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Poster Presentation 1

Using shear stress to drive Diels-Alder cycloaddition

Kueyoung E. Kim, Pranjal Nautiyal, and Robert W. Carpick

Department of Mechanical Engineering and Applied Mechanics, The University of Pennsylvania, Philadelphia, PA

In the pharmaceutical and chemical industries, toxic and carcinogenic organic solvents used in molecular synthesis account for over 80% of waste produced. Mechanochemistry, where reactions are driven via mechanical energy primarily in powder form, has the potential to significantly reduce the environmental impact of industrial scale synthesis by reducing or eliminating toxic solvent use. Although several organic reactions have been conducted mechanochemically via ball milling, the driving force for these reactions is poorly understood due to the large variance in stresses, temperature, and particle size in the reactor. The stress-assisted thermal activation model proposes that applied mechanical stress can reduce activation energies, causing reactions to become thermodynamically favorable at lower temperatures. Here, we investigate shear-driven Diels-Alder cycloaddition using a surface-bound reaction in a ball-on-disc tribometer to elucidate the role of stress-assisted thermal activation in mechanochemical reactions. We modify the surface of a glass disc with anthracene and dissolve maleimide in a mixture of polyisobutylene and alkylated naphthalene, which is then used in the tribometer where shear and normal stresses are precisely measured. We conduct a preliminary reaction in full elastohydrodynamic lubrication at 22.7 MPa of shear stress based on Hertzian contact theory. The substrate is characterized with atomic force microscopy, surface-enhanced Raman spectroscopy and time-of-flight secondary ion mass spectrometry (ToF-SIMS). ToF-SIMS shows that elastohyrodynamic lubrication prevents anthracene removal from the substrate–which is an issue for product characterization–but does not provide evidence of product formation at the selected shear stress, temperature, and reaction time. This work develops reaction conditions and product characterization methods to be used in future study of shear-driven Diels-Alder cycloaddition using a ball-on-disc tribometer, which will ultimately isolate the effects of normal and shear stress on organic reaction kinetics.

Poster Presentation 2

Environmental Factors Influencing Thermally Activated Delayed Fluorescence in NAI-DMAC

Gary Chen, John Swartzfager, and John Asbury

Department of Chemistry, The Pennsylvania State University, University Park, PA

Purpose: Organic Light Emitting Diodes (OLEDs) are becoming increasingly more popular in electronics and technology today. OLEDs have a maximum of 25% efficiency due to the spin-statistics of the excited singlet and triplet states. Thermally Activated Delayed Fluorescence (TADF) molecules are a class of OLEDs that utilize high-lying triplet states so that the electrons can get thermally promoted to the emissive singlet state which leads to a potential of 100% efficiency. By understanding how these TADF molecules interact with the environment, devices can be made with improved efficiencies for better and brighter screens.

Description: NAI-DMAC is a known TADF molecule and studying it in the glass-forming solvent methyl tetrahydrofuran (mTHF) allows us to measure the effects of molecular dynamics on fluorescence and the singlet-triplet energy splitting (ΔEST). An orthogonal orientation of the donor and acceptor moieties results in the smallest ΔEST but very little fluorescence. However, as the molecule leaves orthogonality, the ΔEST increases but results in more fluorescence. In solutions, the solvent allows free rotation between the donor and acceptor to access these necessary conformations given enough thermal energy. In mTHF solution, decreasing the temperature permits comparison of the fluorescence spectrum from the singlet state at 300K to the phosphorescence spectrum from the triplet state at 80K. From this comparison, a value of ΔEST of 0.25eV was obtained. Decreasing the temperature also reduces the variation of molecular conformations in the TADF process, leading to the photoluminescence (PL) intensity decreasing by a factor of 10 between 300 and 80K. However, no such reduction of PL intensity occurs in the solid-state because NAI-DMAC molecules aggregate, allowing energy transfer among molecules of various conformations. The energy transfer process permits the TADF process to occur even at low temperatures but obscures the true ΔEST value so the traditional approach comparing the fluorescence and phosphorescence will result in a ΔEST value of 0.03eV, which is considerably smaller than the solution study.

Poster Presentation 3

Mixer Mill Mechanochemical Metalation of Porphyrin

Julianne M. Dee, Katarina E. Zerbee, Elaina L. Dorchak, Amelia L. Vu, and Edward P. Zovinka

Department of Chemistry, Saint Francis University, Loretto, PA

Green chemistry is a new approach to chemistry that places a focus on limiting the use of toxic chemicals in the environment. Porphyrin ligands are organic molecules that are essential to life of Earth. This ligand often forms complexes with various metal and nonmetal ions. However, it is often synthesized or used in a metalation reaction in labs utilizing large amounts of organic solvents and energy intensive methods, not following the green chemistry approach. Mechanochemistry is a greener approach to the metalation of porphyrin through using force to break bonds in the molecule. Mixer mill machines utilize jars and balls of various materials and sizes to spin reactants in circles to intensely grind together dry, solid reagents so they can react, and metalation can occur. Stainless steel jars and balls were used throughout the research period with varying metals (Cu, Zn, Co, Ni) to see if metalation would occur. Different ratios and frequencies were tested to see if that impacted the outcome of the metalation results. It was found that by reducing the ratio of a metal to the porphyrin, the metalation was still able to occur with varying time lengths at a constant frequency. Additionally, nickel was found to be unable to metalate at a low frequency, but it was found to work at a higher frequency.

Poster Presentation 4

Investigating Liquid-Liquid Phase Separation/Transition and pH Effects on Virus Transmission

Kayla McCreary, Qishen Huang, and Miriam Freedman

Department of Chemistry, The Pennsylvania State University, University Park, PA

Viruses and other respiratory illnesses can be transmitted via respiratory aerosols. The survivability of viruses in aerosols was found to be sensitive to pH and relative humidity (RH) among other factors. It is suggested that aerosols undergo significant pH changes when expelled from the respiratory system. Additionally, RH changes can cause an aerosol particle to undergo a phase transition. This alters the composition of the droplet, consequently affecting virus survivability. There is a need for the development of a better model to describe these aerosol particle behaviors. More specifically, the effects of phase transition and pH in inorganic-protein aerosols on respiratory virus transmission were investigated. Phase transitions are observed via an optical microscope. pH measurements are observed via a fluorescence microscope. The RH during measurements were controlled using an environmental chamber. The model system for respiratory aerosols for investigation of phase transition and pH, respectively, were Bovine Serum Albumin (BSA) with phosphate buffer, and phosphate buffer with fluorescein dye. As a result, it was shown how composition affects phase transition behavior. With increasing phosphate buffer content, the deliquescence RH (DRH) was not affected, while the efflorescence RH (ERH) was slightly increased. In summary, a ratiometric method is being established, using fluorescein to achieve pH measurement. This highlights the importance for better predictors of virus survivability in virus transmission. In the future, we will characterize aerosol droplet pH under different conditions (e.g. changing RH and changing CO_2 concentration) to study how aerosol pH changes in the ambient environment.

