

4-01

**Expanding the Utility and Understanding of Room Temperature Ionic Liquids: Including Micelle Formation and Interactions with Gold Nano-particles**

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Room temperature ionic liquids (RTILs) cannot be adequately characterized on the basis of polarity or any single parameter scale. RTILs are complex entities compared to the relatively simple molecular solvents used in most chemical processes.<sup>[1]</sup> They are capable of a wider range of intermolecular interactions than most other solvents. This includes: dispersive, n- $\pi$ ,  $\pi$ - $\pi$ , dipolar, hydrogen bonding, hydrophobic, and ionic interactions. A multi-parameter scale, that takes into account the many different possible solvent properties, can be used to properly characterize RTILs as well as other solvents.<sup>[1]</sup> Their unique properties appear to induce the formation of solvophobic normal micelles when surfactants are dissolved in RTILs.<sup>[2]</sup> Also, gold nano-particles are more easily formed and dispersed in RTILs than in normal solvents.<sup>[3]</sup> We can now understand why RTILs behave differently than single solvents for organic reactions, and which ones are most promising as MALDI matrixes,<sup>[4]</sup> for extractions and as chromatographic stationary phases.<sup>[5,6]</sup> Chiral ionic liquids and their use will be discussed as well.<sup>[7]</sup>

4-02

**Development of a Universal Method for the Determination of Enantiomeric Compositions of Pharmaceutical Products**

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A new method has been developed for the determination of enantiomeric compositions of a variety of drugs including propranolol, atenolol, and ibuprofen. The method is based on the use of the near-infrared (NIR) technique to measure diastereomeric interactions between an added carbohydrate compound with both enantiomeric forms of an analyte followed by partial least square analysis of the data. The fact that the method works well with all three macrocyclic carbohydrates with different cavity size (i.e.,  $\alpha$ -,  $\beta$ - and  $\gamma$ -cyclodextrin) as well as with sucrose, which is a linear carbohydrate, clearly demonstrates that it is not necessary to have inclusion complex formation in order to produce effective diastereomeric interactions. Rather a simple adsorption of the analyte onto a carbohydrate is sufficient. Since inclusion complex formation is not a requisite, this method is not limited to the amino acids studies here but is rather universal and sensitive as it can, in principle, be used to determine enantiomeric compositions for all types of compounds with only microgram concentration and enantiomeric excess as low as 1.5 %, in water or in a mixture of water and organic solvent. Furthermore, it does not rely on the use of rather expensive carbohydrates such as cyclodextrins but is equally as effective even with a simple and inexpensive carbohydrate such as sucrose.

4-03

### **Determination of Environmentally Important Metal Ions by Fluorescence Quenching in Micellar Solutions**

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This work describes the determination of environmentally important metal ions by fluorescence spectroscopy in micellar solutions. Several metal ions have been used as quenchers of the fluorescence of naphthalene, in aqueous micellar sodium dodecyl sulfate (SDS). The quenching by the metal ions can be described by the Stern-Volmer equation and the detection limits are improved with low SDS concentrations. Apparent Stern-Volmer constants decrease in the order:  $\text{Fe}^{3+} > \text{Cu}^{2+} > \text{Cr}^{3+} > \text{Ni}^{2+} > \text{Pb}^{2+}$  and reflect the sensitivity of the method. Similarly, using the cationic chelating agent 8-hydroxyquinoline (8-HQ), allows the simple, rapid and sensitive assay of  $\text{Zn}^{2+}$  in aqueous micellar solutions of cetyl trimethyl ammonium bromide (CTABr). In the absence of CTABr, the complex formed between 8-HQ and  $\text{Zn}^{2+}$  is insoluble. Micelle-enhanced fluorescence spectroscopy and fluorescence quenching can be used as analytical methods of general application and is an interesting area of research to improve the detection limit of several analytical methods.

4-04

### **Solid-Phase Microextraction: a Link between Micellar Extraction and Gas Chromatography**

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The Micellar Solid-Phase Microextraction (MSPME) is a new technique for sample treatment. MSPME intends to combine the advantages of the micellar extraction with the advantages of the gas-chromatography by means of the solid-phase microextraction (SPME). The present work shows not only the use of MSPME to quantify solutes in solid matrixes but also its ability to determine partition coefficients of solutes between micellar media and aqueous phases.

In the first case, the PAHs contained in a reference marine sediment have been extracted with surfactants. Afterwards, these compounds are removed from the micellar media by using the adequate SPME fiber, and determined by GC-MS. This step is accomplished just desorbing the SPME fiber in the injector of the GC, without needing to remove the surfactant prior to injection. With this new method, the previous treatments in the analysis of any non-polar compound contained in solid samples could be reduced to a stage of solubilization of the same ones in a micellar medium followed by a separation using SPME-GC.

