Supporting Information for

Molecular Origins of Mesoscale Ordering in a Metalloamphiphile Phase

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EXPERIMENTS

Solvent Extraction

Solvent extraction experiments were conducted using the general procedure outlined in our previous publication.1 >99.9% purity DMDOHEMA was provided by Technocomm Ltd (Scotland) whereas all other reagents were purchased from Sigma Aldrich (USA) and were analytical grade. 2 mL of the 0.5 M DMDOHEMA in n-heptane phase was first pre-equilibrated by vortexing for 10 mins in a capped plastic test tube at ambient temperature (23°C) with an equal volume of the aqueous phase (either 3 M HNO3 or LiNO3, with and without Eu(III)). The concentration of Eu(III) used in the aqueous phase was 0.2 M and 0.14 M Eu(III) for solutions (b) and (d) respectively. Phase separation was completely through centrifugation and aliquots of the organic and aqueous phases were withdrawn for analysis. The metal concentration in the aqueous phase was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES). Nitric acid was titrated with standard NaOH after the addition of NaHC2O4 to complex the Eu(III) ion. Organic phase water content was determined using Karl Fisher titration with H2C2O4·2H2O as the standard. To measure the concentration of acid and metal in the organic phase, a sample of the organic phase was stripped of the extracted nitric acid and Eu(III) ion by equilibrating it twice with a double volume of water. Metal and acid in the combined aqueous phase resulting from the strip steps were determined as above.

Scheme S1. Schematic representation of DMDOHEMA, where the hydrophilic headgroups are colored in blue, and hydrophobic tails in red. The C3 represents the central carbon atoms, which is used to roughly stand for the geometric center of the headgroup.

Dynamic Light Scattering (DLS) Measurements
DLS measurement were conducted at 24°C using a ZEN 3600 Zetasizer NanoZS from Malvern (4 mW helium-neon laser of wavelength 633 nm). Detector angle was set to backscattered mode (173°) to minimize the effect of backscattering interference in the concentrated solutions. Triplicate measurements were made with regard to solvent (heptane). The average particle size measurement is presented below along with the raw correlation data and size distribution intensity for the solutions (a) to (d). The particle size determined by dynamic light scattering is the size of a sphere that moves in the same manner as the scatter so that anisotropy is not taken into account. The particle size includes the hydrocarbon chains of the clusters that are ignored in SAXS and lead to larger average measurement. Inelastic collisions that arise from attractive interactions between aggregates will also increase the average particle size measured with DLS as the technique does not distinguish between the small interacting clusters and the larger flocculates.

In solution (a) attractive interactions between aggregates are lowest and the particle size measured with DLS is only slightly larger than that determined from Baxter modelling of SAXS data (18.5 Å versus 11 Å), as would be expected from a sphere that includes that amphiphile aliphatic chains. For solution (b) the DLS size measurement is significantly larger than the Baxter model measurement (54.1 Å versus 19 Å), which could be from the increased inter-cluster interactions measured in this solution. This is true to a lesser extent for solution (c) (36.2 Å versus 17 Å). Solution (d) shows that largest difference between DLS particle size and Baxter model particle size (91.1 Å versus 20 Å), which may be due to this solution having the strongest inter-cluster interactions that would lead to greater flocculation of small aggregates into large particles. The DLS measurements are generally supportive of the SWAXS data analysis in that larger particles form when acid and/or Eu(III) are incorporated into the clusters. They also suggest that the attractive inter-aggregate interactions are leading to larger overall assemblies.
Solution (a). Average particle size = 18.5 Å
Solution (b). Average particle size = 54.1 Å
Solution (c). Average particle size = 36.2 Å
Solution (d). Average particle size = 91.1 Å

**Figure S1.** DLS experimental results.

**Vibrational Spectroscopy**

Vibrational spectra were obtained using a Nicolet Nexus 870 FT-IR spectrometer with an HATR attenuated reflectance accessory containing a diamond resolution element. A drop of organic solution (a-d) was put onto the surface and sealed with a glass adapter to prevent evaporation. IR spectra were obtained from 4000–600 cm$^{-1}$ by collecting 18 scans at 2 cm$^{-1}$ resolution. In the region corresponding to the bands relevant to the aggregating molecular groups, the spectra are complex, showing numerous overlapping peaks, making quantitative analysis difficult. However, some qualitative conclusions may be drawn regarding the coordination interactions between the ligands and metal ion when comparing the spectra in the 1000 to 1700 cm$^{-1}$ range (see figure below). The peaks at 1600-1700 correspond to the C=O stretch of the malonamide ligand, and these shift and change in intensity from (a)-(d). Particularly, the solutions that contain Eu (b and d) show a pronounced peak at 1610 cm$^{-1}$ that is absent in the solutions without Eu. This suggests that the carobonyl malonamide Os are coordinating to the metal ion, in agreement with the MD
simulations (see figure S7) as well as other publications. The different shifts in the peaks at 1300cm\(^{-1}\) may arise from a difference in nitrate density. Our previous work has indicated that monodentate nitrate prevails in malonamide-heptane solutions under acidic conditions whereas significant bidentate mode persists under neutral, which may account for these shifts.

\[ \gamma = \frac{mg}{2\pi r} \] (1)

where \( \gamma \) is the IFT, \( r \) is the radius of the tip of the needle, \( g \) is the gravity acceleration and \( m \) the mass of the drop. Knowing the density of the organic and the aqueous phases, the CCD camera analyzes the shape of the drop through the DSA4 software to determine its volume and therefore its mass \( m \) using the known density of the organic solution.

