Amphiphile-Based Complex Fluids: The Self-Assembly Ensemble as Protagonist

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Multimodal characterization and multiscale simulation reveal new insights into hierarchical self-assembly that challenges simplified interpretations of structured fluids.

Amphiphilic self-assembly leads to the formation of complex, structured fluids whose physicochemical properties can be tuned by the composition and morphological distributions of the assembled species. The generally weak energetic attractions between amphiphilic molecules lead to a large chemical space of structural diversity—an ensemble of species dynamically evolving in time and where specific assemblies may have unique behavior. This attribute supports the ubiquity of these fluids within industry (for example, solvent extraction or cleaning detergents) and basic science (for example, the study of liquid interfaces, shear-induced thinning of emulsions, and the synthesis of nanoparticles).

The thought-provoking work of Motokawa et al.\textsuperscript{1} addresses the historically intriguing and unfolding story of the self-assembly ensemble within the dense-structured fluids that underpin solvent extraction (also called liquid−liquid extraction, LLE). As one of the most industrially important separation methods, LLE is generally performed under conditions where the concentration of extracted species approaches the saturation limit. Discrete molecular-scale complexes are observed to undergo supramolecular assembly, where below the critical concentration, they may be transported to the organic phase. At higher concentrations, a dense phase begins to form at the oil:water phase boundary followed by phase separation.\textsuperscript{2,3} Such third phase formation, and the subsequent efficacy of the separation, is exquisitely sensitive to the exact type and concentration of the amphiphilic extractant introduced to the organic phase, the organic solvent itself, and of the solutes (e.g., metal and inorganic acid) in the aqueous phase.\textsuperscript{4−7}

For many years, the significance of the self-assembly ensemble within both the organic and third phase has not been fully appreciated.\textsuperscript{7} Drawing inspiration from the soft-matter and colloidal communities (and based upon data from small angle neutron scattering, SANS), many studies have interpreted scattering profiles of the third phase using a chemical model consisting of a homogeneous microemulsion of reverse micelles that interact using a simplified interparticle potential like the Baxter Sticky Sphere model (a square well).\textsuperscript{8} The pervasiveness of this micellar model derives from the apparent generality of its ability to describe third phase formation as a phase transition approached by intermicelle attraction energies reaching a value of $\sim 2K_B T$ (where $K_B$ is the Boltzmann constant, and $T$ is the critical temperature).

However, such simplicity lies contrary to the energetic landscape of amphiphilic self-assembly, a highly dimensional space with a nuanced interplay between enthalpic and entropic contributions (Figure 1). In recent years the

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Figure 1. Imagining the free energy landscape of the self-assembly ensemble. Reprinted with permission from refs 1 and 9. Copyright 2018 American Chemical Society. Copyright 2012 Springer Nature.

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First Reactions

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essence of the self-assembly ensemble has begun to emerge. Studies have proposed that, in addition to potential micellar species, there may be percolating networks of clusters of varying length scales and complexity, and that the total fluid may be highly heterogeneous.\textsuperscript{10}−\textsuperscript{12}

With this perspective in mind, the work of Motokawa et al.\textsuperscript{1} is a significant step forward in understanding the structural hierarchy of the self-assembly ensemble, as well as the underlying intermolecular interactions that tune its distribution. The authors focus upon a nonradioactive analogue of the post-extraction organic phase within the plutonium uranium redox extraction (PUREX) process.\textsuperscript{13} PUREX is used to separate high- and low-level radioactive components of spent nuclear fuel; however its general process is quite similar to metal purification strategies found within hydrometallurgy and recycling. Multimodal characterization of the fluid, composed of Zr(NO$_3$)$_4$-HNO$_3$/TBP-n-octane-d$_{18}$, utilized X-ray absorption fine structure (EXAFS) alongside density functional theory (DFT) calculations, to elucidate the local geometry of the Zr(NO$_3$)$_4$(TBP)$_2$ complexes that are generally assumed to be the idealized end-products of solvent extraction at conditions well below the critical concentration. However, importantly, the longer length-scale fluid structure was also probed with SANS complemented by molecular dynamics simulations. Crucially, a concentration dependent series was examined, and as such, the change to both local and extended structural organization was able to be elucidated as the critical concentration was approached in the organic phase.

From this well-designed series, it was observed that the molecular Zr(NO$_3$)$_4$(TBP)$_2$ acts as a building block for larger primary clusters, that in turn may further self-assemble into superclusters (Figure 1). Within conditions that have the Zr(NO$_3$)$_4$(TBP)$_2$ and the primary clusters as the major components of the ensemble, large intermolecular interactions driven by electrostatic forces are implied, which leads to significant nonideality of the fluid as a whole. While the electrostatic interactions appear to drive formation of the primary clusters, diluent solvation appears to contribute to the cluster size and morphology distribution. The distribution of the primary clusters within the fluid is also heterogeneous, where loose assemblies are observed and proposed to be precursors to supercluster formation. Furthermore, the study implies that phase splitting may be driven by changes to the ensemble such that the superclusters become the primary species.

As may be anticipated, the hierarchical detail of the self-assembly ensemble as a function of solution conditions now provides an improved platform to connect the micro- and mesoscopic fluid structure with phase behavior. The community is encouraged to pursue quantitative relationships between the size and shape of the ensemble and its sensitivity to specific solution conditions (Figure 2). Recognizing that under different solution composition there may be different forces that drive self-assembly, and the specific types of assemblages, is absolutely essential toward developing a truly general set of chemical principles the underpin

Figure 2. Illustration of potential self-assembly ensemble with relevant future areas of study highlighted in red. Reprinted with permission from ref 1. Copyright 2018 American Chemical Society.
structured fluids. Indeed, one may consider that it is a grand challenge to predict the energetic landscape that underlies the chemical space of structures available to structured fluids so that one day they may be precisely tailored.

There is also great opportunity in the development of theories that imparts molecular-scale information to the fluid dynamics treatment of such systems. Consider, too, the advancement of chemically informed models of phase transitions, for example, the incorporation of the self-assembly ensemble and its associated range of interparticle interactions, within the context of critical phenomena.\(^{14}\)

Already the current work has indicated that a chemical analoguous to a gas–liquid transition may not be an appropriate model for phase separation within these systems.

Finally, as a necessary counterpart to the thermodynamic equilibrium study described here, it is also relevant to have a mechanistic understanding of how such assemblies form. In practical solvent extractions, it is intuitive that the liquid interface, with its own captivating structural and dynamic complexity,\(^{15,16}\) may play a very important role in assisting self-assembly. For example, one could envision that the initial stages of the building block to primary cluster formation are facilitated by the time dependent evolution of the capillary wave structure of the interface, or that the surfactant laden surface helps template intermediate structures that in turn have decreased barriers to form larger structural architectures. Moreover, it is well-known that, under some operating conditions, thermodynamic equilibrium may in fact not be achieved, and thus metastable self-assembled species may be critical to phase behavior.

Each of these important future areas of study will benefit greatly from the telescoping view of the self-assembly ensemble provided by the current work.

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