Poster Presentation 5

Expression, Purification and Chemical Cleavage of the Human SUMO-Glycophorin A Transmembrane Domain Fusion Protein

Kelsey Leach, and Kyle T. Root

Department of Chemistry, Commonwealth University of Pennsylvania at Lock Haven, Lock Haven, PA

Purpose: The expression and purification of transmembrane peptides is challenging due to their highly hydrophobic character. In this work we have made progress towards optimizing methods for expressing, purifying, and chemically labeling a well-known model transmembrane peptide belonging to human glycophorin A (GlyA).

Description: A number of strategies were employed to enhance expression of GlyA in E. coli (BL21DE3) cells. The protein was expressed as a C-terminal fusion to the small ubiquitin-like modifying protein (SUMO) which acted as a carrier protein and directed expression into inclusion bodies. A hexahistidine sequence was included at the N-terminus to facilitate purification using metal affinity chromatography. We used hydroxylamine (which selectively cleaves the peptide bond between asparagine and glycine) to liberate the carrier protein from GlyA. In addition, we explored the effect of cell growth media richness and inducer concentration on the expression yields. Our purification approach relied on neutrally buffered highly concentrated trichloroacetate solutions to solubilize the SUMO-GlyA inclusion bodies and to maintain solubility during the purification. Once purified, numerous conditions were tested to optimize the liberation of the GlyA peptide from the fusion protein using hydroxylamine.

Evaluation and Outcomes: Using SDS-PAGE analysis, it was found that media choice and inducer strength had a large effect on the amount of fusion protein expressed. It was also determined that the fusion protein could be purified to >90% purity in a single chromatographic step. Despite the surveying of numerous solution conditions to optimize hydroxylamine cleavage, overall cleavage yields tended to be small. Unfortunately, purifying the cleaved GlyA transmembrane domain from the uncleaved fusion protein remained elusive, likely owing to the fact that cleaved GlyA is still able to dimerize with GlyA present within the fusion construct. More work will have to be carried out in order to drive up the yield of cleaved fusion constructs to circumvent this challenging pitfall.

Poster Presentation 6

Binding Analysis of Ubiquitin Ligase SPOP with Intrinsically Disordered Proteins

Nolan P. Jacob, Emery T. Usher, and Scott A. Showalter
Department of Chemistry, The Pennsylvania State University, University Park, PA

Speckle-type POZ Protein (SPOP), a ubiquitin ligase adaptor manages various proteins including transcription factors and cell cycle regulators. Binding of these proteins to the SPOP MATH domain is driven by short linear motifs within intrinsically disordered domains. The ideal substrate protein motif, Puc, has been observed to be (V/P)SS(T/S)(T/S). However, our lab has found through the model system of Pdx1, a transcription factor involved in insulin production, that binding occurs with minimal similarity to this sequence; also of note, the flanking regions of the binding motif play as much a role in binding as the motif itself. Pdx1 contains two binding motifs with amino acid sequences neither like each other nor the ideal Puc motif. More study is still needed to understand exactly how these differences in sequence allow for proper binding and function of the protein. This project aims to address that need by mutating Pdx1 at various points in the sequence that vary significantly with Puc. Through fluorescence anisotropy and protein crystallography, the goal is to further our knowledge of the exact interaction between the two binding motifs of Pdx1 and SPOP. Realizing how each amino acid impacts and alters the binding capabilities will improve generalized models for SPOP MATH substrate interactions. This then provides insight into certain mutations of Pdx1that have been associated with diseases such as diabetes.

Poster Presentation 7

Bronsted basic auxiliary enables synthesis of aza-quaternary centers

Ryan S. Lai and Jonathan L. Kuo
Department of Chemistry, The Pennsylvania State University, University Park, PA

Aza-quaternary centers are important structural motifs in natural products and pharmaceuticals. However, they can be challenging to synthesize. We demonstrate that installing a Bronsted basic auxiliary enables the amination of benzoquinone and catechol derivatives. The amine nucleophile adds to a substituted aromatic carbon, resulting in an aza-quaternary center. We suggest that proton transfer to an auxiliary can offset unfavorable energetics associated with carbon-nitrogen bond formation.

Poster Presentation 8

Coalescence and Solubilization of Ionic Liquid-in-Water Emulsions

Patrick Quinnan, Samuel Birrer, and Lauren D. Zarzar

Department of Chemistry, The Pennsylvania State University, University Park, PA

Ionic liquids are defined as salts with near room temperature melting points. Due to their unique characteristics such as low vapor pressure and nanoscale structure, they are being explored for numerous applications including synthesis, material preparation, and separation. In spite of this, little characterization of the behaviors of ionic liquids in emulsions. To address this, we worked to describe the behaviors of surfactant stabilized ionic liquid-in-water emulsions. With the goals of understanding the emulsion stability, surfactant effectiveness, and emulsified ionic liquids' properties, we measured the long-term coalescence rate through macroscopic observation, the solubilization rate through optical microscopy, and the interfacial tension of the ionic liquid-water interface through pendant drop tensiometry. The results will generate an improved understanding of ionic liquid-in-water emulsions, which could provide more avenues to use ionic liquids in the many existing and new applications to which they are suited.

Poster Presentation 9

Development of Detergent-Free Methods of Membrane Protein Reconstitution into the Lipidic Cubic Phase

Anna Cowfer, Olivia Leitzel, and Kyle T. Root

Department of Chemistry, Commonwealth University of Pennsylvania at Lock Haven, Lock Haven, PA

Purpose: The lipidic cubic phase (LCP) which is spontaneously formed by water-monoolein mixtures and has garnered much attention in that it provides a native-like bilayer with interpenetrating aqueous channels which has facilitated the crystallization of numerous membrane proteins. Proteins are typically stabilized in detergent containing solutions and then are combined with monoolein to reconstitute the protein into the LCP. Unfortunately, it has been found that detergents can destabilize the LCP when present at a high enough concentration. Unfortunately, once this threshold is reached, there is no way to remove excess detergent which could stabilize the LCP.

Description: In this work, we explore the stability of LCP in the presence of chaotropic solutions (urea, trichloroacetate and guanidine hydrochloride) used to solubilize membrane proteins at a variety of concentrations. Utilizing the recently developed ‘cubicon’ method which involves precipitating the LCP by adding excess buffer, we show that chaotropic salts can be easily removed, and the resulting precipitate can be converted back to protein-laden LCP by the addition of a small amount of monoolein. We show that hydrophobic molecules (lipids and membrane proteins) can be incorporated starting from concentrated chaotropic solutions and that the concentration of these species in the LCP can be increased by performing multiple rounds of reconstitution.