In order to determine the monomer concentration to help fit the SAXS data with the Baxter model, a series of tensiometry measurements was performed for each system. IFT was measured for a given
aqueous solution, corresponding to the systems (a), (b), (c) or (d) of this study, at various concentrations of DMDOHEMA diluted in n-heptane. In the plot of the IFT against the concentration of the extractant, as shown in Figures below, the break in slope determines the critical micellar concentration (CMC) or critical aggregate concentration (CAC), which corresponds to the maximum monomer concentration before the formation of aggregates for a given aqueous solution [1-3].

Tensiometry solution (a)
CMC=0.159 ± 0.014 M
Tensiometry solution (b)
CMC=0.08 ± 0.011 M

Tensiometry solution (c)
CMC=0.08
**Figure S3.** Tensiometry results for solutions (a)-(d).

**SWAXS Data Collection**

SWAXS data were collected at the Advanced Proton Source (APS) at Argonne National Laboratory using beamline 12-ID-C. Samples were contained in 2 mm diameter quartz capillary tubes (Charles Supper Co., 20-QZ) at ambient conditions. The incident photon energy of 19.0 keV gave good X-ray transmittance for data acquisition. 2D scattering profiles were acquired in 0.5 s exposure times with a MAR-CCD-165 detector (MAR USA), which has a 165 mm diameter active area and a 2048 by 2048 pixel resolution. The sample-to-detector distance was such as to provide a detecting range for momentum transfer of 0.04 \( \leq q(\text{Å}^{-1}) \leq 2.41 \). The scattering vector, q, was calibrated using a silver behenate standard. The 2D scattering images were corrected for spatial distortion and detector sensitivity and then radially averaged to produce plots of scattered intensity, I(q) versus q, in which q = 4\( \pi \)sin\( \theta \)/\( \lambda \), \( \theta \) is the scattering angle and \( \lambda \) is the wavelength of the X-rays, following standard procedures. The I(q) data were put on an absolute scale \((\text{cm}^{-1})\) by calibration with water (18 MΩcm) scattering after background subtraction.

**SAXS Data Interpretation**

In the absence of aggregation (below the critical micelle concentration), the extractant monomers produce a weak scattering signal. SAXS data were collected from 0.01 M DMDOHEMA solution in n-heptane to establish the scattering contribution from the monomers after subtracting the heptane background. After putting onto absolute scale (as above), this data was used as a second background that was subtracted...
from the heptane-subtracted SAXS data after establishing the monomer concentration in samples (a)-(d) using tensiometry (see below). The double-background subtracted normalized SAXS data were interpreted using the GIFT method and Baxter model as described below.

Figure S4. (i) SAXS data for samples (a)-(d) and the pure heptane solvent after subtracting the background scattering from air and the sample holder. (ii) SAXS contribution from the aggregates after heptane solvent and monomer contributions are subtracted and data put into absolute units.

GIFT Method

As described in our previous publication,1 the GIFT method5-7 was used to obtain p(r) functions (structure information in real space) from scattering data in q space. GIFT interprets the globular particle system, I(q) = nP(q)S(q), where P(q) is the average form factor (corresponding to the shape and size of the scattering particles), S(q) is the average structure factor (from inter-particle interactions), and n is the number of particles per unit volume. P(q) is the Fourier transformation of its real space counterpart, p(r), according to:

\[
P(q) = 4\pi \int_0^\infty p(r) \frac{\sin qr}{qr} \, dr
\]

(2)

This means that, to deduce p(r), the inverse Fourier transformation (IFT) of an experimental P(q) must be calculated. In concentrated interacting systems, such as those involved in solvent extraction, the structure factor, S(q), must be modeled and subtracted from the scattering data, I(q), to give P(q) from which p(r) is derived. The selection of the appropriate structure factor model is key to achieving coherent p(r) functions from GIFT, and the model selected in the present study was the Percus–Yevick (PY) closure relation8 that has been shown to closely approximate the interaction effects of micelles in SAXS studies from numerous solvent extraction systems.9-20

The PY closure relation for hard spheres solves the Ornstein–Zernicke equation on the principle that hard sphere potential is zero if the particles do not overlap, and infinity if they do (approximating the structure factor that results from the excluded volume effect). The resulting structure factor depends on radius and volume fraction of particles, with a modification to include polydispersity with a distribution function.
The PY closure relation structure factor is simple, fast and can even be used for non-hard sphere interaction potentials as many potentials behave similarly to effective hard spheres.\(^5\) According to Glatter,\(^5\) this structure factor model holds true for deviations from hard spheres and for deviations from perfect spherical symmetry, soliciting its use to evaluate scattering data of interacting elongated particles. This has been demonstrated in a string of recent publications by Shrestha and co-workers, who used the GIFT in combination with the PY closure relation to interpret SAXS data from interacting non-ionic surfactant reverse micelle systems in non-polar media (similar to solvent extraction organic phases).\(^{22-26}\) These studies were effective in showing the growth of spherical particles into elongated worm-like aggregates. A detailed discussion of the PY closure relation model in the GIFT treatment of SAXS data is given in a recent review article by Otto Glatter.\(^5\)

