### Ionic Liquid Microemulsions, Templates for Directing Morphology of Cellulose Biopolymer Nanoparticles (Briefing Charts)

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#### Abstract
Briefing Charts
Ionic Liquid Microemulsions, Templates for Directing Morphology of Cellulose Biopolymer Nanoparticles

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Outline

• Background on Cellulose and Ionic Liquids
• Materials and Methods
• Results: Designing an IL/Cellulose µemulsion
• Results: Light Scattering Studies
• Conclusions to Date and Future Work

Introduction to nano Cellulose

Cellulose is the most abundant natural polymer on Earth

- Inexpensive
- Chemically stable
- Nontoxic
- Biodegradable
- Modifiable

Cellulose Chains
- Disordered Region
- Crystalline Regions

Cellulose Nanocrystals
ILs can Dissolve Cellulose

- Cellulose is intra and inter-molecularly connected by hydrogen bonds, and is **insoluble** in water and most organic solvents.
- Solvent dissolution is necessary in multistep processes.
- Drastic conditions such as the viscose method are used for the dissolution of cellulose.
- ILs form electron donor-acceptor complexes with hydroxyl groups of cellulose resulting in separation and dissolution.

Introduction to microemulsions

- Microemulsions are transparent, isotropic, and thermodynamically stable dispersions of two immiscible liquids stabilized by surfactant.
- Applications in chemical reactions and materials syntheses with some peculiar advantages.
- Recently, ILs have replaced water and/or traditional organic solvents to prepare novel IL-based microemulsions.
- Similar to “classic” microemulsions, gradual substructural transition from microdroplets to a bicontinuous structure spans the single-phase microemulsion region.

\[
\begin{align*}
\text{1-Butyl-3-methylimidazolium chloride ([bmim][Cl])} \\
\text{MP} & \approx 70 °C
\end{align*}
\]
Cellulose Nanoparticles

Typical Nanocellulose Morphologies

Emulsion Directed Cellulose Morphology (NOT nanocellulose)

µEmulsion Structure Control

- Microemulsions are thermodynamically stable, clear, colloidal dispersions immiscible liquids, stabilized by surfactant.
- Microemulsions typically have a droplet diameter of approximately 100 nm or less.
- Can be tuned to have cylindrical shapes or several bicontinuous structures.
Related Work: ILs and Cellulose

Micron-sized cellulose particles prepared by the “solvent releasing method” (SRM). Precipitated from Cellulose–[Bmim]Cl–N,N-dimethylformamide (DMF) droplets dispersed in hexadecane (HD) containing dissolved surfactant.

Q: Can cellulose particle size and morphology be precisely controlled by creating a true IL-Cellulose microemulsion?
Materials & Methods

Microemulsion: Quasi-Ternary phase diagram constructed with BmimCl/Span80/Tween20/Sunflower Oil. Warm emulsion technique adapted at 50 °C, for reduced viscosity.

Cellulose Solution: 10 % wt. Microcrystalline cellulose (Sigma Aldrich) dissolved in 10 % wt. DMF:BmimCl solution, for reduced viscosity.

Particle Formation: Two methods explored.
   Frozen phase centrifugation followed by solvent removal
   Anti-Solvent precipitation

Analysis: Direct observation (OM/SEM), Particle Surface contrast (interferometry), time-resolved small angle laser light scattering.
   1. Particles cast of surface
   2. Size, formation and growth vs antisolvent addition
   3. Particle morphology and its relationship to processing
Exploring the Phase Diagram

- Establishing phase diagram for IL-cellulose µE
- Start with fixed ratios and dilute with IL
- Use visual observation and DLS to identify phases
- Repeat with Cellulose solutions

Dilution Line C: Showing Phase transition from a single isotropic phase (1-3) through a 3 phase region (4 & 5) to 2 phases (6).
Particle Size Results

- Dynamic Light Scattering measures the hydrodynamic radius of \( \mu E \) as well as particles in solution.

- Particles deposited on Si wafer can be measured with Interferometer and SEM.

Representative results \( \mu E \) size measurements by DLS:

Y. Gao et al. / Langmuir 2005, 21, 5681-5684

Nanoparticle measurements by Interferometer:

SEM of Cellulose Particle:

![SEM of Cellulose Particle](image)
Conclusions

• Recent work suggests microemulsions can be used to control cellulose particle morphology.
• Size can be controlled by the adjustment of solvent/surfactant ratios.
• Interferometry may be a useful tool for particle characterization.
Future Work

• Continued study of IL-Cellulose microemulsion formulation and phase structures
  – Conductivity and SAXS measurements
  – Study the final particle morphology vs microemulsion structure

• Studies of the solubility of cellulose in different ILs, ie. changing anions (acetate) or alkyl chains

• Measuring the crystallinity of nanocellulose particles using Xray diffractometry (XRD)

• Continued work on particle recovery methods

• Nanoparticle functionalization via known cellulose chemistry