In the second case, the partition coefficients of 16 PAHs and 29 Phenols between ionic and non-ionic micellar media and aqueous phases have been established using MSPME.

The obtained results show that this technique is especially adequate by its simplicity and by leaving the binding equilibrium undisturbed.

4-05

#### **Development of Functionalized Admicelles in Separation Science**

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Surfactant molecules cooperatively sorb on solid surfaces and form aggregates namely hemi-micelles or admicelles in the aqueous solution. Through mixing of surfactants, porous solid materials, and hydrophobic chelating agents or surfactant-conjugated substrates (affinity ligand) in the aqueous solution led to the formation of media for the collection of metal ions or proteins. Different from conventional separation media having chemically bound ligand, the functionalized admicelles have degree of freedom in the preparation. Furthermore, dynamic property and high water permeability of the admicelles can facilitate the interaction of ligand with an objective compound. An admicelle composing of Triton X-100, porous polystyrene-divinylbenzene (Amberlite XAD-4), and Triton X-100-conjugated Cibabron blue 3GA (affinity ligand) was found to be useful for purifying lysozyme from egg white, but was ineffective for the collection of alcohol dehydrogenase (ADH). The uses of octadecylsilyl-silica gel instead of XAD-4 and an affinity ligand having a longer polyoxyethylene moiety were effective for the separation of ADH from bakers' yeast.

4-06

#### **Powerful Preconcentration Method for Ultra Trace Amounts of Polycyclic Aromatic Hydrocarbons and its Application to the Environmental Analysis**

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A preconcentration procedure is one of the most important techniques for the environmental analysis. In this study, lower ppt levels of polycyclic aromatic hydrocarbons (PAHs) in environmental water can be determined by the proposed powerful preconcentration method with high performance liquid chromatography using fluorescence detection (FL/HPLC). The preconcentration method consists of the combination of the blue cotton method (solid-phase extraction) and the homogeneous liquid-liquid extraction. In the case of the homogeneous liquid-liquid extraction, PAHs in the eluate of solid-phase extraction were extracted into micro volume of sedimented phase. The proposed method could completely concentrate 1 liter to 20 microliter within one hour and the 20 microliter of sedimented phase is directly injected into FL/HPLC. The entire preconcentration factor was 50,000-fold. Six kinds of PAHs were determined in the range of  $3.0 \times 10^{-18} \sim 4.5 \times 10^{-11} \text{ mol L}^{-1}$ . These chemicals were also satisfactorily

separated. By changing the combination of various preconcentration methods or instrumental analysis, the various samples could be analyzed.

4-07

#### **Cloud Point Extraction as a Preconcentration Step for the Analysis of Metals in Environmental and Biological Samples**

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Cloud point extraction (CPE) is a powerful separation method with a pronounced capability to preconcentrate trace and ultra-trace metals in diluted samples of diverse origin such as environmental, biological and industrial concern. This procedure have advantages over those currently available including low cost, safety, feasibility for injection of the surfactant-rich phase into any hydrodynamic analytical system and high capacity to concentrate a wide variety of analytes of widely varying nature with high recoveries and very high concentration factors. CPE has been employed for the preconcentration of metal complexes such as mercury, aluminium and rare-earth elements prior to inductively coupled plasma atomic optical emission spectrometry (ICP-OES) and Absorciometry UV-Vis coupled to flow injection (FI). On the other hand, the possibility to preconcentrate lead and aluminium without added chelating agents has been demonstrated. Indeed, the coupling of CPE to Capillary Electrophoresis (CE) was successfully performed to preconcentrate and simultaneously determine lead, platinum/palladium, and iron/dysprosium. The samples under analysis include different water samples, human saliva, urine and industrial samples.