**Baxter Model**

In order to obtain metric information about the aggregation in the different systems, SAXS data were fitted using the Baxter model as used by many before [3-7]. The scattered intensity \(I(q)\), after subtraction of the contribution of the diluent and the capillary, is given by the equation (3):

\[
I(q) = n_P V_P^2 (\rho_P - \rho_S)^2 P(q) S(q)
\]

with \(n_P\) the number of scattering particles per unit of volume, \(\rho_P - \rho_S\) the contrast factor between the scattering particles and the bulk of the solution, i.e. in the case of SAXS experiment the difference of electron density, \(P(q)\) the form factor of the scattered particle, describing the angular scattering distribution as a function of the particle size and shape and \(S(q)\) the structure factor, which relates to the interactions between the scattering particles. As scattering particles exist in different shape, for example spherical, ellipsoidal, rod-shaped etc., the form factor \(P(q)\) can have different analytical expression [8]. However, the structure factor \(S(q)\) has only one known analytical expression. The Percus-Yevick approximation applied to a mono-dispersed spherical particles system has been resolved by Baxter to provide an analytical expression of the structure factor [9]. This model has the advantage to contain two essential characteristics of a real potential, a repulsion of the cores interacting, also called hard sphere volume exclusion effect, and a narrow attractive tail, corresponding to the attractive interaction of the particles leading to a non-elastic collision. The attractive interaction energy \(U(r)\), depending of the distance \(r\) between the interacting particles, is given by the equation (4):

\[
\frac{U(r)}{k_B T} = \lim_{\delta \to d_{hs}} \ln(12 \tau \frac{d_{hs} - \delta}{d_{hs}})
\]

with \(d_{hs}\) is the diameter of the hard sphere, \(d_{hs} - \delta\) represents the width of the narrow rectangular attractive well and \(\tau\) is the inverse of the stickiness parameter \(\tau^{-1}\) which is used in the numerical resolution of the Baxter model.

Therefore, the SAXS data can be fitted using the Baxter model which requires the optimization of three parameters: the monomer concentration, which is determined in this case by the tensiometric measurements for each solution; the average aggregation number \(N\), from which the volume and number of the scattering particles can be derived; and the stickiness parameter \(\tau^{-1}\) which accounts of the attractive interaction between the particles. The interparticle attraction potential energy \(U(r)\) was calculated thanks to the equation (4) with an extremely narrow attractive well, corresponding to a maximum of 10% of the diameter of the hard sphere, using the \(\tau\) parameter determined by fitting the SAXS data.
Figure S5. Baxter model fits to SAXS data from solutions (a)-(d). Like in previous studies, the model only accurately describes the data in the nano- and meso-scale regions at $q < 0.3 \text{Å}^{-1}$.

**ATOMISTIC MOLECULAR DYNAMIC SIMULATIONS**

Classical MD simulations are performed using GROMACS (version 4.5.5). For the molecules of DMDOHEMA, $n$-heptane, the OPLS-AA force field is chosen, with correction for long hydrocarbons (i.e., the L-OPLS force field). The TIP3P-MOD water model is employed as recommended by the L-OPLS force field. The L-OPLS force field has shown to be capable of improving the OPLS-AA force field in reproducing experimental properties for long hydrocarbon chains, e.g., density, heat of vaporization, gel-to-liquid-phase transition, chain conformation, diffusion coefficient, viscosity and solvation free energy. And the utilization of TIP3P-MOD water model has presented good agreements regarding the solvation free energy of several long hydrocarbon organic molecules.

The force field parameters of Eu$^{3+}$ have been reported in Ref. [31], with those of the counterion NO$_3^-$ from the original OPLS-AA force field. The force field parameters of HNO$_3$ are based on the OPLS-AA force field with the atomic partial charges from Ref. [32]. All these force field parameters have been employed in our very recent work.

