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Critical Fluctuations in Liquid-Liquid Extraction Organic Phases Controlled by Extractant and Diluent Molecular Structure

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Abstract

Extractant aggregation in liquid-liquid extraction organic phases impacts extraction energetics and is related to the deleterious efficiency-limiting liquid-liquid phase transition known as third phase formation. Using small angle x-ray scattering, we find that structural heterogeneities across a wide range of compositions in binary mixtures of malonamide extractants and alkane diluents are well described by Ornstein-Zernike scattering. This suggests that structure in these simplified organic phases originates from the critical point associated with the liquid-liquid phase transition. To confirm this, we measure the temperature dependence of the organic phase structure, finding critical exponents consistent with the 3D Ising model. Molecular dynamics simulations were also consistent with this mechanism for extractant aggregation. Due to the absence of water or any other polar solutes required to form reverse-micellar-like nanostructures, these fluctuations are inherent to the binary extractant/diluent mixture. We also show how the molecular structure of the extractant and diluent modulate these critical concentration fluctuations by shifting the critical temperature: critical fluctuations are suppressed by increasing extractant alkyl tail lengths or decreasing diluent alkyl chain lengths. This is consistent with how extractant and diluent molecular structure are known to impact metal and acid loading capacity in many-component LLE organic phases, suggesting phase behavior of practical systems may be effectively studied in simplified organic phases. Overall, the explicit connection between molecular structure, aggregation and phase behavior demonstrated here will enable the design of more efficient separations processes.

Introduction

The selective recovery of critical materials, including metals, enables a wide range of important technologies.[1,2] Owing to its scalability and low input energy requirements, liquid-liquid extraction (LLE) is a predominant method for separations of metals, including rare earth elements,[3–9] actinides,[10,11] and platinum group elements.[12] In LLE, amphiphilic extractant molecules bind metals, transferring them from a polar aqueous phase to an immiscible nonpolar organic phase.[13] The distribution of metals between the two phases depends on the difference in solvation free energy between those phases. As the energy difference needed for effective, reversible separations processes can be relatively small, even as small as the thermal energy, a frontier of separations research is understanding the impact of organic phase structure beyond the primary metal coordination sphere.[7,14–18] To that end, LLE systems are often modeled as microemulsions, where organic phase structure is treated as colloidal particles representing reverse micellar aggregates.[19–43]

An important limitation of LLE is third phase formation,[28,44] a liquid-liquid phase transition where, upon sufficient loading of polar solutes into the nonpolar organic phase, it splits into “heavy” and “light” phases. The heavy phase contains most of the extractant molecules and extracted polar species, while the light phase primarily consists of the organic solvent, also called the diluent.[45] The resulting three-phase system is incompatible with processing equipment, resulting in a limit to the per-contact loading capacity of the organic phase. While organic phase structure has long been linked to its phase behavior,[20,39,43,46–58] we recently proposed that organic phase structure over a wide range of binary extractant/diluent mixtures is consistent with critical fluctuations originating from the critical point associated with the third phase formation phase transition.[59,60] That is, organic phase structuring is consistent with what would be expected from the concentration fluctuations induced by the critical point associated with the liquid-liquid phase transition. For example, the largest length scales are typically observed for extractant volume fractions near 0.5, where the critical composition for the binary extractant/diluent mixture would be anticipated. This organic phase structural mechanism could explain certain limitations to common microemulsion descriptions of LLE systems, such as the presence of structure in the organic phase even in the absence of extracted polar solutes needed to induce the formation of water-in-oil aggregates.[61]

Our recent studies find that the fluctuations in many-component organic phases containing extracted acid, water and metal salts are quantitatively consistent with the theory of critical phenomena.[62] In particular, the scattering obeys an Ornstein-Zernike relation typical of critical fluctuations, with divergent behavior as the critical temperature for phase separation is approached that agrees with predictions for the 3D Ising model.[63,64] Since this universality class of phase transitions includes binary fluid mixtures, this indicates that pseudobinary critical fluctuations develop along a single compositional degree of freedom. This suggests that the theory of critical phenomena may provide a deep, quantitative connection between structure and phase behavior in LLE that can be meaningfully explored through simplified organic phases. To test this applicability of simplified organic phases to complex, realistic LLE organic phases, we investigate critical scaling through temperature dependence of organic phase structure in binary extractant/diluent mixtures, which allows us to compare critical behavior to more complex organic phases. We look to see if well-known relationships between extractant and diluent alkyl chain lengths and their impact on promoting or inhibiting third phase formation[44,65–68] can be reproduced in these simplified systems. If this were the case, it might suggest that screening of compatible extractant/diluent combinations can be conducted in simplified systems that are easier to study experimentally and computationally.

In this study, we explore the role of extractant and diluent molecular structure on organic phase aggregation in binary mixtures of extractant and diluent. (Here, we define compositions by the extractant volume fraction, φ_E.) We consider linear alkane diluents with a family of malonamide extractants, shown in Figure 1, which are commonly applied to lanthanide separations.[69–71] We use small angle x-ray scattering (SAXS) to quantify the concentration fluctuations associated with the phase instability over the full range of extractant/diluent compositions, for diluents and extractants of various molecular lengths. For the organic phase having a critical temperature, T_C, closest to room temperature, we measure temperature-dependent SAXS patterns to obtain critical exponents. Then, we investigate this mechanism of organic phase aggregation with molecular dynamics (MD) simulations. Our findings suggest that critical fluctuations could be responsible for the widely reported nanostructuring found in a wide range of LLE organic phases.

Methodology

Sample Preparation

Purified extractants *N*,*N*'-dimethyl,*N*,*N*'-dibutyltetradecylmalonamide (DMDBTDMA, $>$ 99% purity by HPLC) and *N*,*N*'-dimethyl,*N*,*N*'-dibutylpentylmalonamide (DMDBPMA, $>$ 98% purity by HPLC) were purchased from Technocomm Ltd and *n*-alkanes were purchased from Sigma-Aldrich ($>$ 99% purity). All reagents were used as-received. Samples for each composition were prepared by massing extractant (density of DMDBTDMA = 0.908 g/cm^3; density of DMDBPMA = 0.935 g/cm^3) followed by volumetric dilution with the corresponding diluent. Volume fractions and concentrations of each sample are given in Table S1.

SAXS Experiments

SAXS measurements at fixed temperature, 298 K (25° C), were conducted at beamline 12-ID-C[72] at the Advanced Photon Source (APS). Samples were loaded into a 2-mm-outer-diameter quartz capillary. Data was collected from a Pilatus 2M detector with a 0.000475 Å^{-1} Q-spacing using a 2.133 m sample-to-detector distance and an 18 keV incident energy. Scattering patterns were normalized to an absolute scale after empty capillary subtraction using scattering from pure water.[73] All SAXS patterns were averaged over five one-second exposures. Variable temperature SAXS measurements were conducted at beamline 8-ID-I at the APS, with experimental details the same as those described by Sheyfer et al.[64] Sample temperature was stepped in 0.2 K increments and monitored to 0.1 K accuracy with type K thermocouples.