4-08

#### **Enhanced Organic Photovoltaic Performance from Nanoparticle – Polymer Blends**

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Blends of single walled carbon nanotubes (SWNTs), semiconducting nanostructures, nano-metals (Ag, Au), and/or fullerene derivatives with conjugated polymers (MEH-PPV, PFO, PEDOT, P3OT, P3HT), have been of great interest recently as a mechanism to raise the overall performance efficiency of organically-based, flexible, devices such as photovoltaics, organic light emitting diodes, and more. We have recently developed novel methods for controlling both the electronic properties of the nano-phase and the long range “meso-structure” of the blend. Through the use of selective doping (boron and nitrogen dopants) in carbon nano-structures we have demonstrated control over the donor-acceptor role of the nano-phase in the host, allowing for tailoring of the specific trapping levels introduced. Thus, as we show with time-of-flight, we are able to introduce donor or acceptor states within the HOMO-LUMO gap of the host, and control the relative positions of these states. Secondly, we have demonstrated that an order can be created within the nano-phase, with controlled placement and orientation of the nanoparticles. These ordered nano-blends of conjugated systems exhibit a number of exciting

properties including: modified carrier mobilities, optical absorption, and exciton separation dynamics. In this work we integrate this meta-functional nano-phase blend into a standard flexible organic photovoltaic device. Using commodity polymers, surprisingly high efficiencies can be obtained.

4-09

#### **Morphological Control and Spectrometric Applications of Gold Nanorods**

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Gold nanorods (NRs), rod-like nanoparticles, show characteristic two plasmon bands based on a longitudinal oscillation mode along the long axis (far-red/near-infrared region) and a transverse mode perpendicular to the long axis (visible region). Thus, the NR shows a distinct dichroic property. Quite recently, we developed a novel and simple method for the preparation of gold NRs, by the combination of chemical reduction and subsequent photoirradiation. We have first succeeded in well-dispersed fixing of the gold NRs onto a glass substrate by the layer-by-layer approach. When the NR-modified plate was immersed into the solvent, the longitudinal plasmon band showed substantial red shift, while the transverse SP band showed no substantial shift. The degree of peak shift was roughly correlated with the order of refractive index (dielectric constant) of the solvent. The monoparticle layer film of gold NRs was also prepared at the liquid-liquid interface. The NR film showed distinctly larger Raman scattering signals than the corresponding nanospheres film. We also prepared the aggregate of phosphatidylcholine-modified NRs and DNA. Controlled release of DNA from the aggregates was possible by pulsed irradiation of near-infrared laser light.

4-10

#### **Luminescent Nanoparticles as Labels for Biological Molecules**

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Luminescent nanoparticles such as semiconductor nanocrystals (so called Quantum Dots [QDs]) or rare earth doped nanoparticles gained increasing interest over the past several years. Compared with organic fluorophores, such particles possess substantial optical advantages: For example they don't bleach under excitation, possess a narrow – often tuneable – spectral linewidth and make new detection techniques possible e.g. upconversion luminescence or lifetime multiplexing.

The application of these particles in bioanalytics is promising, but a pre-requisite is, that they are colloiddally stable in biological buffers and can be coupled to appropriate biomolecules. Since high-quality (monodisperse) nanoparticles are usually synthesised in non-polar media as for example trioctylphosphinoxide (TOPO) or high-boiling alkanes, the particle surface must be derivatised in such a way that on the one hand the phase-transfer is possible and on the other hand biomolecules such as proteins or nucleotides can be coupled selectively.

First an overview of luminescent nanoparticles, which are used in bioanalytic applications, is given. Preparation methods regarding those applications are discussed. Furthermore, different possibilities for non-polar/polar phase-transfers are presented. Thereby the encapsulation of single nanoparticles with silica layers will be a special emphasis (cf. figure 1). Moreover, possibilities for the coupling of nanoparticles to biomolecules are discussed. Finally, some examples for the imaging of biological systems with luminescent nanoparticles are presented.

4-11

### **Nanostructure-Assisted Laser Desorption Ionization Mass Spectrometry in Bioanalysis**

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Surface-assisted laser desorption ionization mass spectrometry (SALDI-MS) has drawn considerable attention for its efficiency in detection of species in the low-mass region. Nevertheless, the correlation of the surface property of roughened inorganic substrate with its desorption ionization efficiency remains unclear. We report herein a new nanofabrication method to generate well-controlled surface features and systematically vary the surface geometry with the aim of seeking a fundamental understanding of the SALDI mechanism. Specifically, convective self-assembly is used to generate close-packed 2-D nanoparticle arrays on a flat Si surface. This hexagonal-packed nanoparticle array is then used as a mask in nanosphere lithography to selectively remove portions of Si surfaces in reactive ion etching (RIE) and generates triangle-shaped nanocavities in periodic patterns with pre-defined feature parameters. Mass spectrometry detection of small molecules and peptides on such substrates shows good sensitivity with little fragmentation and minimal background interference. Ordered feature size, shape, and surface density are tailored by varying fabrication conditions. The impacts of surface geometries on MS performance are correlated. The thermal properties of the substrates are investigated. The use of the substrates in metabolite profiling and quantitation of *Arabidopsis thaliana* extracts is also presented.