Evaluation and Outcomes: To probe the stability of the LCP in the presence of denaturant solutions, we utilized three criteria. First, the lipidic cubic phase is optically transparent, which can be assessed visually. In addition, LCP is non-birefringent, and therefore should not scatter light when illuminated and viewed between two crossed polarizing lenses. Finally, LCP is highly viscous and therefore its viscoelastic properties may serve as an indicator of proper phase formation. We have determined a characteristic glass phase transition using (Tg) using dynamic mechanical temperature analysis which corresponds to pure LCP mixtures and can be used to quantitatively provide evidence of well-behaved LCP. Utilizing these three metrics, we have determined the tolerance of LCP to chaotropic agents that are part of the membrane protein purification work flow. Evidence of successful reconstitution of a fluorescently labeled lipid (NBD-DMPE) and a membrane protein (caveolin-1) are provided using fluorescence spectroscopy and SDS-PAGE, respectively.

Poster Presentation 10

Carbon Nanothread Formation from UV Irradiated Benzoquinone

Connor Burns, Margaret Gerthoffer, Morgan Miller, Steven Huss, Sikai Wu, and Elizabeth Elaqua

Department of Chemistry, The Pennsylvania State University, University Park, PA

Carbon nanothreads are a recently discovered 1-D sp^3 hybridized material that forms from the solid-state pressure-induced polymerization of benzene. Nanothreads are theorized to be rigid, strong polymers with a tunable band gap. Since the discovery of the kinetically controlled compression of benzene, discovering new aromatics that form nanothreads with tailored reactivity was deemed possible through the compression of pyridine, furan, and similar aromatic derivatives. Benzoquinone is one such molecule that has been targeted and is believed to lower reaction pressure due to a favorable crystal structure and lower energy within the molecule allowing for Benzoquinone to be closer. While being compressed in a diamond anvil cell (DAC), molecules can be analyzed in situ using Raman spectroscopy, IR spectroscopy, and XRD. Analysis can also be performed after the sample is recovered in addition to XPS and polarized light microscopy. Through experimentation, benzoquinone-derived nanothreads can only be formed via a slow compression (0.1 GPa/min – 0.01 GPa/min), since no sp3 peaks can be observed when a molecule is compressed via IR and a lack of a formed ring in XRD. These occur despite photoluminescence being high during in situ Raman. This research has been expanded to find the limitations of nanothread formation at the lowest pressures possible. As benzoquinone is subject to rehybridization under the presence of UV irradiation into hydroquinone, UV irradiation was performed under pressure to see if this lowers the final polymerization pressure or results in a different polymer product. The products can be distinguished by IR which shows O-H stretching rather easily compared to the difficulty of Raman. Research is ongoing to find the lower limits of nanothread formation in benzoquinone with and without UV exposure which could potentially allow for the commercial production (~6 GPa) of these nanothreads. In the future, extra characterization such as elemental analysis and determination of the band gap would help to characterize these newly discovered molecules and confirm our beliefs about their properties

Poster Presentation 11

NMR analysis of acetylation-induced changes to the histone H4 tail

Emma Kraft, Sophia Dewing, and Scott A. Showalter

Department of Chemistry, The Pennsylvania State University, University Park, PA

Intrinsically disordered proteins (IDPs) and intrinsically disordered regions (IDRs) are proteins or parts of a protein that lack a defined three-dimensional structure. Proteins that are vital in many life-sustaining cellular processes often have IDRs. The discovery of IDPs and IDRs has disproven the hypothesis that three-dimensional protein structure must be static to fulfill its function. IDPs have been connected to functions in allosteric regulation and enzyme catalysis, and they can also be found in transcription factors. IDRs within transcription factors have been found to be post-translationally modified to complete their function. There is no defined set of rules governing how post translational modifications (PTMs) affect the conformational ensembles of IDRs. Changes to the structural ensembles of proteins must be experimentally determined for each protein. IDRs are also found in other vital proteins involved in the storage of genetic material. DNA wraps around histone proteins, which contain intrinsically disordered tails, to keep itself compact. To access DNA that is wrapped around histones, the DNA must be loosened. It has been theorized that lysine acetylation of the intrinsically disordered histone tails results in loosening of the DNA to become available for transcription. It is not known how the conformational ensemble of the histone 4 (H4) tail changes upon acetylation of lysine residues, or how DNA compaction is affected. Nuclear Magnetic Resonance (NMR) spectroscopy was utilized to observe chemical shift perturbations upon lysine acetylation, from which small changes in peptide secondary structure can be determined. Circular dichroism (CD), size exclusion chromatography with multi-angle light scattering (SEC-MALS) and small angle X-ray scattering (SAXS) can be used in conjunction with NMR to provide complementary information to chemical shift perturbations. This information includes the hydrodynamic radius of the peptide, and structural ensemble determination based on nanoscale differences in the density of the molecule. Determination of structural ensemble changes to the H4 tail upon acetylation allows for better understanding of the mechanism of DNA compaction. In addition, this understanding allows for these methods to be applied to other proteins that contain IDRs that also play important roles within protein synthesis.

Poster Presentation 12

C-H Activation of N-heteroaromatic Compounds by Photocatalysis

Kayla Constantini and Eric Nacsa

Department of Chemistry, The Pennsylvania State University, University Park, PA

The substantive decreases in cost and the low environmental impact of using photocatalysis in medicinal and materials chemistry make it an appealing area of research for organic chemists. The relevance of biologically active N-heteroaromatic compounds in drug discovery make a crucial case for developing more efficient functionalization methods that utilize the most basic organic feedstocks. Photoredox catalysis is a viable method of functionalization that makes use of electron-transfer to access new reactive pathways. This summer, high-throughput screening of photochemical reactions was utilized to assess the performance of five different photocatalysts in identical reaction conditions. Herein, we will detail our investigations of using these photocatalysts to perform a C-H activation of the N-heteroarenes we have discovered.

Poster Presentation 13

The Role of DTT and pH in DMS-Stimulated RNA Degradation

Matthew Herne, Catherine Douds, Christy George, and Philip Bevilacqua

Department of Chemistry, The Pennsylvania State University, University Park, PA

RNA is an important molecule central to the translation of genetic information into proteins, and as such, understanding its structure can help us understand its function in gene regulation. Dimethyl sulfate (DMS) is a common probe for RNA which gives us information about its structure, and is often quenched with dithiothreitol (DTT). However, we have seen that DMS degrades the phosphate backbone of RNA in high concentrations and shifted pHs both in vivo and in vitro that could be introducing noise into structure-probing datasets. Other works exploring RNA degradation by DMS mostly involved degradation of the nucleobase rather than the phosphate backbone. To further characterize this phenomenon of DMS-stimulated degradation, my work focuses on the DTT quench. In this work, I address two aims: 1) determine the effectiveness of the DTT quench as a function of pH and 2) investigate the phosphate environment of RNA backbone after DMS and DTT treatment. For the first aim, I used total RNA on an agarose gel to visualize RNA degradation to determine that at low pHs, the DTT quench is ineffective. For the second aim, I used P31 NMR to visualize changes in phosphate environment of poly uridylic acid. From these experiments, I concluded that DMS methylation and subsequent probable DTT demethylation of the phosphate result in chemical shifts. However, I also show that pH changes alone have a great effect on Poly(U) and introduce unknown changes. Future experiments are needed to better characterize these shifts before we can accurately interpret the effects of DMS and DTT on phosphate methylation.