Molecular Dynamics Simulations

The simulation force field details and methodology are the same as we previously reported.[59] Simulation compositions are reported in Table S2. Simulations were conducted with the GROMACS 2016.2 software package.[74] Force field details for DMDBPMA and dodecane are reported in Ref. 61. Initial configurations were created with Packmol,[75] followed by energy minimization using a steepest descent algorithm. Each simulation was equilibrated for 5 ns in the NPT ensemble, followed by 20 ns of equilibration in the NVT ensemble and 50 ns of production in the NVT ensemble. In the NPT ensemble, pressure was set to 1 bar with the Berendsen barostat[76] using a 2 ps coupling time and temperature was set to 300 K using a 0.2 ps coupling time with the velocity rescale thermostat.[76] In the NVT ensemble, temperature was set to 300 K with the Nosé-Hoover thermostat[77] with a 0.2 ps coupling time. Dynamics were conducted using a 2 fs time step using the leap-frog Verlet integrator,[78] with hydrogen-containing bonds constrained using the LINCS algorithm.[79] A 15 Å cutoff was used for Lennard-Jones and short-range electrostatic interactions, with particle-mesh Ewald summation used for long-range electrostatics.[80] Trajectories were sampled for analysis at 100 ps intervals.

Results

Phase Behavior and Effect of Extractant and Diluent Chain Lengths

Practical LLE systems contain an aqueous and organic phase where, after splitting, the dense organic phase is referred to as the third phase. In this study we consider just the organic phase such that the associated phase transition is from one phase to two. In this case, the extractant-rich organic phase of the binary mixtures in this study corresponds to the so-called third phase. Third phase formation is widely associated with organic phase separation upon cooling;[60,63–65,81] Figure 1A shows the T-φ_E diagram with this upper critical solution temperature (UCST) behavior. We consider two extractants: DMDBTDMA and DMDBPMA, shown in Figure 1. The former is commonly applied to rare earth separations while the latter is a more hydrophilic analog that has been used to investigate the role of extractant lipophilicity.[59,82,83] As illustrated in the schematic phase diagrams in Figure 1B, organic phase mixtures are prepared with φ_E increments of 0.10 for combinations of DMDBPMA with hexane, octane, decane, dodecane and hexadecane, and DMDBTDMA mixtures are prepared with dodecane. By varying the lengths of the diluent with DMDBPMA and separating varying the extractant tail length for just dodecane, we can isolate the effects of both molecular structural changes. While the critical temperature for DMDBPMA/hexadecane is measured in the following section, the shape of the coexistence curve and relative location for each mixture are only intended to be schematic and are inferred from the strength of the concentration fluctuations measured at room temperature, as discussed below.

Organic phase structure across the phase diagram is quantified to understand the extent of critical fluctuations in these systems. For aggregation driven by such fluctuations, we expect increased lengthscales associated with compositions near the critical point. Scattering data for the DMDBPMA systems are plotted in Figure 2, and data for DMDBTDMA in Figure 3. Using the Ornstein-Zernike equation,

$$I(Q) = \frac{I_{Q=0}}{1 + (\xi Q)^{2-\eta}} + B, \tag{1}$$

which describes scattering intensity, $I(Q)$, as a function of scattering wavevector, Q, resulting from critical fluctuations,[62] where we fit the scattering at zero wavevector, $I_{Q=0}$, the correlation length, ξ, and background (noncritical) scattering, B, for each mixture. Fits are

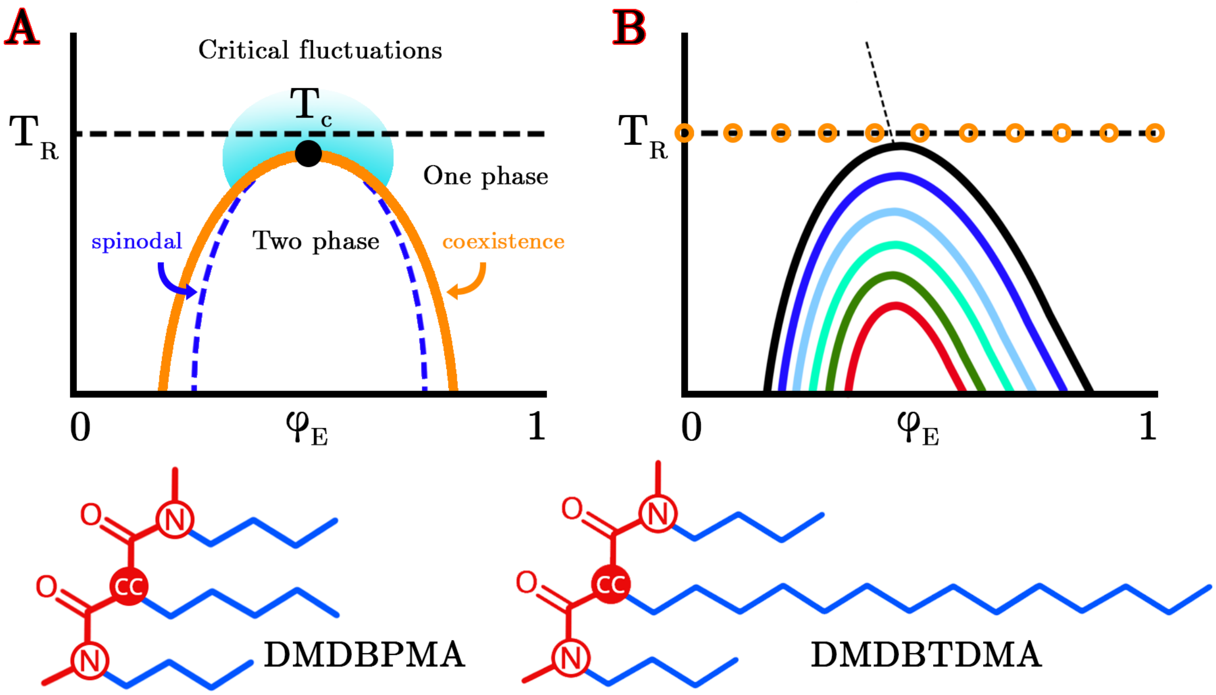

Figure 1: (A) A schematic phase diagram for these organic phases showing a typical upper critical solution temperature, with the region of critical fluctuations above the spinodal curve highlighted. (B) Schematic phase diagrams are shown for different binary mixtures considered in this study. The critical temperature, T_C, decreases with shorter diluent hydrocarbon chains and longer extractant chains: the black curve through the dark green curve in order of descending T_C corresponds to DMDBPMA mixtures with hexadecane, dodecane, decane, octane and hexane, respectively. The red curve corresponds to DMDBTDMA/dodecane. Orange open circles correspond to samples taken at room temperature (T_R) at various extractant volume fractions, φ_E. The Widom line (dashed) is also illustrated for one mixture. Below, the two malonamides of interest, DMDBPMA and DMDBTDMA, are shown with "central carbon" (CC) atoms highlighted.

shown in Figures 4 and 5 for DMDBPMA and DMDBTDMA, respectively, with fitted values plotted in Figure S1. Here, we assume classical Ornstein-Zernike behavior, taking the Fisher dimensional anomaly exponent,[84,85] η, to be zero. Classical Ornstein-Zernike theory assumes spherically symmetric fluctuations. Any asphericity that occurs in real systems lowers the fractal dimension of the fluctuations, resulting in small positive values of η. In the following section, we fit η along with the other static critical exponents using temperature-dependent scattering data.

