Confinement Chemistry in Self-Assembling Polymer-Metal Nanoreactors

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ABSTRACT

Small hydrophobic organic and inorganic solutes undergo spontaneous reactions within 2nm spaces in polymer-metal composite nanoreactors that are endergonic outside the confinement condition. Where the reaction rate can be increased by the system's metal nanocrystals, the reduction of ΔG_{rxn} required to allow thermal initiation of otherwise unfavourable processes is a fundamentally new development. It has been proposed that the phase of water can be radically affected by the hydrophobicity and dimension of a confined reaction space, thereby changing the solvation thermodynamics and reaction environment. This paper presents the results of classical molecular dynamics modeling studies to probe the thermodynamic properties of water and small solute molecules confined within a 1-5nm hydrophobic confinement space. The presence of supercritical phase-like properties strongly implicates solvent effects in the mechanics of nanoreactor confinement chemistry.

Keywords: catalysis, confinement, nanocomposite, nanoreactors, self-assembly

1 INTRODUCTION

Millennia of evolution have produced within living cells highly structured self-assembling macromolecules to promote important chemical reactions: enzymes. Like the large chemical reactors needed for human industry, these biological nanoreactors are essential for energy collection, fuel production and storage, material transport, synthesis, and detoxification. Unlike many industrial reactors, however, enzymatic catalysis manages its task in water at room temperature and pressure. While the enzyme active sites have rightfully been studied for insight into their high catalytic activity, the influence of the surrounding structure over the solvation of reactants within the nanostructure may prove as rich a source for understanding enzymes' enviable properties [1].

We have developed and thoroughly characterized stable polymer-metal nanocomposite reactor systems with hydrophobic inner surfaces 2-3 nm apart, shown in Figure 1 [2]. Previous work has shown that energetically unfavourable reactions, namely pyrrole polymerization and metal salt reduction, become spontaneous under confinement within the polymer nanostructure [3]. Furthermore, the presence of metal nanocrystals formed in situ within the confinement space will catalyze the pyrrole polymerization reaction. Catalytic mechanisms, limited as they are to describing changes in reaction kinetics and not thermodynamics, are insufficient to the task of explaining the surprising decrease of ΔG_{rxn} from a positive to a negative value observed occurring within the supramolecular nanostructure.

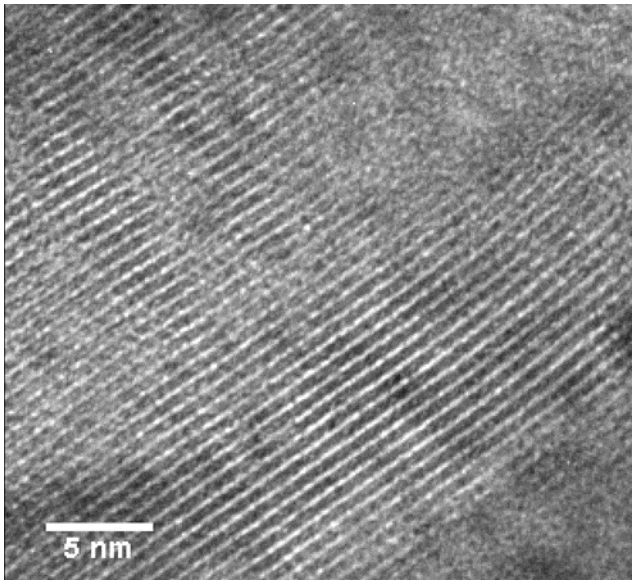

Figure 1: Transmission electron microscopy image of the composite nanoreactor. Parallel lines are self-assembled polymer chains; dark spots indicate platinum nanocrystals grown in the reactor space.

Two parallel hydrophobic surfaces at the 2-3nm distance regime disrupt water's hydrogen bonding network and in general cause spontaneous drying of the confined interior region; an effect credited with hydrophobic attraction in water [4]. However, surfaces that are weakly polarized may be able to suppress the turnover to vapour even at very short distances [5]. Water confined in such a space enters a metastable liquid phase whose solvation characteristics may be closer to that of supercritical water even while the bulk solution remains at room temperature and pressure. Properties of supercritical water such as solvation free

energy, compressibility, and permittivity could explain the disparity between confined and bulk thermodynamics.