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Poster Presentation 14

Synthesis of Electrocatalysts

Hannah Gizenski, Jacob Piane, and Eric Nacsa

Department of Chemistry, The Pennsylvania State University, University Park, PA

Dehydration reactions are indispensable synthetic methods, but often require stoichiometric reagents or acidic conditions. The development of a mild and catalytic dehydration reaction has then been identified to be a top priority by the ACS Green Chemistry Pharmaceutical Roundtable. Electrocatalysts provide a viable alternative to these reactions; with the use of these catalysts, electron-rich and electron-deficient redox can both be reached efficiently with water as the sole byproduct. Throughout the summer, my project focused on the synthesis of various catalysts to be used in dehydration reactions. With the conclusion of these syntheses, I will then evaluate these catalysts.

Poster Presentation 15

Agricultural Bioplastics from Renewable Resources

Jialing Chen[1] and Sibel Irmak[2]

[1]*Department of Food Science, The Pennsylvania State University, University Park, PA*

[2]*Department of Agricultural and Biological Engineering, The Pennsylvania State University, University Park, PA*

Large number of plastics is used in agriculture for various purposes (mulch, greenhouse cover, tunnel, nursery pots, bale wrap, grain bags, etc.) and most of them are single season use polyethylene-based plastics that persists in the environment long after their intended use. Recycling these plastics is a challenge and most of recycling facilities do not accept agriculture plastics since they contain significant residues of soil, plant debris, stones etc. that cause problem in recycling equipment. Biodegradable plastics made from renewable natural resources can be environmentally sustainable alternative to conventional petroleum-based agriculture plastics. While currently there are some efforts to develop biodegradable biobased plastics and improve their performance with additional benefits their biodegradable attributes are limited and there is still a significant gap to overcome in terms of the use of proper raw material(s) for the preparation of such bioplastics.

Present study was designed to develop bioplastics from low-grade, low-cost, abundant, and non-toxic renewables (woody biomass, starch, chicken feather and corn gluten meal) that meet the required properties for agriculture applications. Renewables materials were dissolved under subcritical water conditions and their mixtures in various ratios were plasticized using glycerol. The chemical, thermal, mechanical, and morphological properties of the bioplastics were evaluated by various techniques (FT-IR, TGA, SEM and mechanical testing, etc.). The organic carbon concentrations of the hydrolysate used in bioplastic formulations were determined by total organic carbon analysis.

Bioplastics prepared from carbohydrate-protein mixtures resulted in better film properties compared to only carbohydrate containing blends. The bioplastics made of biomass-gluten meal had better mechanical properties than biomass-chicken feather bioplastics. The liquid formulation of carbohydrate-protein bioplastics has potential to be used as a sprayable mulch in agriculture that can reduce plastic waste in agriculture and reduce environmental pollution while enhancing soil health by releasing of nitrogen to soil during degradation process.

Poster Presentation 16

Purification of homologs of the Listeria monocytogenes ribonucleotide reductase

Jennie Chen, Paoning Chong, Joseph A. Cotruvo, Jr.

Department of Chemistry, The Pennsylvania State University, University Park, PA

Listeria monocytogenes (Lmo) is a pathogenic bacterium responsible for food-borne illness. The bacterium uses the key enzyme, ribonucleotide reductase (RNR), to make deoxynucleotides, the building blocks of DNA, and to reproduce inside the host. The Lmo RNR comprises two subunits, alpha and beta. Alpha has a catalytic site that reduces nucleotides (NDPs) to deoxynucleotides (dNDPs) and beta houses a metal cofactor that is essential for RNR activity. Lmo RNR has been previously characterized to utilize a diferric metal cofactor, but sequence similarity network (SSN) analysis and genetic context suggest that iron may not be the biologically relevant cofactor. In this project, proteins homologous to the Lmo beta from five organisms were expressed and purified to understand general features of the Lmo SSN cluster. These proteins were purified by anion exchange and size exclusion chromatography, and inductively coupled plasma mass spectroscopy (ICP-MS) was conducted to determine the metal composition of the proteins as purified from the cell. Out of the five homologs, two did not purify with our methods and new approaches should be taken for these homologs. For the three purified homologs, unexpected differences in metal loading were observed.

Poster Presentation 17

Development of Detergent-Free Methods of Membrane Protein Reconstitution into the Lipidic Cubic Phase

Anna Cowfer, Olivia Leitzel, and Kyle T. Root

Department of Chemistry, Commonwealth University of Pennsylvania at Lock Haven, Lock Haven, PA

Purpose: The lipidic cubic phase (LCP) which is spontaneously formed by water-monoolein mixtures and has garnered much attention in that it provides a native-like bilayer with interpenetrating aqueous channels which has facilitated the crystallization of numerous membrane proteins. Proteins are typically stabilized in detergent containing solutions and then are combined with monoolein to reconstitute the protein into the LCP. Unfortunately, it has been found that detergents can destabilize the LCP when present at a high enough concentration. Unfortunately, once this threshold is reached, there is no way to remove excess detergent which could stabilize the LCP.

Description: In this work, we explore the stability of LCP in the presence of chaotropic solutions (urea, trichloroacetate and guanidine hydrochloride) used to solubilize membrane proteins at a variety of concentrations. Utilizing the recently developed 'cubicon' method which involves precipitating the LCP by adding excess buffer, we show that chaotropic salts can be easily removed, and the resulting precipitate can be converted back to protein-laden LCP by the addition of a small amount of monoolein. We show that hydrophobic molecules (lipids and membrane proteins) can be incorporated starting from concentrated chaotropic solutions and that the concentration of these species in the LCP can be increased by performing multiple rounds of reconstitution.

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Poster Presentation 18

Characterization of the size dependency of electronic properties of gold nanoparticles

Hannah Priller, Rebecca DiMarco, and Benjamin J. Lear

Department of Chemistry, The Pennsylvania State University, University Park, PA

Gold nanoparticles (AuNPs) have varying applications including but not limited to plasmonic solar cells, photocatalysis, and photothermal heating. These applications are built on the electronic properties of the nanoparticles, which arise from their electronic structure and which can be controlled by ligand identity, ligand size, size of the particle, and more. The electronic change in these particles continues to be a topic of perennial interest. While much focus has been given to the evolution of the plasmon with size, this is not a direct measure of their electronic structure. We present work in which we use measurements of Pauli paramagnetism to directly probe the change in the density of electronic states with particle size. This is in an attempt to characterize where the electronic properties of AuNPs becomes one in the same with bulk gold. AuNPs were synthesized from gold salt ($AuHCl_4$) and octanethiol. Their size and paramagnetism were measured with TEM and Evans method NMR, respectively. We then discuss the dependence of the electronic structure upon the size of the metal core.

