

Spectroscopic characterization of binary and ternary phase diagrams of “green” surfactants in water and ionic liquids (joint NSF-funded project with Professor Van Hecke)

OBJECTIVES

To determine the phase diagrams of binary mixtures of alkyl glucosides/ thioglucosides/ galactosides/ maltosides and water using an innovative fluorescence approach. Detailed phase diagrams present the conditions under which particular surfactant aggregates exist, facilitating utilization of the aggregates in a variety of applications.

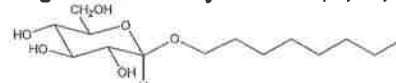
TECHNIQUES

- Fluorescence spectroscopy
- Polarized optical microscopy

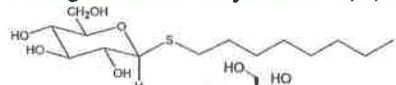


COMPOUNDS STUDIED

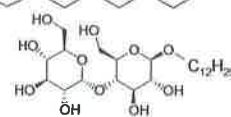
- *n*-alkyl- β -D glucosides – alkyl chain = 8, 9, 10, & 12 C's



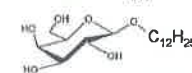
- *n*-alkyl- β -D thioglucosides – alkyl chain = 7, 8, & 9 C's



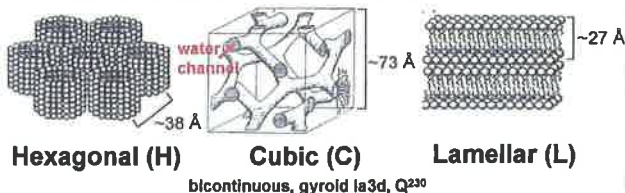
- *n*-dodecyl- β -D-maltoside



- *n*-dodecyl- β -D-galactoside



LYOTROPIC LIQUID CRYSTALS



Non-liquid crystalline:
Micellar (M)



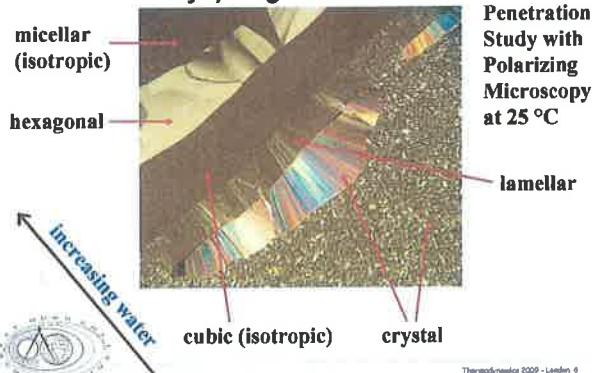
Micellar Cubic (I)
discontinuous, Pm3n



Goodby, J.W. Liquid crystals and Hfs. *Liq. Cryst.* 1998, 24, 23-38.
Patern, A. G. *The Lyotropic States of Matter: Molecular Physics and Living Matter Physics*, Gordon and Breach Science Publishers: The Netherlands, 1999, p 40.
Sedlitz, P.; Seebon, J. M.; Vilh, V. *Liq. Cryst.* 1997, 23, 409-424.

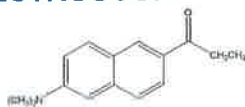
POLARIZED OPTICAL MICROSCOPY

n-octyl- β -D-glucoside + water



FLUORESCENCE SPECTROSCOPY

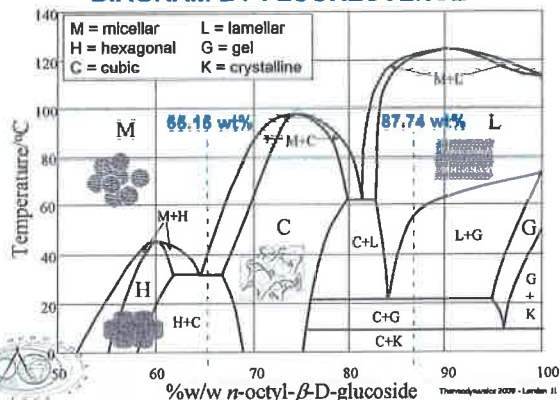
Fluorescent probe: prodan



- Neutral probe soluble in many solvents
- Can distribute throughout microregions of aggregates
- Wavelength of max emission (λ_{max}) depends on polarity of prodan's phase environment allowing identification of phase
- Co-existing aggregates detected since fluorescence signal from each environment is unique and additive.