2 BACKGROUND

Both experimental and modeling results indicate changes in the dynamic behaviour of water in close proximity to hydrophobic surfaces. A 2007 Quasi-elastic neutron scattering (QENS) study revealed a split in the temperature-dependent velocity of water under confinement with an amphiphilic polypeptide (*n*-acetyl-leucine-methylamide); water at the hydrophilic moiety (within 2 nm) moved significantly more quickly than water equally close to hydrophilic regions [6]. This result was corroborated by numerical modeling of the QENS data [7]. Furthermore, previous molecular dynamics simulation has identified far-from-mean reductions in water density within 1.5 nm of extended hydrophobic surfaces [8].

In combination, the literature evidence indicates that water confined within 2 nm of an extended hydrophobic surface is characterized by a substantially higher mean velocity and lower mean density than bulk water at a given temperature and pressure. These properties induce the formation of larger unoccupied areas within the liquid water phase. If the water is confined between two hydrophobic surfaces, a cavity large enough to bridge the surfaces forms the nucleation event for spontaneous drying and the hydrophobic attraction effect [9]. Since cavity distribution is a determinant of solvation free energy and permittivity, confined water that is denied a nucleating event remains in a metastable phase characteristically similar to supercritical. Probing the relationship between hydrophobicity, surface distance, and water phase properties is the major focus of the molecular dynamics simulations currently underway.

Small, non-polar molecules and hydrophobic metal salts should demonstrate greater solubility in the confined phase than in bulk water. Indeed, our lab has observed this effect occurring within the confined reaction space between layers of poly(styrene-alt-maleic anhydride), SMA, an alternating copolymer that self-assembles in neutral water into a well-defined nanostructure [10]. The results of these experiments are briefly described in the following sections.

2.1 Non-Polar Small Molecules

Pyrrole is typical of small, non-polar organic molecules in that it is insoluble in water but readily soluble in aqueous solution of 1% SMA. The change in solvation free energy, as well as the hydrophobic surfaces themselves, would explain the pyrrole solubility in SMA solution. Density functional theory studies have revealed that pyrrole polymerization is energetically unfavourable for oligomers under six units long. Accordingly, pyrrole polymerization does not occur spontaneously in the bulk liquid or in water alone. It does, however, occur spontaneously under confinement in the < 3 nm hydro-phobic space within the SMA nanoreactor. Details of the polymerization reaction and its dependence on confinement have been previously published [11].

The hydrophobicity and separation distances of the SMA nanoreactor are consistent with the conditions required to induce a supercritical confined water phase, as described above. Whether the change in spontaneity of polymerization is a solvation effect in confined water or whether pyrrole accumulation on the hydrophobic surfaces induces vapour nucleation is an open question that the current work seeks to resolve.

2.2 Hydrophobic Metal Salts

Like non-polar organic molecules, hydrophobic metal salts also preferentially accumulate within the confined reaction space of the SMA nanostructure. Also like pyrrole, these salts may undergo energetically unfavourable reactions while under confinement. Details of $PlCl_2$ and AuCl autoreduction in SMA solution has been published elsewhere [12]. In brief, these salts are typically reduced in aqueous solution using a reducing agent such as $NaBH_4$. Our work has demonstrated the reduction of metal chlorides to metal crystals without the addition of a reducing agent into solution. The reduced platinum forms 2 nm nanocrystals within the hydrophobic confinement space and the reduced gold forms a single-atom thick plate on the nanostructure's hydrophilic outer surface, shown in Figure 2.

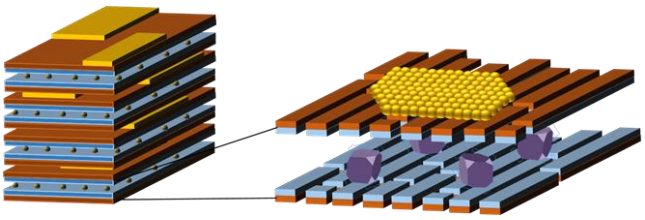

Figure 2: Schematic image of the nanoreactors developed by the Malardier-Jugroot group. Red (dark) and blue (light) regions signify hydrophilic and hydrophobic polymer surfaces, respectively; cubes represent platinum nanocrystals while yellow plates indicate gold nanosheets.