Poster Presentation 19

DSC and Pyrene Luminescence Probe Study of Phase Transitions and Size of Amorphous Domains in 44 mol% PE-co-PVA Copolymer

Steven Ganescu, Faith Hansotte, Nicholas Speitel, and Bratoljub H. Milosavljevic

Department of Chemistry, The Pennsylvania State University, University Park, PA

Previous studies of radiation chemistry of 44 mol% poly(ethylene-co-vinyl alcohol) indicated rather peculiar behavior[1]. More specifically, the hydrated sample containing 10% of water underwent crosslinking while the dry sample underwent scission. More information regarding the copolymer physical chemical properties is needed to understand this phenomenon. Firstly, differential scanning calorimetry was performed on the dry copolymer film, indicating a first-order phase transition centered at 160 °C – the polyethylene crystalline phase melting – and a second-order phase transition centered at 41 °C – the polyvinyl alcohol amorphous glass transition. From room temperature to -150 °C, a monotonous decrease in heat capacity was observed. To further investigate the copolymer's matrix dynamics and domains' sizes, a pyrene luminescent probe was applied. In order to get an idea of the nanodomain size (which differ in polarity), pyrene was embedded in films of polyvinyl alcohol, polyethylene, and the copolymer. Being a very nonpolar compound, pyrene is expected to reside in the nonpolar polyethylene moiety; however, the corresponding absorption and emission spectra indicated a rather strong interaction with the very polar polyvinyl alcohol domains. This can be rationalized as if the nonpolar domains are smaller than 2-3 Å. In order to learn more about the copolymer film dynamics, a laser photolysis experiment was performed at various temperatures from 26 °C to -163 °C. The rate constants of excited state pyrene decay were collected for each trial, and an Arrhenius plot was created, showing a nonlinear plot with two distinct linear regions. The crossover temperature between these two linear regions was -43 °C, which corresponds to the temperature at which a mode in the copolymer film affecting the pyrene excited state is deactivated. The DSC experiment indicated that the corresponding change in heat capacity for this phase transition was too small to be detected.

Reference:

[1] B. H. Milosavljevic and J. K. Thomas. Radiation induced processes in the copolymer, polyethylene–polyvinyl alcohol. Nucl. Instrum. Meth B., 2003, 208, 185-190

Poster Presentation 20

Coarse-grained Molecular Dynamics Simulation Studies of Mechanisms of ClpB Disaggregation Machine

Landon Ashlin, Zhe Zhao, and George Stan

Department of Chemistry, Juniata College, Huntingdon, PA

Department of Chemistry, The University of Cincinnati, Cincinnati, OH

This project investigates the application of molecular dynamics simulations by analyzing the ClpB chaperone activity of rescue proteins from aggregation. ClpB is needed for protein disaggregation, and it is critical to prevent protein aggregation during severe stress conditions. The goal of this project is to optimize scaling parameters of the SMOG coarse-grained model to best match Root Mean Square Fluctuation (RSMF) values with those obtained using the all-atom model.

Previously, a group of students had created an all-atom model to run simulations that analyzed the activity of the ClpB protein while rescuing proteins from aggregation. Due to the complexity, time strain, and heavy computing power required for all-atom models, the desire of a coarse-grained model was introduced. Even though coarse-grained models are more efficient, they produce less significant results. This is where the development of this project stemmed from. Optimizing the parameters of the coarse-grained model and finding additional ways to increase its accuracy is more efficient than running the all-atom model. In order to optimize the coarse-grained model's parameters, simulations were run under different time steps, various temperatures, and both scaled and unscaled trajectories. The results produced from these simulations have gone through a series of calculations to quantify the success of the simulations. These calculations are the Root Mean Square Fluctuation, the Pearson Correlation Coefficient, and the Fluorescence Resonance Energy Transfer. By comparing the differences between these calculations to the ones that were found from previous simulations, it is able to be observed whether the optimization of the coarse-grained model is becoming more or less accurate.

Based on the results collected on the scaled and unscaled trajectories, the scaled trajectory yielded more accurate results. It was also observed that the trajectories that were run for longer time steps produced more substantial results. To measure the success of the simulation, calculations were completed and compared to simulations that were run previously. Seeing that the most recent simulation had the most similar results to the all-atom model thus far, shows that the optimization of the coarse-grained model is getting more accurate. Therefore, continuing to increase the run time of the simulations and optimizing its parameters are making the desired impact on the coarse-grained model.

Poster Presentation 21

Temperature-Resolved Study of *Ru(bpy)$_3^{2+}$ Quenching by TiO$_2$ Nanoparticles

Ethan Fortuna[1] and Bratoljub H. Milosavljevic[2]

[1]Department of Chemical Engineering, The Pennsylvania State University, University Park, PA

[2]Department of Chemistry, The Pennsylvania State University, University Park, PA

As one of the fastest-developing fields, nanotechnology transforms the way scientists and engineers discover new technologies and solutions. TiO_2 nanoparticles garner particular interest due to their photophysical properties and utility in solar energy storage devices. Photosensitizers such as $Ru(bpy)_3^{2+}$ (a common photosensitizer) expand the absorbed (solar) photons' wavelength range. The reaction of interest is the photoinduced electron transfer from $Ru(bpy)_3^{2+}$ (electron donor) to TiO_2 (electron acceptor); anatase crystalline form is the most used. The reaction's temperature dependence requires further study. A study on the reaction between $^*Ru(bpy)_3^{2+}$ (electron donor) and methylviologen (electron acceptor) revealed that this photoinduced electron transfer is thermally assisted; it is efficient at room temperature but stops at 77K[1]. Contrary to this observation, photoinduced electron transfer involving anatase as an electron acceptor linked to the donor was found to be effective at 77K as well[2,3].

In this study, a nanosecond-pulsed laser photolysis technique was used to study $Ru(bpy)_3^{2+}$ quenching by TiO_2 nanoparticles in K_2CO_3 powder as a reaction medium. The comparison of emission decays obtained at room corresponding to samples containing (a) 0.5 mM $Ru(bpy)_3^{2+}$ solubilized in K_2CO_3 pellet and (b) 0.5 mM $Ru(bpy)_3^{2+}$ and 10 wt% of anatase solubilized in K_2CO_3 pellet revealed that the efficient electron transfer occurred. The same experiment was performed at 77K and the data obtained indicated that dynamic quenching of $Ru(bpy)_3^{2+}$ phosphorescence by anatase occurred as well.

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Poster Presentation 22

Redox Reaction of Methyl Viologen

Alexis Nguyen, Cole Clapperton, Max Weissberger, Jincheng Han, and Bratoljub H. Milosavljevic

Department of Chemistry, The Pennsylvania State University, University Park, PA

Oxygen diffusivity is an important parameter that determines the applications of polymers. The most common experimental techniques used for measuring diffusion coefficient of oxygen are sorption and time lag methods. There are experimental problems associated with the use of the aforementioned techniques; these were discussed in a paper which proposes a luminescent probe technique for measuring the diffusion coefficient of oxygen in polymers[1]. In general, the smaller the diffusion coefficient, the more complex the measurements are.