4-12

### **Gold Nanoparticle Matrices for Bioanalysis using Matrix-Assisted Laser Desorption Ionization**

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Nanoparticles, esp. gold nanoparticles (AuNPs), have found wide application in chemical biology and biochemical applications. Importantly, the optical and electronic properties of NPs depend on size, shape, composition, and derivatization. Thus, NPs can be tailored to specific applications, *e.g.* using functionalized AuNPs for selective isolation of target analytes. We present here the utility of AuNPs and surface derivatized AuNPs as potential matrices for matrix-assisted laser desorption ionization (MALDI) mass

spectrometry (MS). These alternative substrates offer a number of advantages over conventional MALDI matrices (*e.g.* small organic acids): (i) greater flexibility in sample deposition conditions (*e.g.* pH, solvents, etc.), (ii) relatively uncomplicated spectra in the matrix region (low mass range), (iii) Au-cluster species as internal standards for mass calibration, and (iv) AuNPs afford a very high shot-to-shot and spot-to-spot reproducibility (<10 % RSD). Furthermore, the surface chemistry of AuNPs also plays an important role in the ionization process, and has been investigated. Surface association of ions and the solvent structure around these species in solution have an effect on analyte interactions with the AuNPs, thus leading to changes in ionization efficiency. These studies present many interesting avenues that can be pursued in various chemical biology systems.

4-13

#### **Chemical Separations Using Nanoparticles**

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The use of chromatographic columns packed with small particle diameters allows the exploration of the theoretical limits in liquid chromatography, as theory predicts that a reduction in particle diameter would provide an increase in separation efficiency with a concomitant reduction in analysis time. Our research group has been exploring such predictions by first synthesizing organosilica particles with diameters in the nanometer range and using them for capillary electrochromatography (CEC) and ultrahigh pressure liquid chromatography (UHPLC). Although a gain is noticeable when using particle diameters below 1  $\mu\text{m}$ , the actual gain combined with practical considerations are factors to consider in the separation formats studied. Using another nanoparticle technology and the nanoscale separation technique of capillary electrophoresis, we also explore the use of fluorescent nanoparticles as “labeling” tags to enhance detection of biomolecules. We will discuss our recent findings as we implement these new technologies in chemical analysis.

4-14

#### **Gold Nanoparticles in Open-Tubular Capillary Electrochromatography and Supercritical Fluid Extraction**

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Nanoparticles exhibit unique size-dependent optical, catalytic, magnetic, and electronic properties compared to their bulk counterparts and can enhance a variety of technologies including chemical processing, medical, electronic, environmental, separation and sensing applications. Gold nanoparticles in particular, are among the most stable metal nanoparticles, and are viewed as key materials and building blocks, with emerging applications in biology, catalysis and nanotechnology.

To-date, very little research has been devoted to the application of nanoparticles in separation science. The significant advances, which have been made in electrophoresis and microchip separations, show the promise to enhance separation performance by using nanoparticles. For example, latex nanoparticles have been used to coat a micromachined channel on-chip, and on-chip ion chromatography of inorganic anions, nitrate, nitrite, and iodide, has been achieved.

In this paper, important new roles for gold nanoparticles in open-tubular electrochromatography (OTCEC), and in the extraction of this precious metal using supercritical carbon dioxide will be highlighted. Specifically, the use of alkylthiolgold nanoparticles in OTCEC to improve the efficiency of separation and the selectivity between selected solutes will be demonstrated, in particular, for hydrophobic test solutes and for selected polycyclic aromatic hydrocarbons (PAHs).

4-15

#### **Development, Evaluation and Application of Nanoparticles as Stationary Phases for Gas Chromatography**

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We are exploring using a thin film of gold-centered monolayer protected nanoparticles (MPNs) as a stationary phase for open-tubular gas chromatography (GC). The MPN films have thermodynamic and mass transfer properties that serve them well, providing good chemical selectivity and high separation efficiencies (high N). High surface area-to-volume ratios of MPNs provide ample sample loading capacity. A majority of our work has been with dodecanethiol MPNs, with a dodecanethiol monolayer linked to a gold nanoparticle. Films of dodecanthiol MPNs ranging from 10 to 60 nm provided efficient separations with various capillary dimensions. The MPNs have a nominal diameter of about 3 nm, so film depths are only a few nanoparticle diameters. High-speed separations with dodecanethiol MPNs in a film depth of ~ 15 nm in a square channeled capillary have been achieved and these results hold considerable promise for the development of “high performance” microfabricated GC. We are also investigating MPN columns for ultra high-speed GC, where separations of several analytes in a fraction of a second are achieved, engendering the notion that GC can function like a chemical sensor. Current development of polar stationary phases utilizing 4-chlorobenzenethiol MPNs and 4-(trifluoromethyl)benzenethiol MPNs will also be discussed.

