. Parameters obtained from fitting the clustering model to the SAXS data for the organic phase obtained after the extraction of 0.02 M lanthanides with TOMA-NO3 or TOMA-SCN from 3M of corresponding background salt solutions

Ln	**Background**	**R_c (Å)**	**R_s (Å)**	**ρ_c (e/Å^3)**	**ρ_s (e/Å^3)**	ϕ_{HS}	**f**	**R_g (Å)**	**d**
water	NO_3^-	3.4±0.1	9.4±0.1	0.71±0.05	0.30±0.01	0.068±0.002	0.7	25.8±0.4	1.1±0.1
La	NO_3^-	3.1±0.1	9.1±0.1	1.00±0.11	0.31±0.01	0.070±0.002	0.7	23.7±0.2	1.0±0.1
Nd	NO_3^-	3.1±0.2	9.3±0.1	1.00±0.15	0.31±0.01	0.071±0.002	0.9	23.8±0.2	1.1±0.1
Gd	NO_3^-	3.1±0.1	9.4±0.1	0.89±0.13	0.31±0.01	0.068±0.002	0.8	23.7±0.2	1.1±0.1
Er	NO_3^-	3.1±0.1	9.4±0.1	0.94±0.1	0.30±0.01	0.070±0.002	0.8	23.4±0.2	1.1±0.1
Lu	NO_3^-	3.1±0.1	9.4±0.1	0.88±0.08	0.30±0.01	0.070±0.002	0.7	24.3±0.4	1.2±0.1
water	SCN^-	3.4±0.1	10.0±0.1	0.74±0.01	030±0.01	0.129±0.001	0.1	*	*
La	SCN^-	3.1±0.1	9.9±0.1	0.86±0.02	0.31±0.01	0.122±0.002	0.1	*	*
Nd	SCN^-	3.4±0.1	9.7±0.1	0.74±0.02	0.31±0.01	0.129±002	0.1	*	*
Gd	SCN^-	3.1±0.1	9.4±0.1	0.85±0.02	0.31±0.01	0.118±0.01	0.1	*	*
Er	SCN^-	3.1±0.1	9.4±0.1	1.00±0.02	0.31±0.01	0.109±0.001	0.6	22.3±0.4	1.1±0.1
Lu	SCN^-	3.1±0.1	9.3±0.2	0.96±0.02	0.30±0.01	0.109±0.011	1.8	20.5±0.4	1.0±0.1

3. Aggregation of TOMA-Cl in toluene

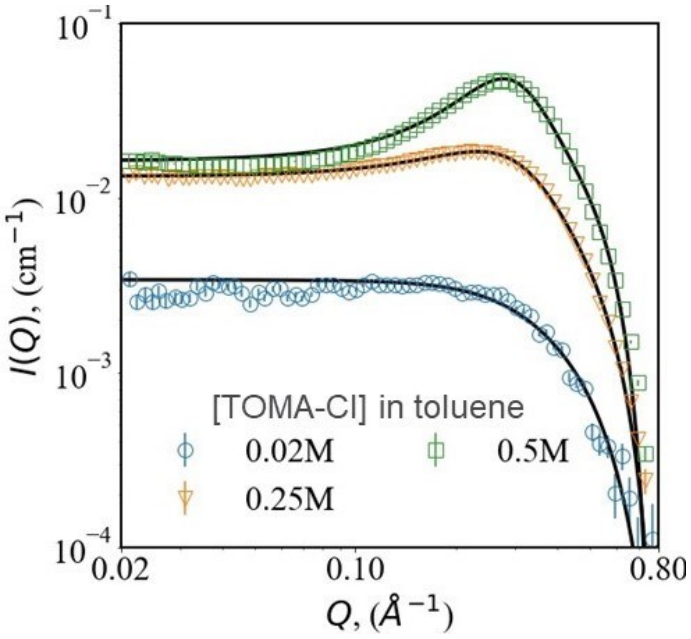

Figure S2. SAXS of TOMA-Cl dissolved in toluene at 0.02M (circles), 0.25M (upside down triangles), and (c) 0.5M (squares). Solid dark lines show the fit from cluster model. Clustering is negligible in these solutions and a clear hard sphere structure is seen. This indicates that the repulsion between the aggregates dominates in these solutions.

Table S3. Parameters from the clustering model fits for SAXS data of TOMA.Cl in toluene.

[TOMA-Cl]	R_c (Å)	R_s (Å)	ρ_c (e/Å^3)	ρ_s (e/Å^3)	ϕ_{HS}	f	R_g (Å)	d
0.02	5.5±0.1	10.5	0.48	0.283	0.015	0	*	*
0.25	5.6	9.5	0.41	0.286	0.11	0	*	*
0.5	5.9	10.4	0.44	0.283	0.22	0	*	*

4. Baxter model

$$\eta = \frac{\phi}{(1-e)^3}$$

$$\lambda = \frac{(1 + {}^{\eta}/_{2})}{(1 - \eta)^2(\tau + \frac{\eta^2}{1-\eta} - \frac{\eta}{12})}$$

$$\mu = \lambda\eta(1 - \eta)$$

$$\alpha = \frac{1 + 2\eta - \mu}{(1 - \eta)^2}$$

$$\beta = \frac{\mu - 3\eta}{2(1 - \eta)^2}$$

$$x = QD$$

$$A = 1 + 12\eta\left\{\alpha\left[\frac{\sin x - x\cos x}{x^3}\right] + \beta\left[\frac{1 - \cos x}{x^2}\right] - \frac{\lambda \sin x}{12\ x}\right\}$$

$$B = 12\eta\left\{\alpha\left[\frac{1}{2x} - \frac{\sin x}{x} + \frac{1 - \cos x}{x^3}\right] + \beta\left[\frac{1}{x} - \frac{\sin x}{x^2}\right] - \frac{\lambda}{12}\left[\frac{1 - \cos x}{x}\right]\right\}$$

$$S(Q) = \frac{1}{A^2 + B^2}$$

These equations are obtained from Menon et al., where they extend the Baxter model to systems with finite well widths.[2]

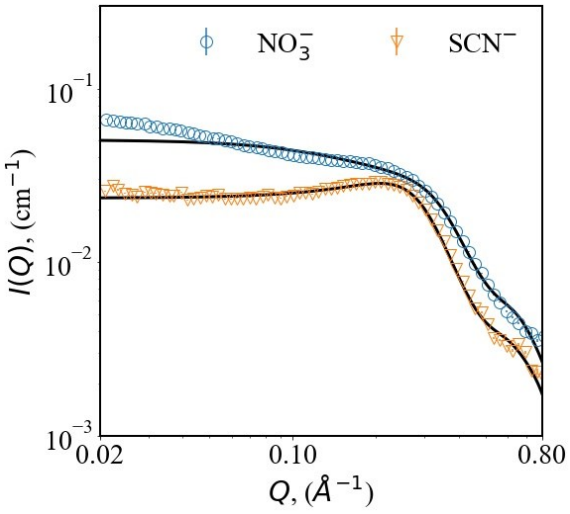

Figure S3. Fits obtained using the Baxter model for sticky hard spheres. This model does not capture the low-Q scattering behavior adequately, especially for the NO_3^- case when clustering behavior is significant

1. J.-P. Hansen and I. R. McDonald, *Theory of simple liquids : with applications of soft matter*, Elsevier/AP, Amstersdam, Fourth edition. edn., 2013.
2. S. V. G. Menon, C. Manohar and K. S. Rao, *J Chem Phys*, 1991, **95**, 9186-9190.