The present research deals with methyl viologen chloride, MV^{2+}, redox reactions in a 44 mol% PE-co-PVA copolymer film. The sample was prepared by soaking a copolymer film in 5 mM aqueous solution of methyl viologen chloride. Subsequently, the sample was exposed to a vacuum at 90 °C for 2 hours. During this procedure, the initially colorless sample turned blue. The UV-Vis spectroscopy analysis indicated a presence of reduced methyl viologen. Since no blue color was noticed in the sample kept at room temperature and exposed to room light, it is concluded that the methyl viologen was created in a thermally driven reaction. The reduced form of methyl viologen reduced in the film of the sample kept in air for two weeks was found to be remarkably stable; the corresponding decrease in absorbance was found to be 0.5 absorbance units. It is well established that reduced methyl viologen, $MV^{+\bullet}$, rapidly reacts with oxygen[2]; therefore, the oxygen radical can act as a relay in the recombination reaction thus accelerating it. The following reaction mechanisms is proposed for the methyl viologen redox reactions in the film:

$$MV^{2+} + polymer \overset{\Delta}{\rightarrow} MV^{+\bullet} + h^{+\bullet} \qquad (1)$$

$$MV^{+\bullet} + O_2 \rightarrow MV^{2+} + O^{2-} \qquad (2)$$

$$O^{2-} + h^{+\bullet} \rightarrow O_2 + polymer \qquad (3)$$

If the oxygen diffusion is slow, the back reaction can occur directly without oxygen acting as an electron relay:

$$MV^{+\bullet} + h^{+\bullet} \rightarrow MV^{2+} + polymer \qquad (4)$$

Either reaction mechanism indicates that the oxygen diffusion in the dry copolymer is very slow. The EPR experiment is needed to clarify the reaction mechanism and will allow the aforementioned methyl viologen reaction to be used in order to determine the oxygen diffusion coefficient in the copolymer film.

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Poster Presentation 23

Molar Decadic Absorption Coefficient and Kinetics of Formation of Silver Nanoparticles Produced in Reduction of Ag_2O with Hydrogen Gas

Josserand de Monts de Savasse and Bratoljub H. Milosavljevic

Department of Chemistry, The Pennsylvania State University, University Park, PA

The synthesis of silver nanoparticles, AgNP, via reduction of silver (I) oxide with hydrogen gas was published [1,2] and the plasmon absorption spectra as well as the corresponding absorption coefficients were reported. However, no details regarding the reaction kinetics were presented. In this work, using a modified synthetic procedure, we determined the reaction rate constants and reexamined the absorption coefficients values. The reduction of silver(I) with H_2 gas can be presented as[1]:

$$Ag_2O(aq) + H_2(g)\ 2Ag(s) + H_2O(l)$$

Since the solubility of silver(I) oxide in water is 2.2×10^{-4} mol Ag kg^{-1}, in order to have all the silver in the form of Ag^+, in our experimental work we used 10 mg Ag_2O per 3 L of water. The H_2 pressure and temperature were maintained constant (P = 10 psi, T = 70°C). The pH was adjusted to be 10. Typically, it took ~ 3 hours for the AgNP synthesis to go to completion. The AgNP size was estimated from the plasmon spectrum wavelength maximum[2,3]. Our plasmon spectral maxima were in the range from 398 to 405 nm. The lowest wavelength in Reference 2 for which the corresponding particle diameter is reported to be 417 nm. An attempt to extrapolate the lowest six wavelength values failed because there was no apparent trend in the graph. Reference 3 does report the relation between the maximum wavelength and particle size as well as the corresponding extinction coefficients and we used them to calculate the final concentration. Since the total concentration of reduced silver was known, the final concentration AgNP was also determined using that value; the values obtained are about two times larger. The reasons for the discrepancies could be (a) the AgNP synthesis reported in Reference 3 was performed using citrate as a stabilizing agent, which affects the extinction coefficient, (b) the shape of our AgNP is not known and an electron microscopy experiment is needed to comment on this factor. The UV-Vis absorption spectra were measured during the synthesis in order to get an idea about the AgNP formation rate. It was found that the AgNP formation rate was linear in the first two hours of synthesis; the corresponding rate of formation was found to be $(1.4 \pm 0.2) \times 10^{11}$ particles per minute at 70°C and at 24 psi hydrogen pressure. This project is funded by Stephen and Patricia Benkovic Summer Research Award in Chemistry.

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Poster Presentation 24

Designing New Experiments for Contemporary General Chemistry Laboratory Part 1. Gravimetric Determination of Universal Gas Constant

Taylor Hufnagel and Bratoljub H. Milosavljevic

Department of Chemistry, The Pennsylvania State University, University Park, PA

In the current structure of our STEM educational system, laboratory learning and classroom learning are mutually beneficial. However, the efficacy of laboratory practices, especially when high quality demonstrations are available at the click of a button, is often called into question. As pointed out by S. L. Bretz in the paper "Evidence for the Importance of Laboratory Courses," laboratory instruction can be quite financially draining[1]. One question S. L. Bretz asks, "What arguments and data would your department amass to defend laboratory instruction if your university administration decided that virtual laboratories and simulations would be a far less expensive pedagogy that does not compromise student learning?" In response, M. Seery argued that the laboratory is an irreplaceable place where students learn how to do chemistry[2]. We agreed with his statement and designed a lab that allows students to gain hands on experience with essential laboratory skills as well as experience with data processing and error analysis. These skills are also important in preparing students for undergraduate research.

The project/experiment title is: Gravimetric study of pressure vs. amount of nitrogen relationship under isochoric and nearly isothermal conditions. Because the relation $P = f(n)$ has never been published and included in general chemistry textbooks, outcomes are not known to the students; therefore, the project successfully mimics a project that produces new knowledge. The second advantage of this project is that the students have all the necessary background knowledge so that they can have full ownership of it. The experimental data obtained are such that the data processing and error analysis can also be learned and practiced. In the poster to be presented, the inquiry-based introduction of the project to the students as well as the guidance throughout the project are detailed. The project experimental setup and procedures are fully described and explained. The corresponding reports and PowerPoint presentations by four students are analyzed and the learning gains are discussed.