The concentrations of all the solute species in the four systems (a) – (d) are based on the experimental data, which are provided in Table 1 in the main text. In the experimental neutral systems, the Li$^+$-NO$_3^-$ aqueous phases, with (b) or without (a) Eu(NO$_3$)$_3$, come in contact with the $n$-heptane organic phase containing 0.5 M DMDOHEMA. The concentrations of LiNO$_3$ and Eu(NO$_3$)$_3$ in the aqueous solution was varied to adjust the equilibrium concentrations of water and Eu(NO$_3$) in the organic phase. Note that Li$^+$ ions can’t diffuse into the oil phase. Whereas in the experimental acidic systems, the nitric acid aqueous phases, with (d) or without (c) Eu(NO$_3$)$_3$, coexist with the $n$-heptane organic phase containing 0.5 M DMDOHEMA. The concentrations of nitric acid and Eu(NO$_3$)$_3$ in the aqueous solution was changed to control the equilibrium concentrations of HNO$_3$ and Eu(NO$_3$) in the organic phase. Note that Lefrançois et al. have confirmed that nitric acids are fully associated in the organic phase in the malonamide -
heptane solution. In the present work, only the four organic solutions (a)-(d) are employed for the convenience of comparison. The numbers of the compounds are listed in Table S1.

| System | n-heptane | DMDOHEMA | H2O | HNO3 | Eu(NO3)3 | Time (ns) |
|--------|-----------|----------|-----|------|----------|-----------|
| control | 1550      |          |     |      |          | 10/10     |
| a      | 12400     | 1200     | 360 |      |          | 25/50/25  |
| b      | 12400     | 1200     | 360 | 144  |          | 25/50/50  |
| c      | 12400     | 1200     | 792 | 744  |          | 25/50/25  |
| d      | 12400     | 1200     | 792 | 744  | 144      | 25/50/25  |

1 MD simulation time: annealing(small box)/equilibration(small box)/production(large box)
2 Annealing/production simulations, both using simulation box length of around 7.2 nm.

To speed up the self-assembly process, two methods were employed. Firstly, smaller initial structures were employed, which are 1/8 as large as the targeted solution in Table S1. As illustrated in Figure S6, all the species were randomly distributed initially using the package Packmol. After some preliminary equilibration, the annealing method was subsequently employed. During the annealing process, the temperature of the system was increased from 298K to 363 K in the duration of 0.5 ns, maintained at 363 K for another 0.5 ns, and then cooled down to 298 K within 0.5 ns. The system was finally maintained at 298 K for another 3.5 ns. See Figure S7. The solution density and total potential energy were recorded (Figure S8). Moreover, the C3-C3 radial distribution function (RDF) was calculated based on the frames in the last 3 ns of each annealing cycle (298 K). The annealing process was repeated for 3 or 5 times until the obtained C3-C3 RDF becomes converged (Figure S8). Note that in the annealing simulations, all the simulation parameters are the same as those used in the production simulations below.
**Figure S6.** Snapshot of the initial structure of the system (b). Eu$^{3+}$, NO$_3^-$ and waters are highlighted with Eu/N/O/H colored in pink/blue/red/white, respectively. Note that initially the simulation box length is a bit of larger than 8 nm to conveniently accommodate all the molecules using Packmol.$^{35}$

**Figure S7.** Temperature of the annealing simulations.
Figure S8. Convergences of the annealing simulations. (a) The obtained density and the potential energy as a function of time in the annealing simulations. (b) Radial distribution function between the C3 atoms of DMDOHEMA molecules under 298 K in the annealing simulations.

Figure S9. Snapshots of the last simulation frames in the four systems (a)-(d). In plots (a’)-(d’) only solute molecules (water, HNO₃, Eu⁺, NO₃⁻) are provided.

The annealing simulations were followed by further equilibration of 50 ns at 298 K. These simulation boxes were enlarged $2 \times 2 \times 2 = 8$ times larger (in $X \times Y \times Z$ dimensions), leading to the simulation sizes in Table S1. The simulation parameters were the same as those in the production simulations below.
In the production simulations, the NTP ensemble (constant number of particles, temperature, and pressure) was used. The reference temperature was set to be 298 K, with the solvent \((n\text{-heptane})\) and solute separately coupled using the velocity rescaling algorithm. The pressure of the system was coupled to 1 bar using the Parrinello-Rahman algorithm. The three-dimensional periodic boundary condition was employed. The neighbor searching was performed up to the distance of 1.5 nm. The long-range Coulomb interactions were calculated using the Particle Mesh Ewald (PME) method with a grid real spacing of 0.12 nm and cubic interpolation. The switch function between 1.0 nm and 1.2 nm was employed for the van der Waals interactions to smooth the forces and potential function, in combination with the long-range dispersion correction for energy and pressure. A simulation integration timestep of 2.5 fs was used with all the covalent bond lengths constrained via the LINCS algorithm. Each of the simulations was performed for the duration of at least 25 ns (Table S1). The snapshots of the last frames were provided in Figure S9.

**Scheme S2.** Schematic representation of the simulation methodology. (a) All the molecules were randomly distributed initially in a box \(~8\) nm in each dimension (Figure S6). (b) The annealing simulation was performed to speed up the aggregation behavior, whose convergence is justified by Figure S8. (c) The systems were further equilibrated for 50 ns. (d) Each of the simulation is enlarged to be 8 times larger \((\sim 16\) nm in each dimension), which is necessary for the calculation of the low-\(q\) range of the SWAXS. The snapshots of the last frames are provided in Figure S9.

