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The Role of Microenvironment Reagent Solubility on Reaction Kinetics of 4-Nitrophenol Reduction

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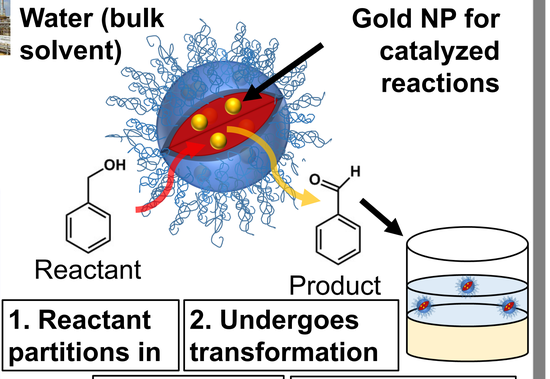
Motivation

Transform conventional unit operations (i.e. fixed bed reactor, liquid-liquid extraction) to multifunctional polymer nanoreactor

Polymer Nanoreactor

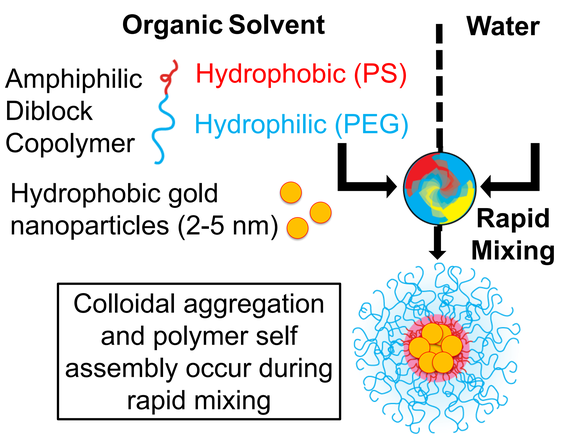


- Although 90% of all chemical processes use catalysts, progress in catalyst development has outpaced advances in reactor design.
- Thus, advances in multifunctional reactors are needed to fully utilize catalyst potential and increase processing efficiency.

Approach

- Hydrophobic microenvironments of self-assembled polymeric micellar systems provide avenues to carry out a range of organic reactions using water as the bulk solvent.

Nanoreactor Synthesis

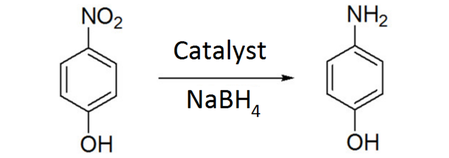


Colloidal aggregation and polymer self assembly occur during rapid mixing

Confined impinging jet mixers are used to achieve high energy mixing. Micellization of amphiphilic block copolymers direct nanoreactor self-assembly.

Methods

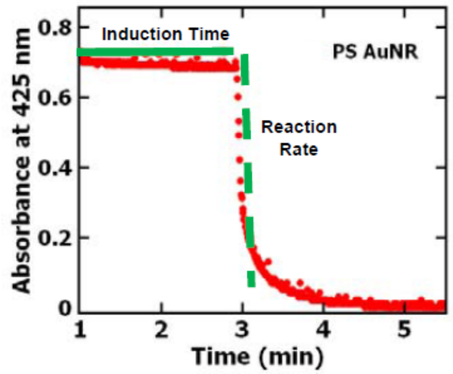
4-Nitrophenol Reduction



4-nitrophenol — 4-aminophenol

4-nitrophenol (4NP) is catalytically reduced by sodium borohydride to 4-aminophenol in water using AuNP. The reaction rate can be studied by tracking the UV-Vis absorbance of 4-nitrophenolate.

Representative UV-Vis data depicting a typical 4-Nitrophenol reduction. The induction time is characteristic of a zero-slope region with the reaction rate corresponding to a distinct change in absorbance (dA/dt).

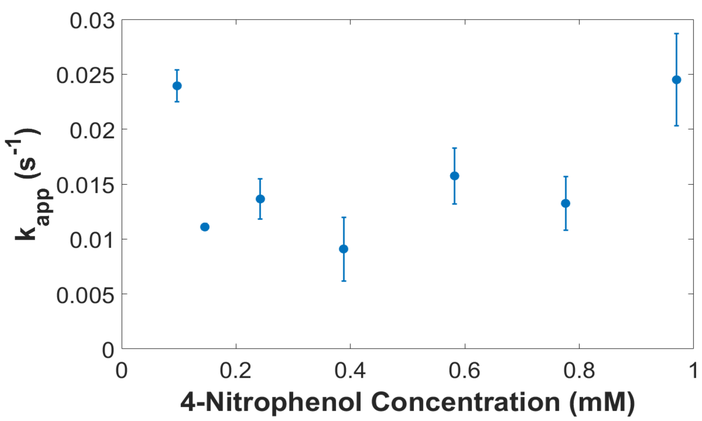


$$Rate = \frac{dA}{dt} = k_{app} \cdot C_{4NP}$$

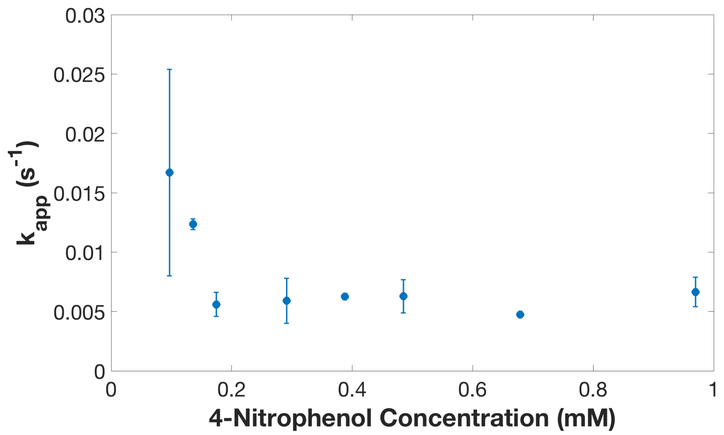
Results

Effect of Reactant Concentration

- No change in k_{app} observed above standard concentration (0.097 mM) when varied in constant ratio, indicating that the localized concentration of 4-nitrophenol is not changing.



Results Continued



- Decrease of k_{app} with increasing 4-nitrophenol at constant [$NaBH_4$] is indicative of Langmuir-Hinshelwood kinetics.

Solubility of 4-Nitrophenol in Reactor Microenvironments

- Reaction kinetics behavior could be explained by chemical potential gradients within the nanoreactors.
- Saturated reagent concentrations were measured for ethanol using UV-Vis and for chloroform-D using ^{1}H NMR.

Solvent	4NP Solubility (x 10^3 g/mL)
Chloroform-D	2.13
Ethanol	1010 ± 10

Conclusions

- Increasing total reagent concentration appeared to have no significant effect. This could be explained by the difference in solubility in the microenvironments.
- Increasing the [4NP] had a detrimental effect on apparent rate, potentially explained by a diffusion-limited scenario.
- Reaction kinetics in this system are highly dependent on reagent partitioning due to chemical potential gradients.

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