

Chemical Engineering Doctoral Defense

Molecular Dynamic Simulations of Diffusion and Phase Behaviors of Colloidal Particles in Two-Component Liquid Systems

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abstract

The interface of biphasic liquid systems has attracted great attention because it offers a simple, flexible, and highly reproducible template for the assembly of a variety of nanoscale objects. This can find many potential applications in catalysis, emulsion, sensing, and drug delivery. However, certain important fundamental issues about the diffusion and self-assembly of such nanoscale objects in biphasic liquid-liquid systems have not been fully explored, especially when the size of the object is comparable with the liquid molecules. In our first Molecular Dynamic (MD) simulation system, the diffusion and self-assembly of nanoparticles with different size, shape and surface composition were studied in an oil/water system. We found that a highly symmetrical nanoparticle with uniform surface (e.g. buckyball) can lead to a better-defined solvation shell which makes the “effective radius” of the nanoparticle larger than its own radius, and thus, lead to slower transport (diffusion) of the nanoparticles across the oil-water interface.

PNIPAM is a thermoresponsive polymer with a Lower Critical Solution Temperature (LCST) of 32°C in pure water. It is one of the most widely studied stimulus-responsive polymers which can be fabricated into various forms of smart materials. However, our understanding about the diffusive and phase behaviors of PNIPAM in ionic liquids/water system is very limited. Therefore, two biphasic water-ionic liquids (ILs) systems were created to investigate the interfacial behavior of PNIPAM in such unique liquid-liquid interface. It was found the phase preference of PNIPAM below/above its LCST is dependent on the nature of ionic liquids. This potentially allows us to manipulate the interfacial behavior of macromolecules by tuning the properties of ionic liquids and minimizing the need for expensive polymer functionalization. To seek a more comprehensive understanding of the effects of ionic liquids on the phase behavior of PNIPAM, in another component of this thesis, PNIPAM was studied in two miscible ionic liquids/water systems. We elucidated the thermodynamic origin for the reduction of LCST of PNIPAM in imidazolium based ionic liquids/water system. Energy analysis, hydrogen bonding calculation and detailed structural quantification were presented in this study to support our conclusions.

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