4-16

#### **Non-Cross-Linking Aggregation of DNA-Carrying Nanoparticles for Single-Base Substitution Assay**

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The graft copolymer consisting of poly(N-isopropylacrylamide) (PNIPAAm) and single-stranded DNA was prepared as a DNA-conjugated material. Interestingly, the DNA-conjugate was found to form nanoparticles above physiological temperature (*Langmuir*, **20**, 313-319 (2004)). We found that non-cross linking aggregation of the nanoparticles was induced by the hybridization of the surface-bound DNA with the full-match complementary DNA, but not with one-base mismatch. The results demonstrated that the non-cross linking aggregation of DNA-carrying nanoparticles is useful for analyzing various SNPs. The core material is not restricted to PNIPAAm; DNA-functionalized gold nanoparticle (15 nm diameter) was found to show a similar aggregation phenomenon induced only by the fully-complementary DNA, resulting in rapid color change within 3 min at ambient temperature (*J. Am. Chem. Soc.*, **125**, 8102-8103 (2003)). This methodology is general in principle and applicable for wide variety of clinical diagnosis.

4-17

### **Enzymatic Amplification of Chemical Signals Inspired by Biological Signal Transduction**

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Intermolecular communication between a receptor and an effector on the biomembrane surface plays a pivotal role of the information processing in biological system. We have recently developed an artificial intermolecular communication system on colloidal lipid vesicles, as a molecular device, inspired by the biological signal transduction. The system is constituted in combinations of an artificial ditopic receptor, an enzyme as an effector, and a bilayer-forming synthetic lipid. The cationic bilayer membrane formed with the synthetic peptide lipids or the Cerasome-forming lipids was an effective platform for self-assembling of such functional molecules. On the membrane surface, the enzymatic activity was effectively synchronized with ditopic recognition of the receptor toward an external signal and a mediator species between the receptor and the effector. Marked signal selectivity which is characteristic to the aqueous colloidal interface was observed. The signal transduction efficiency was sensitively tuned with gel to liquid-crystalline phase transition of the matrix membrane. The present molecular device acts as a unique sensing system, in which the information on the molecular recognition of various biologically important species by the receptor is transmitted to the enzyme and amplified chemically as the catalytic reaction.

4-18

### **Triggered Drug Release from Membrane Coated Silica Nanoparticles**

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The presentation will focus on the recent development of a new and improved nanoparticle formulation for drug delivery applications. It is based on the idea that it is possible to increase the density of drug molecules in nanometer-sized particles compared

to micrometer-sized particles because of the increased surface area. The increasing loading efficiency may prove useful in applications require high dose of drugs. Furthermore, because of their small dimensions the particles could permeate through cells and tissues and even through the blood brain barrier. Recent studies in our laboratory focused on the synthesis of drug containing phospholipids-coated silica nanoparticles and their utility as drug carriers. Drug release from these particles is triggered by exposing them to anti microbial peptides at micromolar levels. When combined with selective targeting capabilities the drug containing nanoparticles could target cells and then release their drug content in response to a trigger signal. The chemical and physical features of the particles and their interaction with cells in cell culture will be discussed.

4-19

#### **Analytical Measurements Using Polymeric Surfactants**

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Over the past several years, we have employed polymeric surfactants as analytical reagents, particularly as mobile phase additives for separations in capillary electrophoresis. We have shown that our polymeric surfactants are broadly applicable to the separation of a variety of analytes, including the separation of chiral compounds by use of chiral polymeric surfactants. More recently, applications for the development of novel nanomaterials in the presence of polymeric surfactants have been explored. Our studies have shown that these polymers are more suitable than conventional micelles for both separations and spectroscopic applications. In this talk, I will focus on the use of polymeric surfactants as separation reagents and for the development of spectroscopic probes. The advantages of these reagents in comparison to regular micelles will also be discussed, particularly with regard to the wide variety of applications. A comparison of the use of polymeric surfactants for separations and spectroscopy will also be made directly to separations and spectroscopy by use of conventional (unpolymerized) micelles.