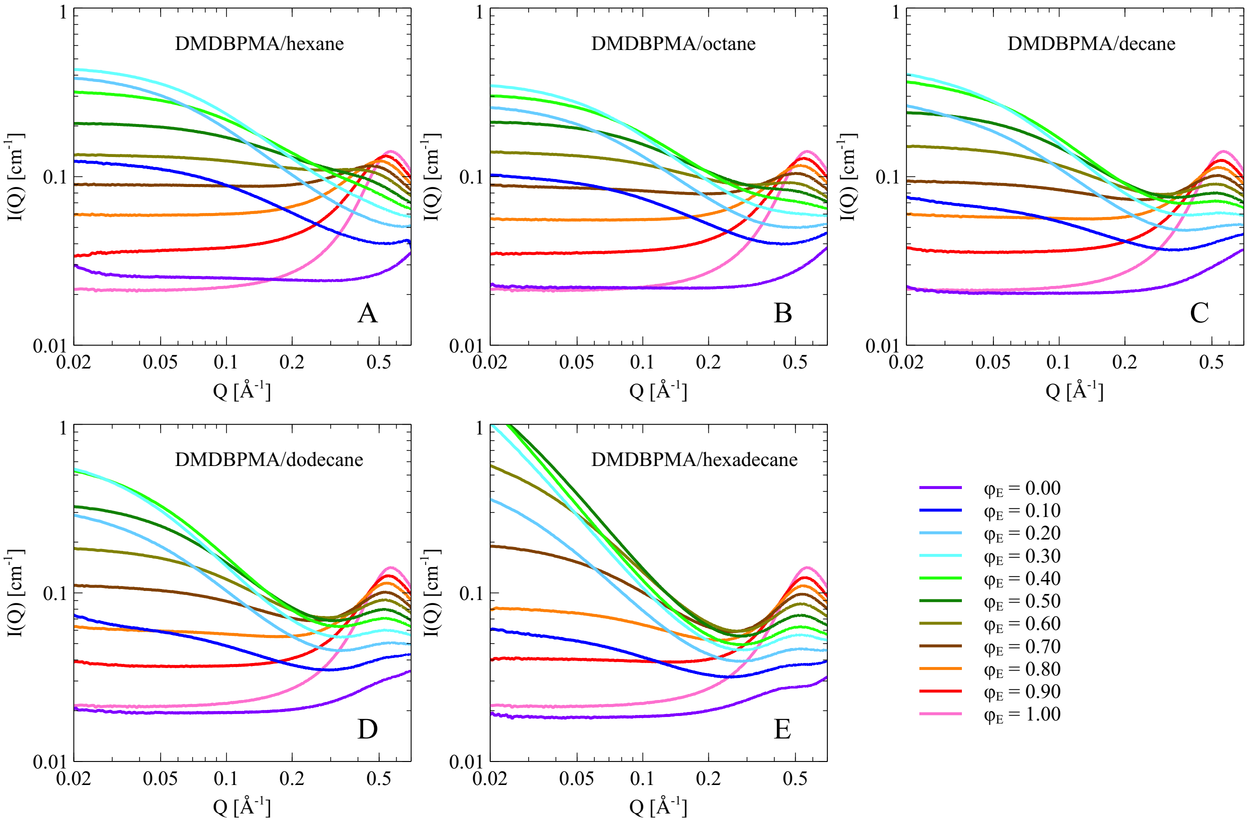

Figure 2: The SAXS patterns for each DMDBPMA mixture, defined by extractant volume fraction, φ_E, are shown in panels A-E for increasing diluent chain length from hexane to hexadecane.

While the above approach provides good fits for many of our systems, the behavior of the fitted parameters are inconsistent at high values of φ_E, where the strength of the critical fluctuations are weakest, as shown in Figures S1. In particular, best-fit values of $I_{Q=0}$ can become negative and the fitted background scattering, B, increases with φ_E compared to

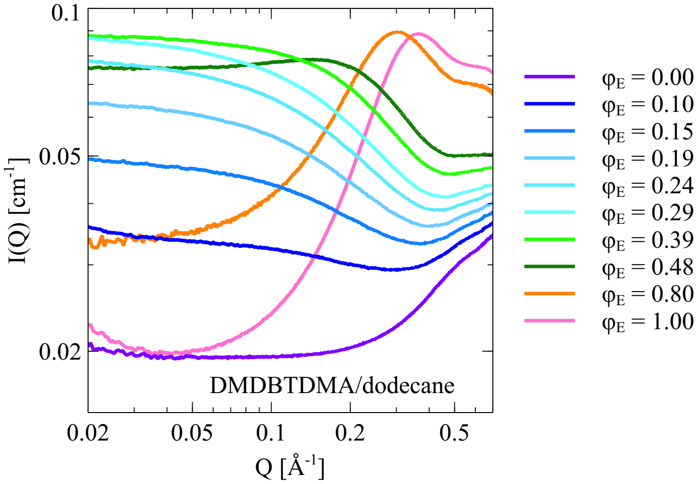

Figure 3: The SAXS patterns are plotted for each DMDBTDMA mixture with dodecane.

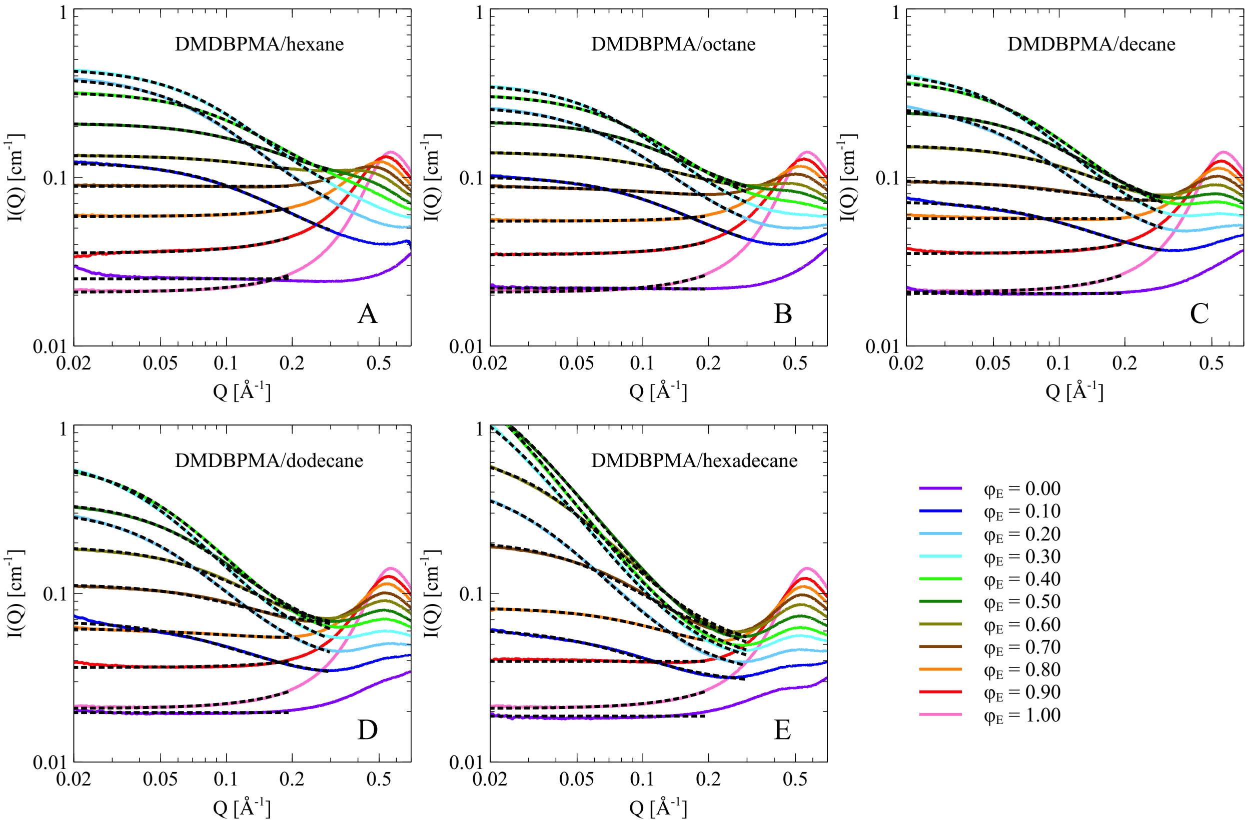

Figure 4: Ornstein-Zernike fits to the lower Q region of the total scattering intensity, as given in Eq. 1, are shown for each DMDBPMA/alkane mixture.