**Calculation of the Scattering Intensity of SWAXS From Atomistic MD Simulations**

As far as we know, Guilbaud and co-workers performed the first calculations of SWAXS for amphiphile-oil systems with \(^{37}\) or without \(^{38}\) metal ions by means of atomistic MD simulations in 2014. In their work, the structure factor \(S(q)\) was calculated using the package nMoldyn. \(^{39}\)

\[
S(q) = \frac{1}{N} \langle |\sum_{j,k} Z_j Z_k \exp[-i q (r_j - r_k)]|^2 \rangle.
\]  

(5)
where $q$ stands for the wave vector, $Z$ for the atomic number, $N$ for the total number of diffusing sites, and $r$ for the their position vector. However, it is the scattering factor $I(q)$ which is directly obtained from SAXS experiments. To make the scattering experiment and simulation calculations comparable, an effective atomic form factor is required.

$$I(q) = S(q)\tilde{f}^2(q),$$

where $\tilde{f}(q)$ denotes the effective atomic form factor averaged over all the existing element types in the simulation boxes.\(^\text{40}\)

In the present work, we are using a different method, which is capable of calculating the scattering intensity $I(q)$ directly. That is to say, no assumption of the effective atomistic form factor is necessary. In GROMACS, the program g_saxs, which is the same as “g_rdf – sq” in GROMACS versions earlier than 5.0, prints out the rescaled scattering intensity $I(q)$, which is normalized by the amount of atoms per simulation frame.

$$I(q) = \frac{1}{N}\langle|F(q)|^2\rangle A(q),$$

where the polarization factor $A(q) = [1 + \cos^2(2\theta)]/2$. Note that under the Bragg’s law, $q = 4\pi \sin \theta / \lambda$, where $\theta$ is the scattering angle and $\lambda$ denotes the wavelength of the incident X-ray. It is necessary to note that in this algorithm, all other correction terms other than the polarization correction are ignored, e.g., X-ray adsorption, temperature (i.e., the B-factor). And $\langle\rangle$ stands for the average over all the orientations of the reciprocal vector $q = (h, k, l) = 2\pi(n_x/X, n_y/Y, n_z/Z)$ in the three dimensional space, where $n_x, n_y$ and $n_z$ are integer numbers, and $(X, Y, Z)$ represents the box edge length in the corresponding dimension. Therefore, the reciprocal vector $q$ is varied by systemically adjusting $n_x, n_y, n_z$. The structure factor $F(q)$ is:

$$F(q) = \sum_{j=0}^{N} f_j(q) \exp(-iqr_j),$$

or equivalently,

$$F(h, k, l) = \sum_{j=0}^{N} f_j(h, k, l) \exp[2\pi * i(hx_j + ky_j + lz_j)].$$

$r_j = (x_j, y_j, z_j)$ denotes the coordinate of atom $j$. The atomic scattering factors $f(q)$ have been reported by Cromer and Mann using Hartree-Fock wave function, and fitted using the following analytical function:

$$f\left(\frac{\sin \theta}{\lambda}\right) = \sum_{i=1}^{4} a_i \exp\left(-b_i \frac{\sin^2 \theta}{\lambda^2}\right) + c.$$  

The fitting parameters, $a_i, b_i$, and $c$ ($i = 1, 2, 3, 4$), have been obtained for neutral atoms from He to Lw and for most ions through Lu\(^{3+}\). Note that the atomic scattering factor becomes the atomic number $Z$ under the condition of $\theta = 0$ (i.e., $q = 0$).

The scattering intensity, Eq. (7), is consequently rewritten as

$$I(q) = \frac{1}{N} A(q) \langle|\sum_{j,k} f_j(q) f_k(q) \exp[-iqr_j - qr_k]|\rangle.$$  

### Calculation of the Dipolar Energy between Neighbor Aggregates from Atomistic MD Simulations

Given the overall charge neutral feature of metal-centered reverse micelles in the systems investigated, the monopole interactions between the neighbor, charge neutral aggregates is reasonably expected negligible. The attractions between neighbor aggregates are supposed to originate from dipolar interactions or higher levels of multipolar interactions between them. To quantify this hypothesis, the
dipolar interactions are calculated between neighbor metal-centered mononuclear aggregates. It is obtained in the follow processes:

1) The distances between all Eu-centered mononuclear aggregates, \( r \), are calculated, with all the higher levels of oligomers excluded. Those Eu-Eu neighbors whose distances are within the range of 1.0 nm and 1.2 nm are labeled. These calculations are based on the coordinates of Eu\(^{3+}\) ions, which serve as the centers of the aggregates. This distance range corresponds to where the inter-cluster interactions dominate, as illustrated in Figure 8 in the main text.

2) All the ligands (water, nitrate, and DMDOHEMA) which are directly coordinating the labeled Eu\(^{3+}\) ions are marked. The cutoff distances from Eu to oxygen (water), nitrogen (nitrate) and the central carbon (i.e., C3) on DMDOHEMA are obtained from the minima after the primary correlation peaks on the corresponding \( g(r) \), which are 0.3, 0.38, and 0.52 nm, respectively. Note that under this algorithm, it is assumed that all the coordinating waters, nitrates, or DMDOHEMA headgroups are directly coordinating the central Eu\(^{3+}\) ions. This assumption works in system (b), but is not necessary true in system (d), where higher amounts of waters and DMDOHEMA headgroups are distributed in the second coordination shell of Eu\(^{3+}\) ions.