***n*-OCTYL- β -D-GLUCOSIDE/WATER PHASE DIAGRAM BY FLUORESCENCE**

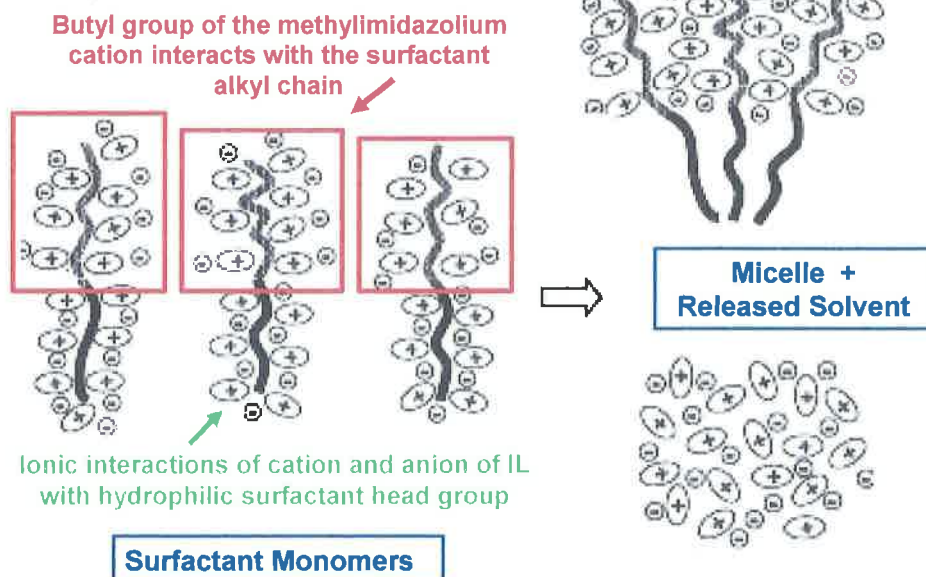


Why should surfactants self-assemble in ionic liquids?

Consider the ionic liquid 1-n-butyl-3-methylimidazolium tetra-fluoroborate, a hydrophilic molecule consisting of a methylimidazolium cation and a tetrafluoroborate anion. The solvophobic solvation by this ionic liquid is created by a network of ionic interactions (rather than the hydrogen-bonding interactions in aqueous solvent), and the bmim⁺ cation binds to a surfactant hydrophobic chain by directing the butyl group toward the hydrophobic chain.

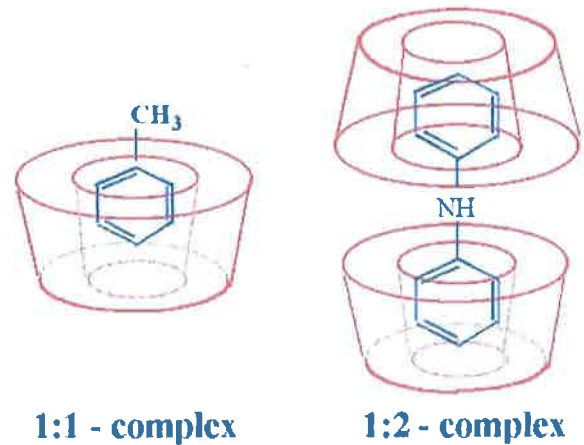
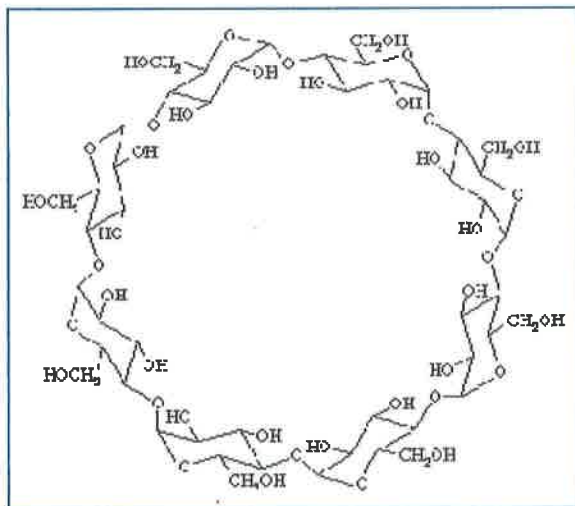


