

Spectroscopic Studies of Aqueous Iodine Equilibria

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I N D I A N A P O L I S

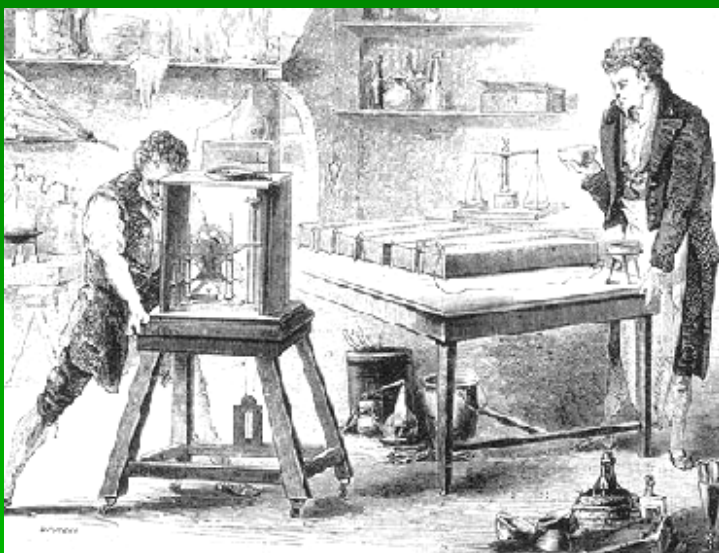
The Big Picture

- Iodine – discovered in 1811
- Forms Complexes:
 - Donor-Acceptor and Host-Guest
- Starch-Iodine Blue Complex
 - Has been known for almost 200yrs but is not well understood
- Goal – to understand the complex interactions of Iodine
- Starch is a biologically benign delivery vehicle – better medicines

How are Iodine and this man Connected?



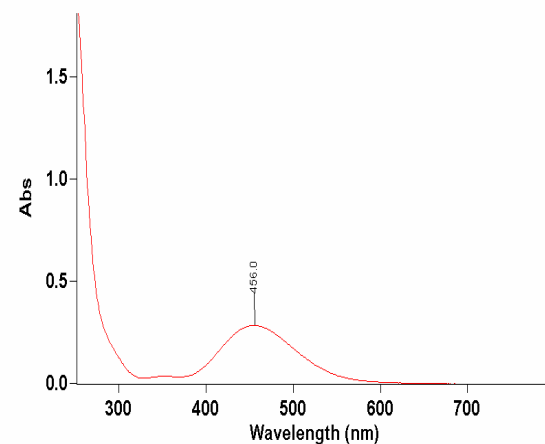
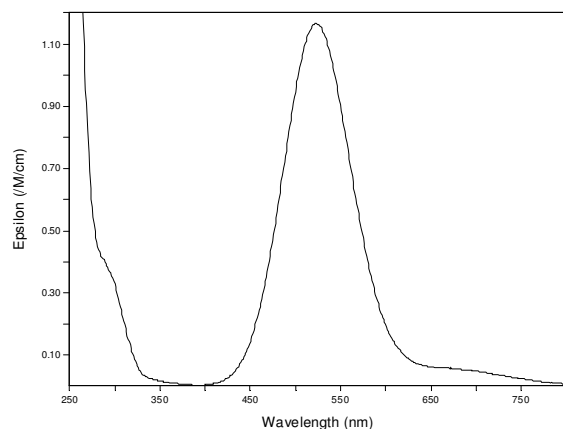
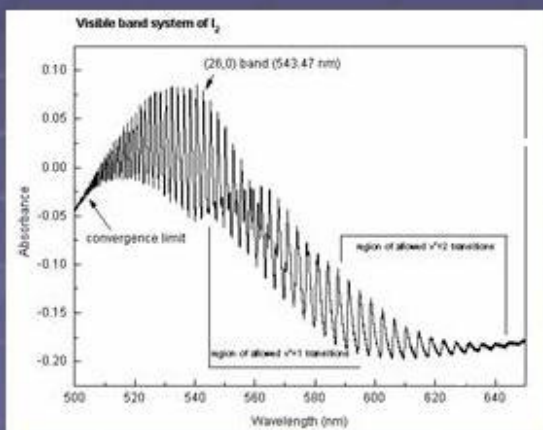
The History of Iodine



- Result of military research for Napoleon
- Discovered by Courtois in 1811
- Humphry Davy determined it was in the same group as chlorine
- Starch-iodine complex known since 1814

Absorption Spectra of Iodine

- Vibronic Spectrum – gas phase
- Broadening of vibrational structure in “inert” solvents



Gas Phase

$\lambda_{max} \sim 540\text{nm}$

In cyclohexane

Water Spectrum

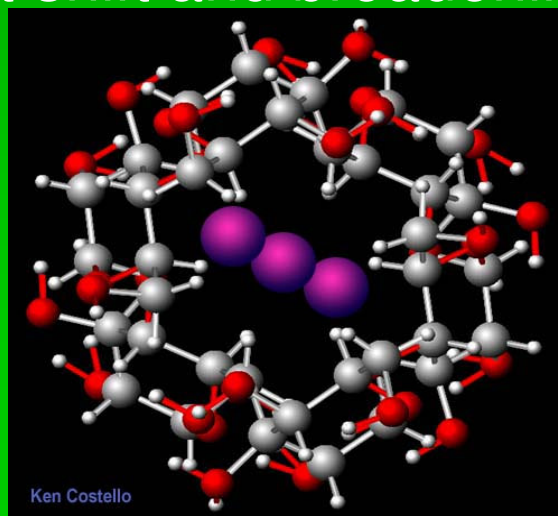
Donor-Acceptor Complexes

- Cause spectral shifts in water and other electron pair donors
- Exact structure of the iodine-water complex not known
 - One or two water molecules?