4-20

#### **Liposome Enhanced Firefly Bioluminescent Assay of ATP in the Presence of Surfactants**

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The firefly bioluminescence (BL) assay has been widely used for the determination of ATP in living cells. In this assay, the ATP extractants such as surfactants are required for the release of ATP from cells, but they often inhibit the BL enzyme, luciferase. On the other hand, surfactants are known to incorporate into liposomes composed of vesicular lipid bilayers. In addition, cationic liposomes were found to enhance the BL intensity. Thus, a cationic surfactant being used as an extractant, liposomes can eliminate the inhibitory extractant and can transform into the BL-enhancer, cationic liposomes, by incorporating cationic surfactants. In this study, we exploited such a double advantage of

liposomes for the BL assay of ATP in the presence of cationic surfactants. Liposomes consist of phosphatidylcholine and cholesterol were prepared by the extrusion method using a polycarbonate filter. Benzalkonium chloride (BAC) was used as an ATP extractant. The detection limit for ATP in the mixtures containing 0.06% BAC was 25pM in the absence of liposomes. On the other hand, the BL intensity was remarkably increased by the addition of liposomes into the assay mixture, resulting in the enhancement of the sensitivity for ATP. The detection limit was improved to be 400fM.

4-21

### **Structure and Dynamics of Cationic and Nonionic Micelles: Neutron Scattering Studies**

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Micellar morphology in aqueous micellar solutions of cationic surfactants such as CTAX and CPyX can be manipulated by changing the counterion. Organic counterions that penetrate the micellar interface, such as salicylate and tosylate, produce very large, semi-flexible wormlike micelles. Flexibility depends on the surfactant's head group, the counterion, and the concentration of added salts. Increasing concentrations of NaSal or NaTos cause the micelles to undergo size reversion back to globules; the salt concentration at which this occurs is counterion-dependent. SANS data that allow micellar contour lengths, persistence lengths and cross-sectional radii to be determined will be presented, and size reversion will be found to correlate with the unfavorable energetics of decreasing radii. Our fitting protocol incorporates changes to the widely-used Pedersen-Schurtenberger scattering functions.

Neutron spin-echo studies on the local dynamics of linear and branched wormlike cationic and nonionic micelles will also be presented, as well as of saturated micellar networks.

4-22

### **Studies of Reversible Guanosine Gels**

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Guanosine gels (G-gels) are self-assembled networks of hydrogen-bonded guanine tetrads formed by guanosine nucleosides and nucleotides. G-gels combine desirable properties, such as reversibility, tunability, aqueous solubility, and biocompatibility, with the unique ability to non-covalently and reversibly introduce functionality directly into the G-tetrad network of the gel via hydrogen bonding. Their degree of organization and viscosity are dependent upon monomer concentration, temperature, pH and cation

content, providing a variety of parameters that can be used to control their formation/disassembly and to reversibly modulate their properties. This talk will present results of experiments in which Ggels are used for chiral separations in capillary gel chromatography and molecular probe studies of these gel phases related to their performance in chiral separations. Results will also be presented for gels that are under investigation for bioencapsulation.

4-23

#### **Hydrogen Bonded Molecular Macrocluster Formation at the Solid - Liquid Interface**

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Liquid molecules at the solid-liquid interfaces often exhibit different properties from those in the bulk, which is attributed to the surface-induced structuring of liquids. Elucidation of these properties is important in nanoscience and nanotechnology. We recently have found that liquid molecules with the hydrogen bonding functionalities (alcohol, carboxylic acid, and amide) form a hydrogen bonded organized structure, which we call “molecular macrocluster”, on the silica (glass and oxidized silicon) surface when they are adsorbed from their mixtures with non-polar solvents. The surface silanol groups are essential for this structure formation. FTIR-ATR spectroscopy demonstrates the hydrogen bonding interactions between the surface silanol groups and adsorbed molecules in addition to those between adsorbed molecules. Surface forces measurement reveals the long ranged attraction (e.g. extending to 30 ~ 40 nm for normal monohydric alcohol in cyclohexane) due to the contact of the opposed adsorption layers. Half the attraction range is close to the adsorbed layer thickness, which is extraordinarily long range. Interesting differences are observed in the mode of adsorption depending on the chemical groups. Dynamic properties of adsorbed molecules, ethanol on glass in cyclohexane, are studied by NMR spectroscopy. We utilize this molecular macrocluster for preparing polymer thin-films on solid surface.