Micelle Formation in Imidazolium Salt Ionic Liquids

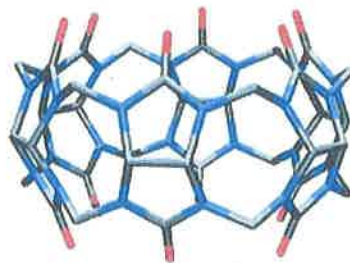
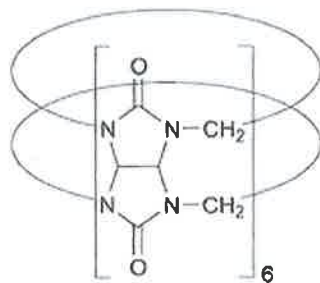


Spectroscopic characterization of solutes encapsulated within the nanocavities of cyclodextrins and cucurbiturils

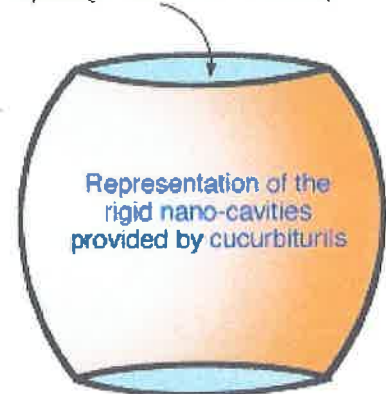
- cyclodextrins** are water-soluble compounds with six, seven, or eight glucopyranose units in which the overall macromolecule is toroidal-shaped with a hydrophilic exterior and a hydrophobic interior cavity with a maximum diameter of 5.7-9.5 Å, respectively



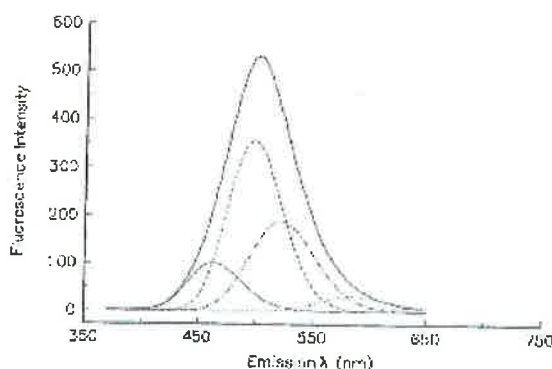
- cucurbiturils** are water-soluble compounds composed of six, seven, or eight glycouril units in which the overall macromolecules is pumpkin-shaped with a hydrophilic exterior and a hydrophobic interior cavity with a diameter of 5.8-8.8 Å, respectively



opening / window of the cavity



Peakfit of 7.5 μ M Prodan in β -cyclodextrin



Fluorescence spectrum of prodan in β -cyclodextrin. The spectrum is fit to a sum of Gaussian-shape curves. The two curves at high wavelength - centered at 521 nm and 585 nm - reflect prodan in water. The peak at 497 nm corresponds to a 1:1 inclusion complex and the peak at 460 nm corresponds to a 2:2 inclusion complex formed from the association of two 1:1 complexes via hydrogen bonding. Work of Abigail Kritzer '99.