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Poster Presentation 25

DSC and Ru(bpy)$_3^{2+}$ Luminescent Probe Study of Fully Hydrated Nafion® Membrane in Sub-Zero Temperature Range

Yin-Jen Chang[1] and Bratoljub H. Milosavljevic[2]

[1]*Department of Chemical Engineering, The Pennsylvania State University, University Park, PA*

[2]*Department of Chemistry, The Pennsylvania State University, University Park, PA*

Nafion® membrane has been widely used as a key component in high performance fuel cells due to its high proton conductivity and slow chemical aging characteristics[1]. Although many studies have been published on this subject, the membrane performance at low temperatures is not fully understood[2]. In this presentation, we report our DSC study results as well as the data obtained using the Ru(bpy)$_3^{2+}$ luminescence probe. The DSC thermogram obtained using 10 °C/min heating and cooling rates reveals that the frozen water in Nafion® membrane melts at -22 °C, which is consistent with the previously established fact that the water freezing/melting temperatures are sample size dependent[3]. The enthalpy of melting of water was found to be 253 J/g, which can be rationalized as that 24 wt% of water remains unfrozen when the sample was cooled to -150 °C. The difference in enthalpies of the water freezing and the ice melting peaks indicate water freezing starts at -38 °C; about 34 wt% of water is frozen at -65 °C and water continues to freeze as the temperature decreases to -150 °C. To understand this peculiar water behavior, the Ru(bpy)$_3^{2+}$ luminescence probe, which is sensitive to spatial confinement, is applied[4]. The emission spectrum maximum was measured as a function of temperature; the uninterrupted hypsochromic shift down to -105 °C was observed. Two crossover points were noticed (-30 °C, -71 °C); they can be attributed to some phase transitions of the polymer matrix. The crossover at -105 °C can be attributed to the complete freezing of water since the Ru(bpy)$_3^{2+}$ spectrum hypsochromic shift is negligible below that point. The NMR measurements reported in Reference 2 were performed in the temperature range from +25 °C to -70 °C, while our measurements were performed in the temperature range from +25 °C to -150 °C and that is the reason for the discrepancy in the frozen water percentage determined.

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Poster Presentation 26

Solvent Effects on Photophysical Properties of Dansyl Chloride: Study Using Ethanol-Water Mixtures

Gary Chen, Juliana Redisi, Ziqiao Wang, Shae Johnstone, Bratoljub H. Milosavljevic

Department of Chemistry, The Pennsylvania State University, University Park, PA

Dansyl chloride, 5-(dimethylamino)naphthalene-1-sulfonyl chloride, DNSC, has the ability to react with the N-terminus of amino acids, which does not hinder its role in biological processes. Due to its fluorescence properties, DNSC is useful in protein sequencing, amino acid labeling and studying the mechanisms of biological macromolecules[1,2]. However, the understanding of the photophysical properties of DNSC itself is incomplete. First, in this work, the photophysical properties of DNSC were studied in anhydrous ethanol; the absorption spectrum exhibited a maximum at 366 nm and the corresponding extinction coefficient was found to be 3,500 M^{-1} cm^{-1}. The DNSC emission spectrum maximum is centered at 526 nm; the Stokes shift at room temperature is 8,308 cm^{-1}. This Stokes shift was compared to that of PRODAN (7,056 cm-1), which is known to have an increase in the dipole moment of 5 Debye upon electronic excitation[3]. This indicates that upon electronic excitation, the dipole moment of DNSC increased more than 5 Debye. The aforementioned difference in dipole moments can be attributed to the stronger electron withdrawing ability of the sulfonyl group in comparison to that of carbonyl group in PRODAN. Addition of small amount of water (1 v/v%) resulted in a hypsochromic shift of the absorption spectrum (2,256 cm^{-1}), which could be attributed to the fast dissociation of chloride anion followed by either an acid or ethyl ester formation. These reactions are accompanied with a formation of new fluorescent species whose peak is centered at 519 nm and comprises of two components. Further increase in water concentration increases intensity of the spectrum centered on shorter wavelengths while intensity of the spectrum at higher wavelengths decreases; the isosbestic point is centered at 513 nm; this change in spectral shape can be attributed to the acid – ester equilibrium. The future work will include the emission lifetime and quantum yield measurements as well as the related thermodynamic and kinetic studies.

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Poster Presentation 27

Rapid Detection and Identification of Microplastics using Nile Red

AnQi Chen and Dan Sykes

Department of Chemistry, The Pennsylvania State University, University Park, PA

Microplastics have become an issue of increasing concern in recent years due to their ubiquitous presence in the environment and the risk of injuries or ingestions by organisms at all trophic levels. The purpose of the current research is to develop a method to identify nano- and micro-plastics via fluorescence labeling. The fluorescent dye, Nile Red, has a well characterized solvatochromatic shift in both excitation and emission spectra. A fundamental premise of our study is that Nile Red will exhibit a similar shift as function of the dielectric constant of plastics. We measured the dielectric constants of eight common plastics; dielectric constants shifted from 2.04 F/m for Teflon to 3.45 F/m for Nylon which correlates to the polarity of the functional groups. The solvatochromatic shift of Nile Red emission adsorbed on to the surfaces of the plastics linearly scales with dielectric constant (R^2=0.8928). We are currently in the process of acquiring micro-reflectance UV-Vis spectra to determine if there is a solvatochromatic shift in the excitation spectra of Nile Red. Based on these results, we are exploring possibility of a flow-through cell method of detection to distinguish between plastic types. This project is funded by Stephen and Patricia Benkovic Summer Research Award in Chemistry.

Poster Presentation 28

Synthesis and Characterization of Porphyrin Building Blocks

Minmay Duplanty, Ngoc Troung, and William Ames

Department of Chemistry, Juniata College, Huntingdon, PA

The syntheses of meso-substituted dipyrromethane (DPM) and bilane have been accomplished. The small-scale experiments involve the reaction of an aldehyde and pyrrole in the presence of an acid catalyst under nitrogen gas. The excesses are later removed, and white crystals are expected to be the final products. Upon synthesis of the DPM and bilane, characterization is completed using 1H NMR, mass spectrometry, and IR-spectroscopy. This standard DPM synthesis was being compared with a new novel synthesis of meso-substituted DPM in sodium dodecyl sulfate (SDS) micelles. The synthesis of bilanes has been less challenging than the synthesis of DPMs. The purpose of these experiments is to prepare building blocks for the ultimate synthesis of porphyrin hybrid materials.

Poster Presentation 29

Thermodynamic properties of A ⥋ 2B reversible gaseous chemical reaction

Wezi D. Mkandawire[1] and Bratoljub H. Milosavljevic[2]

[1]*Department of Chemical Engineering, The Pennsylvania State University, University Park, PA*

[2]*Department of Chemistry, The Pennsylvania State University, University Park, PA*

The determination of the thermodynamic properties of A ⥋ 2B reversible gaseous chemical reaction (the dissociation of propionic acid dimers in the gaseous phase) is a valuable and pedagogically rich undergraduate physical chemistry experiment. The experiment learning goals are (i) to understand the logic behind the design of an experiment, (ii) to calibrate laboratory equipment and operate an apparatus to collect pressure vs. temperature data under isochoric and constant mass conditions, (iii) to apply knowledge related to the calculation of thermodynamic parameters of reversible first-order reactions, (iv) to become familiar with the estimation of uncertainties and errors of data collected, and (v) to write an evaluative lab report and produce a PowerPoint presentation. By comparing the measured P = f(T) data to corresponding data calculated using the ideal gas law, students provide evidence for the existence of acid dimers at room temperature. Further data processing produces the equilibrium constant Kp for acid dimer dissociation as a function of temperature. By applying the van't Hoff equation, they determine the reaction enthalpy change ΔrH; subsequently, the entropy change ΔrS, and free energy ΔrG can be calculated. The analysis of possible interactions between the propionic acid molecules indicates that the hydrogen bonding between the carboxylic groups is responsible for the dimer formation; the corresponding bond strength can be obtained from the ΔrH. To further analyze the data, the students use the Maxwell distribution of molecular velocities to compare the kinetic energy of monomers and dimers to that of hydrogen bonding in dimers.