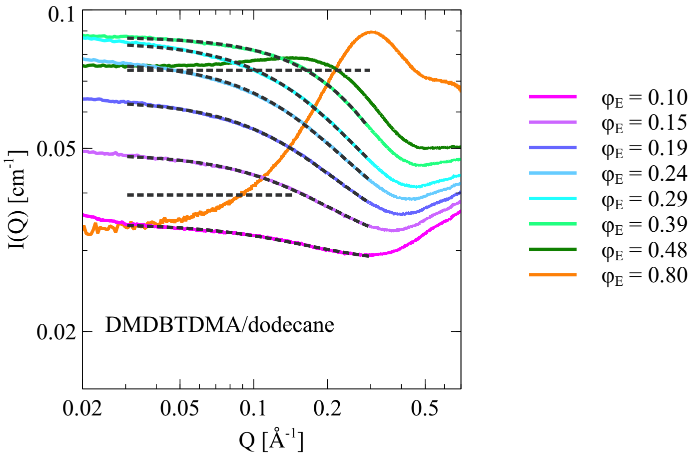

Figure 5: Ornstein-Zernike fits to the total scattering intensity between Q = 0.03 and 0.3 Å^{-1}, as given in Eq. 1, are shown for DMDBTDMA/dodecane mixtures.

the weighted average of the pure components. To address this, we instead fit $I(Q)_{\text{sub}}$ to the Ornstein-Zernike equation,

$$I(Q)_{sub} \equiv I(Q) - [\varphi_E I(Q)_{\text{ext}} + (1-\varphi_E) I(Q)_{\text{dil}}] = \frac{I_{Q=0}}{1+(\xi Q)^2}, \tag{2}$$

where we have subtracted the weighted average of the scattering of the pure extractant and diluent, $I(Q)_{\text{ext}}$ and $I(Q)_{\text{dil}}$, respectively, from $I(Q)$. By subtracting the pure component scattering patterns, the remaining scattering results from the structural correlations present in the solution: in this case, the structure factor associated with the concentration fluctuations. The Ornstein-Zernike fits to $I(Q)_{\text{sub}}$ are shown in Figures 6 and 7 for DMDBPMA and DMDBTDMA, respectively, with comparisons of the fitted ξ and $I_{Q=0}$ values from $I(Q)$ and $I(Q)_{\text{sub}}$ in Figure S1. Comparing the trends with φ_E for these two fitting approaches, it is clear that we obtain better fits after subtracting the weighted average of the pure components. At middling extractant volume fractions where the fluctuations are strongest, the trends in ξ and $I_{Q=0}$ are the same, with larger absolute values using $I(Q)$. However, at high φ_E where the Ornstein-Zernike scattering is relatively small, its fit is disrupted by the higher-Q pre-peak near 0.5 Å^{-1} that is characteristic of the pure extractant SAXS patterns. As a result, subtracting the pure component scattering patterns provides a significant improvement to the fitting (see Figure S1). Additionally, the fit to background scattering, B, is also strongly affected by the pre-peak for the fit to $I(Q)$. As B is proportional to the volume fraction-weighted average of the two pure components—which is removed when calculating $I(Q)_{sub}$—it is effectively fixed and removed from the fit. Therefore, we proceed with our analyses using this approach.

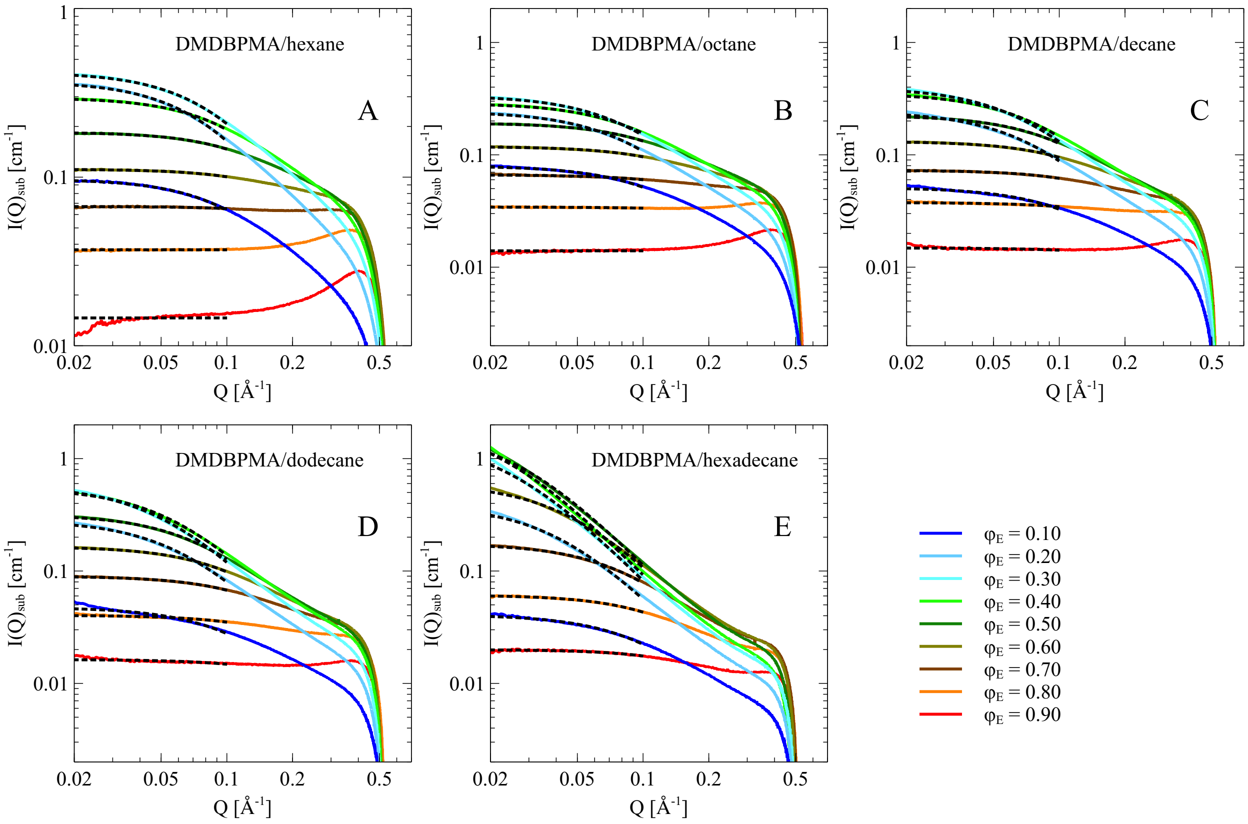

Figure 6: Ornstein-Zernike fits to the lower Q region of the scattering intensity with weighted average of the pure components subtracted, as given in Eq. 2, are shown for each DMDBPMA/alkane mixture.