The mechanism of noble metal salt reduction under in aqueous SMA solution is yet to be elucidated. Density functional theory modeling demonstrates that disassociation of chlorine gas and atomic platinum requires a ΔG_{rxn} = 406 $kJ \cdot mol^{-1}$ that must be overcome by the potential energy provided either through confinement or another interaction with the polymer. If the formation and collapse of cavities in the confined water can be modeled as nanobubbles, then the

internal pressure of the cavity can be calculated using the Young-Laplace equation:

$$\Delta P = \frac{2\gamma}{r} \quad (1)$$

where γ is the surface tension at the interface: 0.073 Nm^{-1} for water at 293 K. A bubble formed within the 2-3 nm confinement space would therefore carry 2.74 $N{\cdot}nm^{-2}$ surface area and release 2.4 $MJ{\cdot}mol^{-1}$ upon its collapse, a sufficient amount to overcome the energy of dissociation. Evaluation of the cavity size distribution and solvation free energy of model salts such as $PtCl_2$ via molecular dynamics simulation will provide evidence concerning possible reduction mechanisms.

3 EXPERIMENTAL

Studies currently underway examine the effect of nanoconfinement on water and small solute particles by two complementary methods: molecular dynamics simulation and systematic nanoreactor experiments. The present work focuses on the results of initial molecular dynamics simulations.

The TIP4P-Ew long-range water model was selected for its high quality interfacial thermodynamic and dynamic properties and relatively low computational cost [13]. The hydrophobic surfaces are modeled in a flat graphene topology to control for artefacts of surface roughness and geometry. Interaction with the surfaces are determined by Lenard-Jones modeling to permit tuning their specific hydrophobicity.

The properties of the water model will be measured while under 2-dimensional confinement ranging from 1 – 5 nm, as well as allowing systems of a given number of molecules to freely equilibrate confinement distance, to judge the effect of distance on cavitation and phase stability. All simulations are being run in the LAMMPS molecular dynamics software as implemented on the High Performance Computing Virtual Laboratory (HPCVL) servers.

Thermodynamic behaviour of the water model under confinement will be elucidated, specifically those properties identified in the above sections and including the solvation energy for various small molecules such as organics, metal ions, and gases, under precisely controlled values of surface hydrophobicity and polarization.

Characterization of the experimental system, including a study on the effect of SMA molecular mass on morphology, is ongoing and will continue in concert with simulation. While these tests are beyond the scope of the present discussion it bears mentioning that all simulation results will continue to be validated by comparison to experimental results of reactions under confinement within our polymer-metal nanoreactor systems.

4 CONCLUSION

By offering control over both the kinetics and thermodynamics of chemical reactions in neutral water at room temperature and pressure, composite nanoreactors hold immense potential for science and technology. Our nanoreactors were designed to mimic the confined and catalyzed cavities of enzymes so the thermodynamic effects revealed by this study will provide insight into the mechanisms of biomolecular reactions. Supercritical water is an excellent solvent yet has not been broadly adopted in industry due in part to the cost of maintaining high pressure and temperature at scale. If the same effectiveness can be achieved with low cost nanoreactors, high value industrial processes such as carbon dioxide conversion could be achieved at a fraction of present capital and energy expenditures. Understanding the chemical physics of water and reactant molecules within nanoreactors will allow industry, like nature, to use what is abundant to optimize what is scarce.

REFERENCES

[1] McTaggart, M.R. et al. “Biomimetic Soft Polymer Nanomaterials for Efficient Chemical Processes” in Green Processes for Nanotechnology, Springer International Publishing: 277-301, 2015.

[2] Patent no. PCT/CA2013/000738

[3] Groves, M. et al, Chem. Phys. Lett., 612, 309-312, 2014.

[4] Berne, B.J. et al., Ann. Rev. Phys. Chem., 60, 85-103, 2009.

[5] Giovambattista, N. et al, Ann. Rev. Phys. Chem., 63, 179-200, 2012.

[6] Malardier-Jugroot, C. and Head-Gordon, T., Phys. Chem. Chem. Phys., 9, 1962-1971, 2007.

[7] Malardier-Jugroot, C. et al, Phys. Chem. Chem. Phys., 10, 4903-4908, 2008.

[8] Patel, A.J., Phys. Chem. B., 1632-1637, 2010.

[9] Leung, K. et al., Phys. Rev. Lett. 90, 065502 (4).

[10] McTaggart, M. et al, Chem. Phys. Lett., 636, 216-220, 2015.

[11] Li, X. et al, Macromolecules, 46, 2258-2266, 2013.

[12] McTaggart, M., et al., Chem. Phys. Lett., 636, 221-227, 2015.

[13] Horn H.W. et al, J. Chem. Phys., 120, 9665-9678, 2004.