In conclusion, the experimental values produced are reproducible and compare well with previously published experimental data. The most recent version of this laboratory experiment was updated four years ago and has been utilized in CHEM 457, the experimental physical chemistry course at Penn State, since then. Based on the evaluation of graded students' reports, it proved itself a valuable learning experience.

Poster Presentation 30

Solvent Effects on Photophysical Properties of PRODAN in Ethanol-Water Binary Mixture

Yin-Jen Chang[1], Sijing “Vivian” Wang[1] and Bratoljub H. Milosavljevic[2]

[1]*Department of Chemical Engineering, The Pennsylvania State University, University Park, PA*

[2]*Department of Chemistry, The Pennsylvania State University, University Park, PA*

PRODAN, *6-propionyl-2-(dimethylamino)naphthalene*, is a non-polar luminescence probe of the naphthalene family. In order to make it sensitive to medium polarity, a dimethylamino group (electron donating) and a carbonyl group (electron accepting) were attached to the 6 and 2 positions, respectively. In the original paper, it was estimated that upon excitation the dipole moment of PRODAN increases 20 Debye units[1]. Later, it was determined theoretically[2] and measured experimentally[3] that the dipole moment increase is 5 Debye units. PRODAN is not soluble in water; it forms aggregates in aqueous media[4], which obscures the related studies.

In this work, several solvents as well as the ethanol-water binary mixture of various compositions was used to learn about the PRODAN photophysical properties in (predominantly) water-containing media. The PRODAN emission spectra were measured in cyclohexane (e = 2.02), toluene (e = 2.38), 50 wt% ethanol-toluene, ethanol (e = 24.5), 50 wt% ethanol-water (e = 50.4), and 2 wt% ethanol-water (e = 79.5). As expected, the larger bathochromic shift was observed in a solvent of the highest dielectric constant, the 2 wt% ethanol-water mixture (Stokes shift = 5,781 cm^{-1}). The wavelengths corresponding to the absorbance maxima of absorption spectra of PRODAN in ethanol-water mixtures were plotted as a function of molar fraction; the extrapolation to x_{water} = 0 resulted in l_{max} = 358 nm. The same data processing was applied to the PRODAN emission spectra; the emission maximum wavelength corresponding to pure water was found to be 523.6 nm. The preferential solvation analysis indicated that the PRODAN solvation shell composition deviates from the ideal behavior (the weighted linear combination of the water and ethanol contributions); the highest deviation (75 %) was observed at $x_{ethanol}$ = 0.35 mol%. The temperature dependence of fluorescence maximum wavelength was studied using a 33.2 mol% ethanol-water binary mixture; a hypsochromic shift was observed on increasing temperature. There is a number of factors that can contribute to this effect (increased kinetic energy of solvent molecules, hydrogen-bonding between solvent molecules, changes in entropy, etc.). Dynamic molecular simulations are required to fully elucidate the observed temperature effect.

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Poster Presentation 31

Matrix Dynamics Study of Hydrated Copolymer 44 mol% PE-co-PVA Using Ru(bpy)$_3^{2+}$ Luminescence Probe

Sindy Liu, Sushmita Barua, Melisa Slye, Ryan Lai, and Bratoljub H. Milosavljevic

Department of Chemistry, The Pennsylvania State University, University Park, PA

Poly(ethylene-co-vinyl alcohol), PE-co-PVA, possesses unique physicochemical properties as it combines the convenient rheological/mechanical/chemical properties of polyethylene, PE, with the low gas permeability of poly(vinyl alcohol), PVA. For example, oxygen permeability of 44 mol% PE-co-PVA in the dry state is approximately three orders of magnitude less than that of PE[1]. However, PE-co-PVA copolymers are hydrophilic and their hydration increases oxygen permeability. Much like PE, PVA-co-PE can be crosslinked by ionizing radiation and that provides a pathway to reduce the hygroscopicity. The previous research revealed that water (10 wt%) embedded in the 44 mol% PE-co-PVA has a marked effect on the radiation-induced crosslinking drastically increasing its efficacy, but no insight into the reaction mechanism was offered[2]. Since it is likely that water is solubilized in the PVA hydrophilic domains, in this work, it was intended to characterize their dynamics as a function of temperature; the Ru(bpy)$_3^{2+}$ fluorescent probe was used for that purpose. Previous research has indicated that the excited state of Ru(bpy)$_3^{2+}$ is sensitive to spatial confinement and its excited electron orbital strongly interacts with medium modes[3].

A 44mol% PE-co-PVA copolymer film was soaked into a 2 mM solution of Ru(bpy)$_3$Cl$_2$ and heated above its glass transition temperature (Tg). Subsequently, optical absorption and emission spectra of the probe were taken and compared to that obtained in bulk water medium. From the slight bathochromic shift in the UV-Vis absorption spectrum (2 nm) and the slight hypsochromic shift (7 nm) in the emission spectrum, it was concluded that that the Ru(bpy)$_3^{2+}$ molecule can relax upon excitation almost as freely as in bulk water. The emission peak shifts continuously as temperature decreases from +38 ℃ to -150 ℃ indicating that neither (apparent) first nor second order phase transitions occur in this temperature region . The Arrhenius plot of the Ru(bpy)$_3^{2+}$ inherent unimolecular decay of the excited state exhibits a crossover at -18.5 ℃, which can be attributed to the deactivation of a polymer matrix mode(s) that strongly interact with Ru(bpy)$_3^{2+}$ excited electron orbital. The mode(s) deactivation only slightly affects the copolymer heat capacity as found in the corresponding DSC experiment.

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Poster Presentation 32

A Molecular Dynamics Investigation of Ternary Phase Diagrams

Benjamin Cunningham and William Ames

Department of Chemistry, Juniata College, Huntingdon, PA

Molecular dynamics (MD) simulations allow for a molecular scale picture of the motion and interactions of molecules. In this work, ternary phase diagrams from experimental titrations and MD simulations are compared, all work done at Juniata College. The ternary system in question contains mixtures of 1-propanol, hexane, and water. This ternary system results in either a single homogeneous phase or two liquid phases depending on the relative amounts of each component. Initial MD topologies were produced by the CHARMM-GUI website. The as-constructed topologies built by the CHARMM-GUI were minimized and equilibrated at 300 K using the GROMACS molecular dynamics software package with the defaults provided by the CHARMM-GUI. Production runs of each equilibrated system of 1.0 ns were analyzed using density profiles to determine relative mass % of each liquid phase. After finding incoherent data, the production runs were lengthened to 10.0 ns, which provided more discernable data. MD simulation mass % results were then compared to experimental results to determine that MD simulations provide qualitative approximations. However, results show these simulations may only achieve quantitative agreement after fine adjustments to the duration of runs.

--End of Abstracts--