3) The dipole moment of the aggregate is thus calculated by

\[
\vec{\mu} = \sum_i \left[ (\vec{x}_a - \vec{x}_{Eu}) \cdot q_a \right].
\]  

(12)

Note the Eu\(^{3+}\) ion is considered as the center of the aggregate, and \( \vec{x}_a \) denotes the coordinate of atom \( a \) on the coordinating ligands. It is noteworthy that only the headgroup atoms of the DMDOHEMA molecules are taken into account in Eq. (12). It is noteworthy that these Eu-centered mononuclear aggregates are calculated to be exclusively charge neutral throughout the simulation trajectory, which is a prerequisite for a unique definition of dipole moment. 41

4) The dipolar interaction energy between clusters \( i \) and \( j \) is thus obtained by

\[
U = \frac{1}{4\pi\varepsilon_0 r^3} \left[ (\vec{\mu}_i \cdot \vec{\mu}_j) - 3(\vec{\mu}_i \cdot \hat{r})(\vec{\mu}_j \cdot \hat{r}) \right],
\]

(13)

where \( \vec{\mu}_i, \vec{\mu}_j \) is the dipole moment of clusters \( i \) and \( j \), respectively; \( \hat{r} \) stands for the unit vector between the two Eu\(^{3+}\) ions whose distance \( r \) is within the range of 1.0 and 1.2 nm.

5) The calculations (steps 1 - 4) are performed for all the aggregates throughout the simulation durations. The distribution of the calculated dipolar energies is provided in Figure S10.
Figure S10. Distribution of the dipolar interaction energies between two Eu-centered mononuclear aggregates with the Eu-Eu distance of 1.0 - 1.2 nm in the system (b). The attractions (< 0) dominate over the repulsions (> 0). The average dipolar energy is -0.6 ± 1.5 k_BT. This value is in good agreement with the effective inter-aggregate interactions of ΔG ≈ -0.7 k_BT estimated from the peak height on Eu-Eu g(r) (see Figure 8 and related discussion in the main text). It thus highlights the predominant contribution of the dipolar interactions to the effective inter-aggregate interactions.

SUPPORTING FIGURES
**Figure S11.** RDF between Eu-Eu and Eu-DMDOHEMA headgroup. The C3 atom (Scheme S1) is used to approximately represent the center of the DMDOHEMA headgroup. Two short Eu…C3 peaks in the RDF appear at around 4.1 Å and 4.7 Å, corresponding to bidentate and monodentate malonamide binding mode, respectively. Published crystal structures of Pr(III) nitrate complexes with alkyl malonamide ligands (although not DMDOHEMA as this does not crystalize) show bidentate Pr…C3 distances of 4.021 Å, which is close to the bidentate Eu…C3 distance measured in our simulations. Only bidentate mode appears in the solid state structures for lanthanide-malonamide complexes and unfortunately no crystal structures of Eu(III) nitrate with coordinatively bonded malonamides showed up in our search of the crystallography database.

![RDF between Eu-Eu and Eu-DMDOHEMA headgroup](image)

**Figure S12:** Snapshot of the trigonally-arranged trinuclear Eu-centered aggregate in system (d). Eu$^{3+}$ ions are colored in pink. The size of the disk-shaped structure of the hydrophilic region of this aggregate is given in the right.
**Figure S13.** One example of an elongated aggregate at the absence of Eu$^{3+}$ ions in solution (d). Hydrogen atoms of DMDOHEMA are omitted for the display.

**Figure S14:** A 7-member chain of self-associated DMDOHEMA molecules in solution (a). Hydrogen atoms of DMDOHEMA are omitted for the display.

**References:**

1. Qiao, B.; Demars, T.; Olvera de la Cruz, M.; Ellis, R. J. How Hydrogen Bonds Affect the Growth of Reverse Micelles around Coordinating Metal Ions. *J. Phys. Chem. Lett.* 2014, **5**, 1440-1444.
2. Gannaz, B.; Antonio, M. R.; Chiarizia, R.; Hill, C.; Cote, G. Structural study of trivalent lanthanide and actinide complexes formed upon solvent extraction. *Dalton Trans.* 2006, **(38)**, 4553-4562.
3. Iveson, P. B.; Drew, M. G. B.; Hudson, M. J.; Madic, C. Structural studies of lanthanide complexes with new hydrophobic malonamide solvent extraction agents. *J. Chem. Soc., Dalton Trans.* 1999, **3605-3610**.
4. Ellis, R. J.; Antonio, M. R. Coordination Structures and Supramolecular Architectures in a Cerium(III)-Malonamide Solvent Extraction System. *Langmuir* 2012, **28**, 5987-5998.
5. Fritz, G.; Glatter, O. Structure and interaction in dense colloidal systems: evaluation of scattering data by the generalized indirect Fourier transformation method. *J. Phys.: Condens. Matter* **2006**, *18*, S2403-S2419.