Overall, we find the low-Q region of $I(Q)_{\mathrm{sub}}$ in all of the mixtures for each extractant and diluent pair are described well by the Ornstein-Zernike equation. The fitted values of ξ and $I_{Q=0}$ are shown in Figure 8A-B for each system. In each binary mixture, these properties exhibit maxima near $\varphi_E = 0.20 - 0.40$. This behavior is consistent with the compositional isotherm for $T > T_C$ crossing the Widom line in the single-phase region. The Widom line, illustrated in Figure 1B, is defined as the locus of correlation length maxima extending from

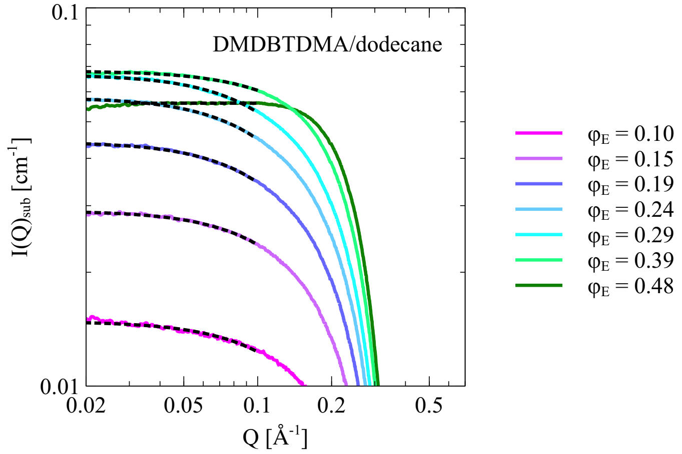

Figure 7: Ornstein-Zernike fits to the region between $Q = 0.03$ and 0.15 Å^{-1} of the scattering intensity with weighted average of the pure components subtracted, as given in Eq. 2, are shown for DMDBTDMA/dodecane mixtures.

the critical point into the single phase region.[86–92] Along the critical isotherm, $T = T_C$, the correlation length diverges at the critical composition; for $T > T_C$, it instead reaches a maximum at the Widom line with the strength of this maximum increasing as T approaches T_C (see discussion of temperature scaling in the following section). The Widom line is often conceptualized as demarcating the transition between low- and high-density-like mixtures, such as liquid-like and gas-like regions above T_C for a liquid-vapor critical point,[89,92] or low- and high-density-like water mixtures above the liquid-liquid critical point in supercooled water.[86,88,90] For the liquid-liquid critical point associated with third phase formation, the low-density compositions corresponds to extractant clustering within the nonpolar alkane diluent, while the high-density corresponds to the inverse case. While there is no thermodynamic phase transition separating extractant-in-diluent mixtures from diluent-in-extractant, the location of the Widom line at a given T represents the composition at which the two components are most strongly interspersed.

The molecular structure of the extractant and diluent strongly affects the critical fluctuations at room temperature, both in magnitude and the location of the Widom line. Figure 8 shows how decreasing diluent chain length reduces the strength of fluctuations. Shorter diluent alkyl chain lengths result in diluent molecules that more easily solvate, or "wet,"

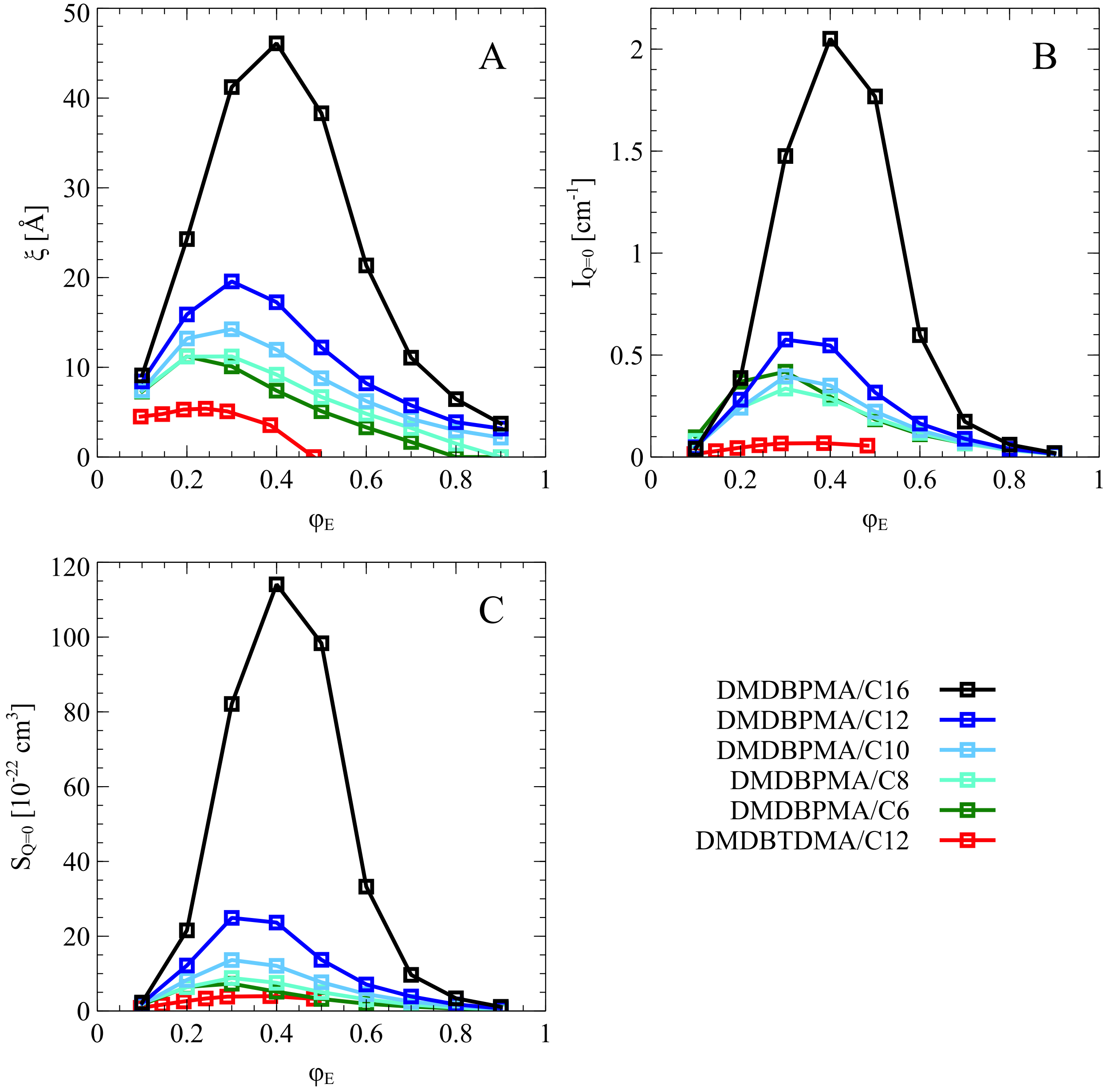

Figure 8: The fitted ξ (A), $I_{Q=0}$ (B) and $S_{Q=0}$ (C) values are plotted for each binary mixture.