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#### **Distribution of *tert*-Butylhydroquinone in Food-Like Emulsions Stabilized by C<sub>12</sub>E<sub>6</sub>**

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We have developed a new approach for estimating the distributions of antioxidants in opaque, surfactant based, macroemulsions based on the pseudophase model for homogenous microemulsions. The distribution of *t*-butylhydroquinone, TBHQ, in emulsions composed of tributyrin, C<sub>12</sub>E<sub>6</sub>, and acidic water is described by two partition constants between the oil and interfacial,  $P_O^I$ , and the water and interfacial,  $P_W^I$ , regions. To estimate values for  $P_O^I$  and  $P_W^I$  requires fitting two independent data sets with two independent mathematical relations and solving two equations simultaneously. One data set was obtained by electrochemical determination of the observed rate constant,  $k_{obs}$ , for

reaction of TBHQ with an arenediazonium ion probe as a function of  $C_{12}E_6$  volume fraction. The second data set was obtained by determining the partition constant,  $P_O^W$ , of TBHQ between tributyrin and water in the absence of surfactant by UV-Visible spectrometry,  $P_O^W = 0.015$ . The values of the partition constants in the emulsion are:  $P_O^I = 11$  and  $P_W^I = 7.11 \times 10^2$ . Application of this approach to a variety of antioxidants in emulsions containing different food oils and emulsifiers should provide new insight into the factors controlling antioxidant distributions and may lead to a development of a new scale of antioxidant efficiency.

4-25

#### **Partitioning of Polar Aromatic Compounds to Organogels and Application for their Extractive Removal from Organic Solvents**

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Organogels are formed by the addition of gelatin to Aerosol OT [bis(2-ethylhexyl) sodium sulfosuccinate] reverse micelle solutions at elevated temperatures followed by cooling. The “solid” organogels have been shown to retain many of the general properties exhibited by traditional reverse micelle solutions. Some of the general features and characteristics of these materials will be described. Results regarding the stability of organogels in a variety of organic solvents and aqueous mixtures will be presented. Partitioning data for the interaction of polar aromatic compounds (such as substituted anilines, phenols, naphthols) with the AOT organogels will be presented and compared to the partitioning observed for the same interaction with solution AOT inverted micelles. The use of organogels to remove (extract) and/or concentrate organic solutes from organic solvents will be discussed and the relevant extraction parameters summarized. In addition, the use of such an approach as a preconcentration technique prior to spectroscopic chemiluminescent determinations will be illustrated. Preliminary data obtained using CTAB [hexadecyltrimethylammonium bromide] based organogels will also be presented.

4-26

#### **Analytical Applications of Metal Nanoparticles**

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Palladium nanoparticles are of particular interest as catalyst for the synthesis of specialty chemicals, nuclear waste and environmental applications. The objective of this work was to develop a reliable experimental procedure for the synthesis and analytical applications of Pd-based nanoparticle. In designing advanced materials for nanosensors and environmental remediation, nanomaterial synthesis procedures are increasingly required to control the shape and size. Consequently, we have synthesized palladium nanoparticles through the reduction of Pd (II) acetate using polyamic acid (PAA) as a reducing agent in an organic medium at room temperature. The approach is based on subsequent capping

and stabilization of the resulting palladium nanoparticles by the PAA. The Pd-based nanostructured materials were characterized using UV/Vis spectroscopy, scanning electron microscopy and transmission electron microscopy (TEM). TEM image analysis showed the synthesized PAA-metal hybrid as well dispersed particle of different shapes (Spherical, pyramidal and octahedral). The particle sizes were in the range of 8.3-13.0 nm. In this presentation, we will show that palladium nanoparticles of variable shape may be synthesized using a simple one step procedure involving the reduction of a palladium salt by polyamic acid at room temperature. The possibility of fabricating a PAA-metal hybrid material for environmental remediation and biosensing would be presented.

4-27

#### **Colloidal CdSe Quantum Dots as Novel Luminescent Probes for Selective and Sensitive Analytical Determination of Trace Amounts of Ions in Water Samples**

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Recent developments are stressing the importance of adequate surface chemistry in the development of highly luminescent, water-soluble and biocompatible quantum dots (QDs) for applications in bioanalysis and diagnostics [1, 2]. Moreover, analytical chemists have also started to explore these nanomaterials for the development of a new generation of luminescence optical probes.

Luminescence of QDs is very sensitive to their surface states; therefore, it is reasonable to expect that eventual chemical or physical interactions between a target chemical species with the surface of the nanoparticles would result in changes on their surface charge affecting the efficiency of the core electron-hole recombination.

Following this approach, water-soluble surface-modified CdSe QDs have been synthesized and evaluated as optical probes for selective and sensitive determination of trace amounts of small ions (free cyanide and copper (II)) in aqueous solutions based on fluorescence quenching measurements.