6. Fritz, G.; Bergmann, A.; Glatter, O. Evaluation of small-angle scattering data of charged particles using the generalized indirect Fourier transformation technique. *J. Chem. Phys.* **2000**, *113*, 9733-9740.

7. Brunner-Popela, J.; Mittelbach, R.; Strey, R.; Schubert, K. V.; Kaler, E. W.; Glatter, O. Small-angle scattering of interacting particles. III. D$_2$O-C$_{12}$E$_5$ mixtures and microemulsions with n-octane. *J. Chem. Phys.* **1999**, *110*, 10623-10632.

8. Percus, J. K.; Yevick, G. J. Analysis of classical statistical mechanics by means of collective coordinates. *Phys. Rev.* **1958**, *110*, 1-13.

9. Dejugnat, C.; Dourdain, S.; Dubois, V.; Berthon, L.; Pellet-Rostaing, S.; Dufreche, J.-F.; Zemb, T. Reverse aggregate nucleation induced by acids in liquid-liquid extraction processes. *Phys. Chem. Chem. Phys.* **2014**, *16*, 7339-7349.

10. Dejugnat, C.; Berthon, L.; Dubois, V.; Meridiano, Y.; Dourdain, S.; Guillaume, D.; Pellet-Rostaing, S.; Zemb, T. Liquid-Liquid Extraction of Acids and Water by a Malonamide: I-Anion Specific Effects on the Polar Core Microstructure of the Aggregated Malonamide. *Solvent Extr. Ion Exch.* **2014**, *32*, 601-619.

11. Berthon, L.; Testard, F.; Martinet, L.; Zemb, T.; Madic, C. Influence of the extracted solute on the aggregation of malonamide extractant in organic phases: Consequences for phase stability. *C. R. Chim.* **2010**, *13*(10), 1326-1334.

12. Nave, S.; Mandin, C.; Martinet, L.; Berthon, L.; Testard, F.; Madic, C.; Zemb, T. Supramolecular organisation of tri-n-butyl phosphate in organic diluent on approaching third phase transition. *Phys. Chem. Chem. Phys.* **2004**, *6*(4), 799-808.

13. Erlinger, C.; Belloni, L.; Zemb, T.; Madic, C. Attractive interactions between reverse aggregates and phase separation in concentrated malonamide extractant solutions. *Langmuir* **1999**, *7*(7), 2290-2300.

14. Erlinger, C.; Gazeau, D.; Zemb, T.; Madic, C.; Lefrancois, L.; Hebrant, M.; Tondre, C. Effect of nitric acid extraction on phase behavior, microstructure and interactions between primary aggregates in the system dimethyl dibutyl tetradecyl malonamide (DMDBTDMA) n-dodecane water: A phase analysis and small angle X-ray scattering (SAXS) characterisation study. *Solvent Extr. Ion Exch.* **1998**, *16*, 707-738.

15. Chiarizia, R.; Stepinski, D.; Antonio, M. R. SANS study of HCl extraction by selected neutral organophosphorus compounds in n-octane. *Sep. Sci. Technol.* **2010**, *45*(12-13), 1668-1678.

16. Antonio, M. R.; Chiarizia, R.; Gannaz, B.; Berthon, L.; Zorz, N.; Hill, C.; Cote, G. Aggregation in solvent extraction systems containing a malonamide, a dialkylphosphoric acid and their mixtures. *Sep. Sci. Technol.* **2008**, *43*, 2572-2605.

17. Chiarizia, R.; Briand, A.; Jensen, M. P.; Thiagarajan, P. SANS study of reverse micelles formed upon the extraction of inorganic acids by TBP in n-octane. *Solvent Extr. Ion Exch.* **2008**, *26*, 333-359.

18. Gannaz, B.; Chiarizia, R.; Antonio, M. R.; Hill, C.; Cote, G. Extraction of lanthanides(III) and Am(III) by mixtures of malonamide and dialkylphosphoric acid. *Solvent Extr. Ion Exch.* **2007**, *25*(3), 313-337.

19. Chiarizia, R.; Briand, A. Third phase formation in the extraction of inorganic acids by TBP in n-octane. *Solvent Extr. Ion Exch.* **2007**, *25*, 351-371.

20. Chiarizia, R.; Stepinski, D. C.; Thiagarajan, P. SANS study of third phase formation in the extraction of HCl by TBP isomers in n-octane. *Separation Science and Technology* **2006**, *41*(10), 2075-2095.

21. Barker, J. A.; Henderson, D. Perturbation theory and equation of state for fluids. II. Successful theory of liquids. *J. Chem. Phys.* **1967**, *47*, 4714-21.

22. Shrestha, L. K.; Shrestha, R. G.; Aramaki, K. Intrinsic parameters for the structure control of nonionic reverse micelles in styrene: SAXS and rheometry studies. *Langmuir* **2011**, *27*, 5862-5873.
23. Shrestha, L. K.; Yamamoto, M.; Arima, S.; Aramaki, K. Charge-free reverse wormlike micelles in nonaqueous media. *Langmuir* **2011**, *27*, 2340-2348.