the bulkier extractant molecules, thereby increasing the solubility of the extractant and reducing T_C. This is consistent with how shorter alkane diluents are widely understood to promote inhibit third phase formation.[44,65–68] The fact that trends in third phase formation are consistent with trends in concentration fluctuations of the binary mixture suggests a similar mechanism of extractant/diluent compatibility in both cases. The description of shorter alkane diluents better wetting or solubilizing the metal-extractant complexes/reverse micelles, inhibiting their self-association, is consistent with the reduced concentration fluctuations we observe in simplified binary organic phases. Interestingly, some compositions of the DMDBPMA/hexane mixture have larger values of $I_{Q=0}$ (but not ξ) than longer alkanes. This can be attributed to the larger density difference between shorter alkane diluents and the extractant than for longer alkanes (DMDBPMA has a mass density of 0.935 g/cm^3 compared to 0.750 g/cm^3 for dodecane and 0.655 g/cm^3 for hexane[93]), which contributes to $I_{Q=0}$ but not ξ.[94,95] Decreasing diluent chain length reduces the correlation length of fluctuations less and less at smaller chain lengths, but the decrease in diluent density remains roughly linear with chain length. Therefore, the contribution to $I_{Q=0}$ from the increasing difference in density between the two components out-competes the decrease in concentration fluctuations at sufficiently low diluent chain length. We account for this by converting $I_{Q=0}$ to a structure factor using

$$S_{Q=0} = \frac{I_{Q=0}}{r_e^2(\rho_{e,ext} - \rho_{e,dil})^2}, \tag{3}$$

where $\rho_{e,ext}$ and $\rho_{e,dil}$ are the electron densities of the extractant and diluent, respectively, and r_e^2 is the Thomson scattering length.[96] The relationship between $S_{Q=0}$ and composition is plotted for each system in Figure 8C, demonstrating that fluctuations decrease monotonically with decreasing diluent chain length.

We find that increasing the extractant chain length also reduces T_C, which is consistent with the widely reported impact of extractant chain length for malonamides[66] and other classes of extractant.[67] The solubility of the extractant in the diluent is driven by the lipophilicity of the partially polar extractant molecule, such that longer alkyl chain lengths result in an extractant that is more soluble in the nonpolar diluent. As with the role of diluent chain length above, this indicates the phase stability of simple binary mixtures can provide insight into more complex organic phases. However, another change in structure along the room temperature isotherm occurs as T_C is lowered: the correlation length maximum moves to lower extractant volume fractions. That is, more extractant is needed to maximize fluctuations the stronger those fluctuations are. This is attributed to the negative slope of the Widom line in the $\varphi_E - T$ phase diagram that is imparted by the asymmetry in the high- and low-density branches of the liquid-liquid coexistence curve. This impacts the slope of the line of rectilinear diameters, which the Widom line tracks into the single phase region.[92,97,98]

Temperature Scaling and Critical Exponents

To definitively demonstrate that the structural heterogeneities observed from small angle scattering are dominated by critical fluctuations—and to measure the associated critical exponents—we investigate the temperature scaling of the extractant/diluent mixture having its critical point closest to room temperature. For this mixture, DMDBPMA and hexadecane, we select the composition with the strongest room-T critical fluctuations: $\varphi_E = 0.40$. We measure the scattering at low Q while lowering T toward T_C. In this regime, we can fit the data with Eq. 1 with $B = 0$. From critical point theory, the temperature scaling of ξ and $I_{Q=0}$ are expected to follow power laws given by

$$\xi(\epsilon) = \xi_0 \epsilon^{-\nu} \tag{4}$$

and

$$I_{Q=0}(\epsilon) = I_0 \epsilon^{-\gamma}. \tag{5}$$

Here, ϵ is the reduced temperature, defined as

$$\epsilon \equiv (T - T_{sp})/T_{sp}, \tag{6}$$

where T_{sp} is the spinodal temperature, which is equal to T_C at the critical composition. The critical exponents, γ and ν, and the Fisher dimensional anomaly exponent are expected to be related through[84,85]

$$\gamma = \nu(2 - \eta). \tag{7}$$

As shown in Fig. 9A, the scattering patterns for this mixture show increased critical fluctuations with decreasing temperature, as expected for UCST behavior. Also shown is a simultaneous fit of the scattering at all temperatures using independent values of ξ and $I_{Q=0}$ at each T, but a single value of η, as done previously in Ref. 64. Using these values, all curves collapse onto a single master curve, Fig. 9B. Values of exponents γ and η and the associated T_{sp} are obtained from fits shown in Fig. 10A and reported in Table 1. The fitted critical exponents are consistent with the 3D Ising model, having reported values of $\nu = 0.63$ and $\gamma = 1.24$.[99] The temperature scaling observed here is the same as we previously reported for complex, five-component malonamide/dodecane organic phases.[64] This highlights the universality of critical phenomena in its ability to describe a wide range of LLE organic phases, even when the nature of the aggregation is driven by different types of intermolecular interactions, i.e., amphiphile self-association versus clustering of extractant-metal complexes.

Aggregation from Molecular Dynamics Simulations

Molecular simulation can provide a real-space description of solution structure, revealing the microscopic origins of aggregation. Figure 11A illustrates the nanoscale heterogeneities in extractant concentration that are evident from visual inspection of the simulation trajectories. In our previous Letter,[59] we quantified extractant clustering from simulation in this

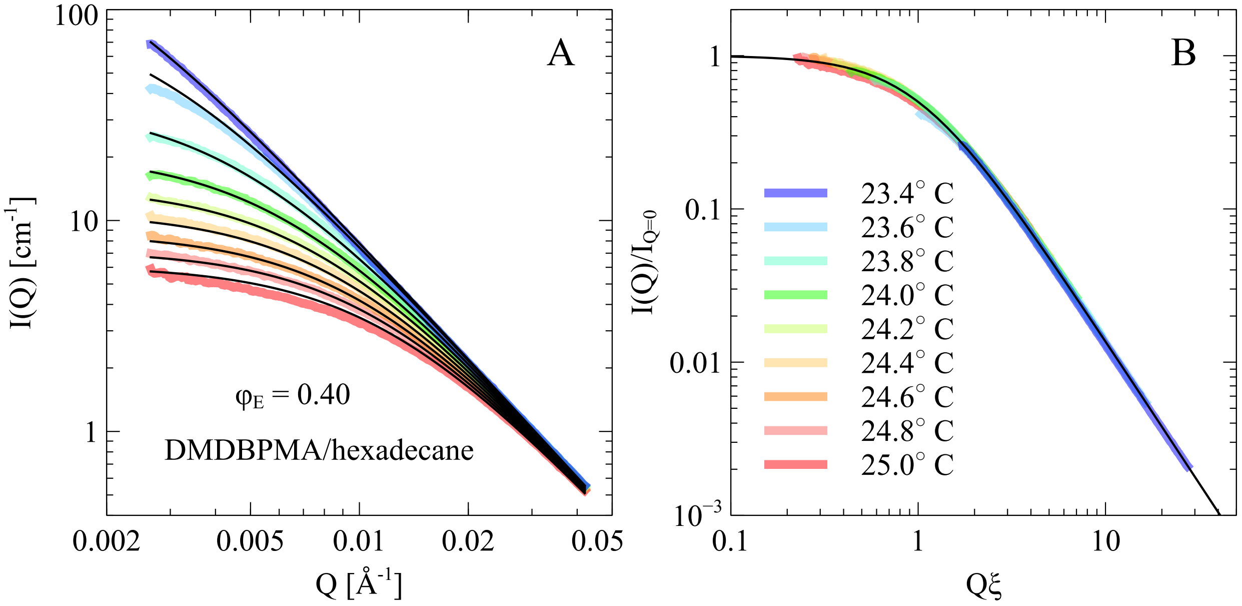

Figure 9: SAXS patterns (A) and master curve (B) for the $\varphi_E = 0.40$ DMDBPMA/hexadecane mixture is shown for each temperature.