After QDs synthesis, a photostimulation was necessary in order to obtain a stabilized emission profile resulting in reliable responses to the presence of the analytes. Moreover, the addition of surfactant agents to the measured aqueous solution was found to greatly stabilize the colloidal QDs and the fluorescent signals, resulting in a very high sensitivity for analyte detection (detection limits in the low  $\text{ng ml}^{-1}$  range are obtained) [3].

4-28

#### **Synthesis of Semiconductor Nanoparticles as Probe to Detect Supersaturated Dissolved Oxygen**

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High-quality ZnS nanocrystals are synthesized with a coordinating solvent (i.e. high boiling-point long chain amine) using zinc stearate and elemental sulfur as the precursors. Spherical ZnS nanoparticles (~2nm) were obtained and characterized using several different techniques (XRD, SEM, TEM and UV-Vis). Fluorescence intensity and decay rate of ZnS were acquired using a fluorometer. The ZnS nanoparticles have a good fluorescence at 400 nm and a long decay time (~2.5ms). The fluorescence intensity and decay time are inversely proportional to the dissolved oxygen concentration. Calibrating this relationship allows one to determine the concentration of dissolved oxygen by measuring the fluorescence intensity and/or the fluorescence decay rate. The slow decay rates and bright fluorescence make ZnS nanoparticles potential probes for measuring supersaturated dissolved oxygen, which is difficult to obtain using other techniques.

4-29

#### **Hybridization of DNA Functionalized Silver and Gold Nanoparticles in Aqueous Dispersions and on Gold Films**

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Silver and gold nanoparticles were successfully functionalized by 12mer oligonucleotides and hybridized onto gold nanoparticles in dispersions. The optical and hybridization properties of DNA linked gold-silver, silver-silver and gold-gold colloidal nanoparticles are described. In addition, the self-assembly of homo-oligonucleotides on gold films and their hybridization with their complementary pairs, unlabeled or labeled by gold and silver nanoparticles, were detected by Polarization Modulated Fourier Transform Infrared Reflection Absorption Spectroscopy (PM-FTIRRAS). PM-FTIRRAS was found to be capable to detect the base pairing between DNA strands and distinguish between the types of oligonucleotides (adenine or thymine) attached to the nanoparticles.

4-30

#### **Novel Evaluation Method of Nanoparticle Dispersibility in Nanocomposites by TEM-Computerized Tomography and 3D Image Analysis**

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We propose a novel evaluation method to characterize three-dimensional (3D) structures of nanoparticles in nanocomposites by using 3D images obtained from a transmission electron microscopy assisted by computerized tomography (TEM-CT). Since physical properties such as transparency, dimensional stability and thermal durability depend on the dispersibility of nanoparticles in a nanocomposite, it is crucial to reveal the 3D structures of nanocomposites.

The silica nanoparticle/epoxy nanocomposite evaluated is a model material to figure out our proposed method. First, the nanocomposite 3D images are reconstructed by TEM-CT. Second, the nanoparticle images are separated from the nanocomposite by binarization. Third, the summation of the shortest distances between each separated particle is normalized by an ideal distance between two particles under fcc structure, which is defined as Universal Factor (UF) as an index of the particle dispersibility to quantitatively evaluate the 3D structure of nanoparticles. It is found that silica nanoparticles in the nanocomposite are well dispersed because the UF of the nanocomposite is 0.85.

We also show the simple analytical validation in order to estimate the error of the length subject to the novel evaluation method.

4-31

#### **Systems Based on Polymeric Surfactant – Polyvinylpyrrolidone and Organic Reagents: Properties and Utilization in Analysis**

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The influence of polymeric surfactant - polyvinylpyrrolidone (PVP) for various molecular masses ( $8 \cdot 10^3$  -  $360 \cdot 10^3$ ) on spectroscopic, protolytical and complex formation properties of organic reagents (dyes of different classes) is established with the methods of UV-, visual and IR-spectroscopy. It is shown that addition PVP in solution of azo-, triphenylmethane and trioxylfluorone dyes leads to shift of absorption strips maximum of reagents, displacement of reagent dissociation. One can use PVP to modify complex formation of organic reagents with ions of metals: it is shown in increase of contrast and sensitivity of analytical reactions. On the basis of PVP adducts with organic reagents we propose manufacturing of electrochemical sensors for direct determination of polymer content in solution. The conditions of sensors work are established in model and real solutions of medicine. The complex techniques of spectroscopy and electrochemical determination of PVP concentration in medicine, bioobjects, waste water, spectrophotometry techniques of determination of average molecular mass of PVP in substation and metal ion content in different objects are developed.