24. Shrestha, L. K.; Sato, T.; Dulle, M.; Glatter, O.; Aramaki, K. Effect of lipophilic tail architecture and solvent engineering on the structure of trehalose-based nonionic surfactant reverse micelles. *J. Phys. Chem. B* **2010**, *114* (4), 12008-12017.

25. Sharma, S. C.; Shrestha, R. G.; Shrestha, L. K.; Aramaki, K. Viscoelastic wormlike micelles in mixed nonionic fluorocarbon surfactants and structural transition induced by oils. *J. Phys. Chem. B* **2009**, *113*, 1615-1622.

26. Shrestha, L. K.; Sharma, S. C.; Sato, T.; Glatter, O.; Aramaki, K. Small-angle X-ray scattering (SAXS) study on nonionic fluorinated micelles in aqueous system. *J. Colloid Interface Sci.* **2007**, *316*, 815-824.

27. Hess, B.; Kutzner, C.; van der Spoel, D.; Lindahl, E. GROMACS 4: Algorithms for Highly Efficient, Load-Balanced, and Scalable Molecular Simulation. *J. Chem. Theory Comput.* **2008**, *4* (3), 435-447.

28. Jorgensen, W. L.; Maxwell, D. S.; Tirado-Rives, J. Development and Testing of the OPLS All-Atom Force Field on Conformational Energetics and Properties of Organic Liquids. *J. Am. Chem. Soc.* **1996**, *118* (45), 11225-11236.

29. Siu, S. W. I.; Pluhackova, K.; Bockmann, R. A. Optimization of the OPLS-AA Force Field for Long Hydrocarbons. *J. Chem. Theory Comput.* **2012**, *8* (4), 1459-1470.

30. Sun, Y.; Kollman, P. A. Hydrophobic solvation of methane and nonbond parameters of the TIP3P water model. *J. Comput. Chem.* **1995**, *16* (9), 1164-1169.

31. van Veggel, F. C. J. M.; Reinhoudt, D. N. New, Accurate Lennard-jones Parameters for Trivalent Lanthanide Ions, Tested on [18]crown-6. *Chem. Eur. J.* **1999**, *5* (1), 90-95.

32. Benay, G.; Wipff, G. Liquid-Liquid Extraction of Uranyl by an Amide Ligand: Interfacial Features Studied by MD and PMF Simulations. *J. Phys. Chem. B* **2013**, *117* (24), 7399-7415.

33. Meridiano, Y. *These de Doctorat Theses*. Paris XI: Orsay, 2009.

34. Lefrançois, L.; Delpuech, J.-J.; Hébrant, M.; Chrisment, J.; Tondre, C. Aggregation and Protonation Phenomena in Third Phase Formation: An NMR Study of the Quaternary Malonamide/Dodecane/Nitric Acid/Water System. *J. Phys. Chem. B* **2001**, *105* (13), 2551-2564.

35. Martínez, L.; Andrade, R.; Birgin, E. G.; Martínez, J. M. PACKMOL: A Package for Building Initial Configurations for Molecular Dynamics Simulations. *J. Comput. Chem.* **2009**, *30* (13), 2157-2164.

36. Hess, B. P-LINCS: A Parallel Linear Constraint Solver for Molecular Simulation. *J. Chem. Theory Comput.* **2008**, *4* (1), 116-122.

37. Rodrigues, F.; Ferru, G.; Berthon, L.; Boubals, N.; Guilbaud, P.; Sorel, C.; Diat, O.; Bauduin, P.; Simonin, J. P.; Morel, J. P.; Morel-Desrosiers, N.; Charbonnel, M. C. New insights into the extraction of uranium(VI) by an N,N-dialkylamide. *Mol. Phys.* **2014**, *112* (9-10), 1362-1374.

38. Ferru, G.; Gomes Rodrigues, D.; Berthon, L.; Diat, O.; Bauduin, P.; Guilbaud, P. Elucidation of the Structure of Organic Solutions in Solvent Extraction by Combining Molecular Dynamics and X-ray Scattering. *Angewandte Chemie International Edition* **2014**, *53* (21), 5346-5350.

39. Róg, T.; Murzyn, K.; Hinsen, K.; Kneller, G. R. nMoldyn: A program package for a neutron scattering oriented analysis of molecular dynamics simulations. *J. Comput. Chem.* **2003**, *24* (5), 657-667.

40. Schottl, S.; Marcus, J.; Diat, O.; Touraud, D.; Kunz, W.; Zemb, T.; Horinek, D. Emergence of surfactant-free micelles from ternary solutions. *Chemical Science* **2014**, *5* (8), 2949-2954.

41. Dommert, F.; Schmidt, J.; Qiao, B. F.; Zhao, Y.; Krekeler, C.; Site, L. D.; Berger, R.; Holm, C. A comparative study of two classical force fields on statics and dynamics of [EMIM][BF[sub 4]] investigated via molecular dynamics simulations. *J. Chem. Phys.* **2008**, *129* (22), 224501-10.

42. Jackson, J. D. *Classical Electrodynamics 3rd Edition*. John Wiley & Sons, Inc.: 1999.