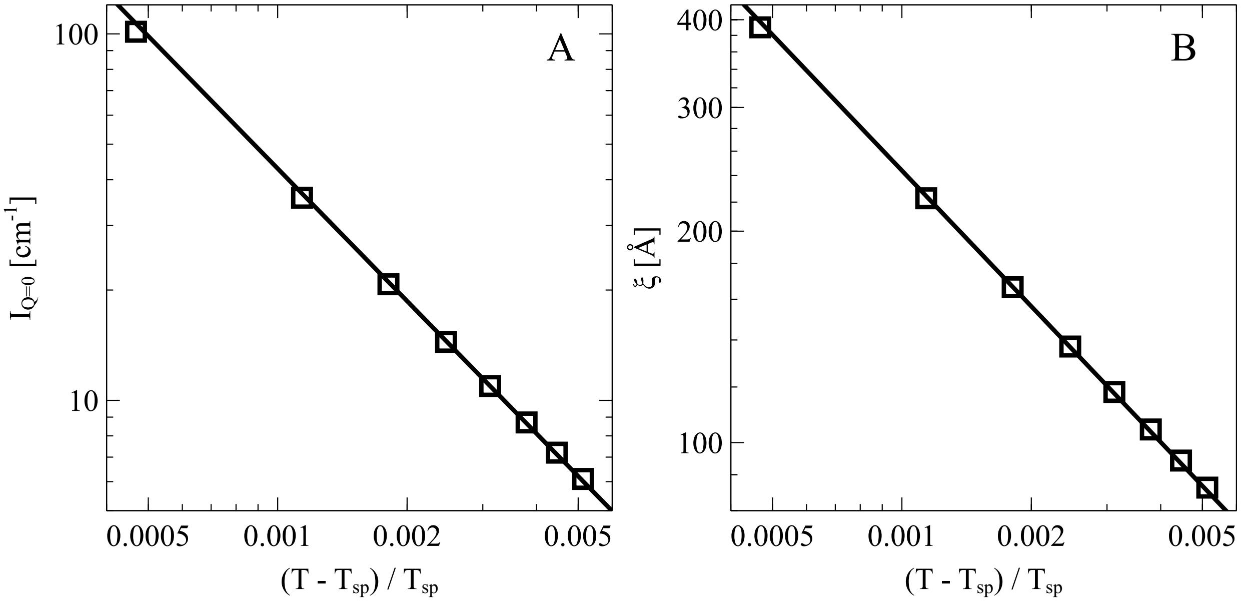

Figure 10: Power law fits of temperature scaling for the $\varphi_E = 0.40$ DMDBPMA/hexadecane mixture are shown for $I_{Q=0}$ (A) and ξ (B).

Table 1: Fitted parameters and critical exponents from DMDBPMA/hexadecane mixture for $\varphi_E = 0.40$.

Fisher exponent η	0.13 ± 0.01
Critical exponent ν	0.64 ± 0.02
Critical exponent γ	1.20 ± 0.04
$(2-\eta)\nu$	1.20
Correlation ampl. ξ_0 [Å]	2.89 ± 0.34
Scattering ampl. I_0 [cm^{-1}]	0.0107 ± 0.0027
T_{sp} from ξ [K]	296.63 ± 0.01
T_{sp} from $I_{Q=0}$ [K]	296.63 ± 0.01

system, discussing the relative locations of the percolation and Widom lines and qualitatively comparing extractant cluster size distributions to the 3D Ising model. Here, we select four simulation compositions from the data reported in that study for DMDBPMA/dodecane mixtures to describe extractant aggregation under different conditions with increasing φ_E: below the percolation threshold, at the percolation threshold, above the percolation threshold, and for pure DMDBPMA.

Extractant aggregation is quantified by using both geometric and thermodynamic descriptions. For the geometric description, a graph-theoretic cluster analysis is performed on the extractant molecules[59,61,100] using the position of the carbon connecting the two amide groups and a distance cutoff of 10 Å, taken from the first minimum in the radial distribution function (RDF) for pairs of that atom type (see Figure 11). At low φ_E ($\varphi_E = 0.08$), we find that the cluster sizes are exponentially distributed. At $\varphi_E = 0.18$, the distribution is a power law with exponent consistent with the percolation critical exponent for cluster size in three dimensions, $\tau = 2.19$.[101] Then, at higher φ_E, a spanning cluster exists in dynamic equilibrium with exponentially distributed clusters of finite size. Lastly, with $\varphi_E = 1.00$, there is a single spanning cluster. Overall, these broad distributions of cluster sizes indicate that extractant self-association does not feature characteristic aggregate sizes in any concentration regime. Monodisperse particle models, such as the spherical tetramers or larger rod-like reverse micelles[82] that have been proposed in the literature are, therefore, not necessarily appropriate for organic phases dominated by critical concentration fluctuations of

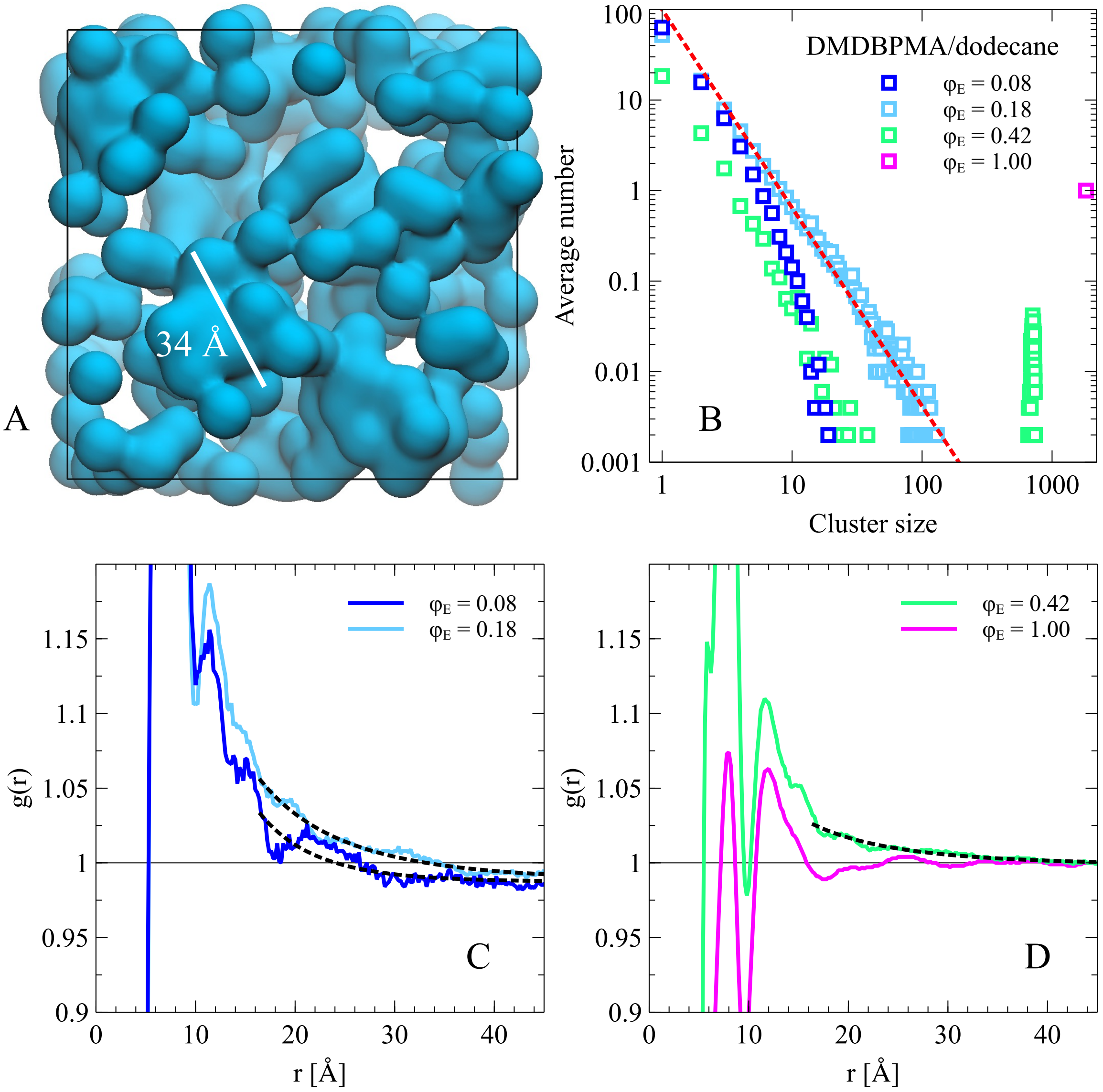

Figure 11: Panel A shows a snapshot from the $\varphi_E = 0.18$ DMDBPMA/dodecane mixture with a surface representation of the extractant molecules using the positions of the "CC" amide-bridging carbon atoms. Diluent is omitted for clarity. Panel B shows the extractant cluster size distributions for each of the four simulations. The red dashed line is the power law distribution for cluster sizes in three dimensions from percolation theory. Panels C and D show the CC-CC RDFs for each simulation, with fits to the long-range decay using the experimental correlation lengths drawn with dashed black lines.

the binary extractant/diluent mixture. The temperature dependence of scattering patterns or other measures of particle size, such as diffusivity,[36] may assist differentiation of structure factor and particle factor contributions to scattering. As we previously noted,[59] geometric and thermodynamic descriptions of solution structure are not identical and the divergence of the mean cluster size and the maximum of the Ornstein-Zernike correlation length do not generally coincide.[59,92,102] For a second approach to quantifying solution structure, next we directly measure the thermodynamic concentration fluctuations observed from the simulations.

For the thermodynamic approach, we quantify the critical fluctuations using the same Ornstein-Zernike approach as applied to the experimental scattering data. While directly fitting the correlation length from simulation scattering patterns is not possible due to finite simulation sizes and the large Q-spacing of the Fourier transformed pair correlation functions at low Q, we can observe the concentration fluctuations in real space. The total density-density correlation function decays as $r^{-1}e^{-r/\xi}$ in classical Ornstein-Zernike theory[62,103,104] for a unary system, where this functional form is obtained from the Fourier transform of the Ornstein-Zernike equation (Eq. 1) with $\eta = 0$. For the binary mixture here, where self-association of the extractant drives concentration fluctuations, we consider the long-range decay of DMDBPMA head group correlations defined by the same RDF described above. Figure 11C-D plots these RDFs with fits to $g(r) = Ar^{-1}e^{-r/\xi} + C$, where A and C are constants that are fit and ξ is taken from the experimental fit of the closest corresponding experimental volume fraction. (By fitting C, rather than assuming a value of unity, we allow for deviation to slightly lower values due to finite size effects of the simulation box where local concentration enhancement depletes the observed bulk concentration.) The simulation data are consistent with this form of the long-range decay, particularly at the higher extractant concentrations where the statistical accuracy of the RDF is best. No long-range decay in $g(r)$ is observed for the pure DMDBPMA simulation as there are no concentration fluctuations in the pure phase. We note that the fitted values of the correlation length are sensitive to the range of r values over which the data are fit, and we expect that longer simulation trajectories and larger simulation box sizes would improve the accuracy of fitted correlation lengths. Overall, simulation data suggest that extractant clustering is consistent with critical concentration fluctuations lacking characteristic aggregates sizes. The combination of long-range decay of concentration fluctuations (from the CC-CC RDFs in Fig. 11) with the lack of characteristic cluster size (no peak in cluster size distributions at finite non-spanning cluster sizes) indicates that the mechanism of structural heterogeneity observed in simulation is consistent with critical concentration fluctuations.

Conclusions

Organic phase aggregation is an important—yet poorly understood—phenomenon in LLE. While its connection to third phase formation has been implicitly understood in the literature, we have only recently proposed that the mechanism of aggregation is associated with the liquid-liquid critical point. Here, we demonstrated this explicit relationship by quantifying organic phase structure over a wide composition range for binary extractant/diluent mixtures. We expand on our previous work on binary malonamide-based organic phases[59] by performing SAXS measurements for combinations of extractant and diluent alkyl chain lengths, as well as measuring temperature scaling for one mixture. We find that structure in these simple binary systems are dominated by critical fluctuations that are characterized by 3D Ising exponents. Molecular dynamics simulations are consistent with this mechanism of extractant aggregation, showing a lack of characteristic aggregate size.

As the complex multicomponent organic phases that we previously studied[63,64] also feature 3D Ising exponents, interpreting structure in organic phases using the theory of critical phenomena is likely generalizable and approachable with simplified model systems. The systems we study here contain no aqueous solutes, such as metals or coextracted acid or water, demonstrating critical fluctuations are fundamental to the extractant/diluent mixture and the same scaling laws can describe structure in both simple and complex organic phases. We find well-known relationships between phase behavior and extractant and diluent molecular structure are the same as for metal- and acid-containing LLE systems: increasing extractant chain length or decreasing diluent chain length suppresses third phase formation and therefore the critical fluctuations. This suggests that high-throughput screening of compatible extractant/diluent pairs that suppress third phase formation might, to first order, be achievable by considering simplified binary mixtures. This could dramatically simplify experimental testing and computational modeling.

Many studies on organic phase aggregation report small angle scattering patterns that could be consistent with critical fluctuations,[21,23,33,35,37,39,41,42,49,105–113] potentially representing a different or additional mechanism driving aggregation than the formation of water-in-oil reverse micellar nanostructures. The universality of critical phenomena means that critical fluctuations are similar between chemically different systems once each system is scaled to its respective critical temperature, even when the molecular-level interactions driving the phase transition are fundamentally different. The correlation length obtained from the Ornstein-Zernike equation represents a characteristic length over which the concentration fluctuations decay. As we find a single diverging lengthscale with temperature scaling consistent with the binary 3D Ising model in both simple and complex systems, Lorentzian-shaped low-Q scattering alone cannot be taken as evidence of any particular nanostructure, such as reverse micellization. Future studies should investigate whether structure in more complex systems is dominated by concentration fluctuations of the extractant or the formation of larger, discrete aggregates or some combination of the two. Overall, this study suggests how critical phenomena theory may provide an explicit, quantitative connection between structure and phase behavior under a wide range of solution conditions encountered in LLE.

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Supporting Information

Sample and simulation compositions, and comparison between Ornstein-Zernike fitting methods are provided in the Supporting Information.

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