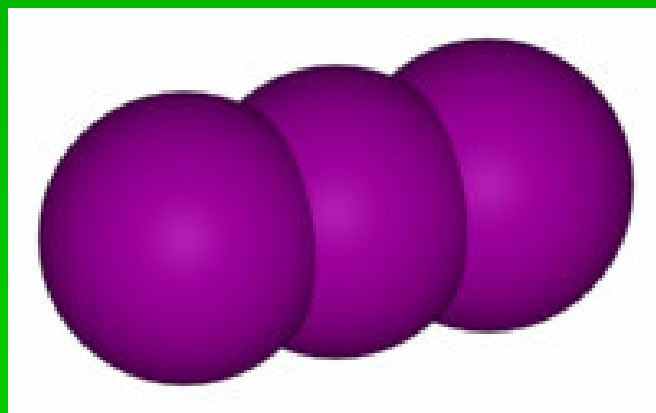
Host-Guest Complexes

- an example of supramolecular chemistry
- Best known host-guest complex is the starch-iodine complex
 - Used as iodimetric end-point indicator
- Raman spectroscopy and X-ray diffraction studies of structure exist
- The amount of charge in the complex (I_2/I^-) and the origin of spectrum are not known (Kuhn free-electron model/solvent shift and broadening).



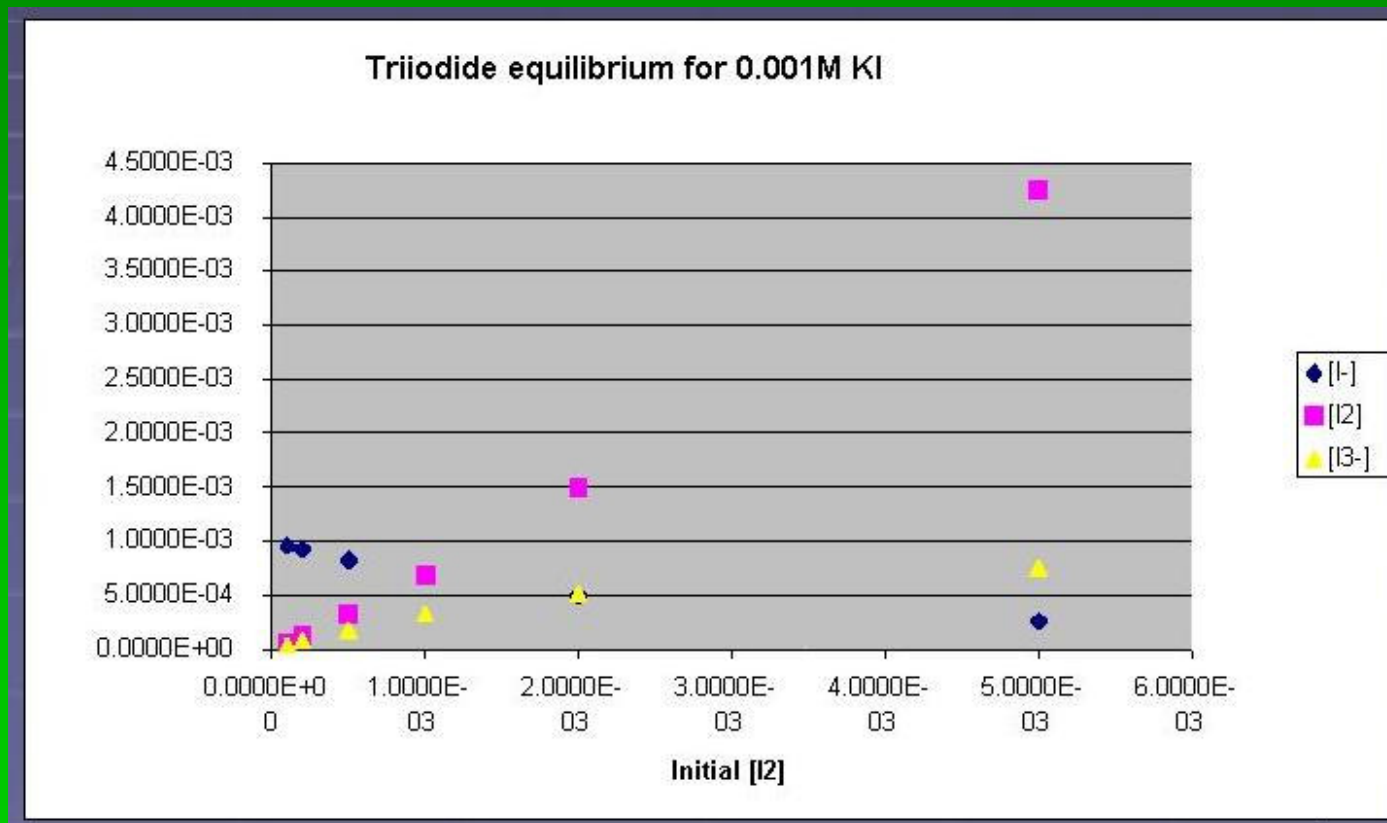
Triiodide Equilibrium

- When I^- is added to an I_2 solution, an equilibrium occurs between I_2 , I^- , and I_3^-
- $I_2 + I^- \rightleftharpoons I_3^-$
 - $K_{eq} = 7 \times 10^2$



Iodine and Triiodide Spectra

Calculations of triiodide equilibria in mixtures



$$[I_3^-] = \frac{(a + b + 1/K) + \sqrt{(a + b + 1/K)^2 - 4ab}}{2}$$

Proposed Starch/Iodine Studies

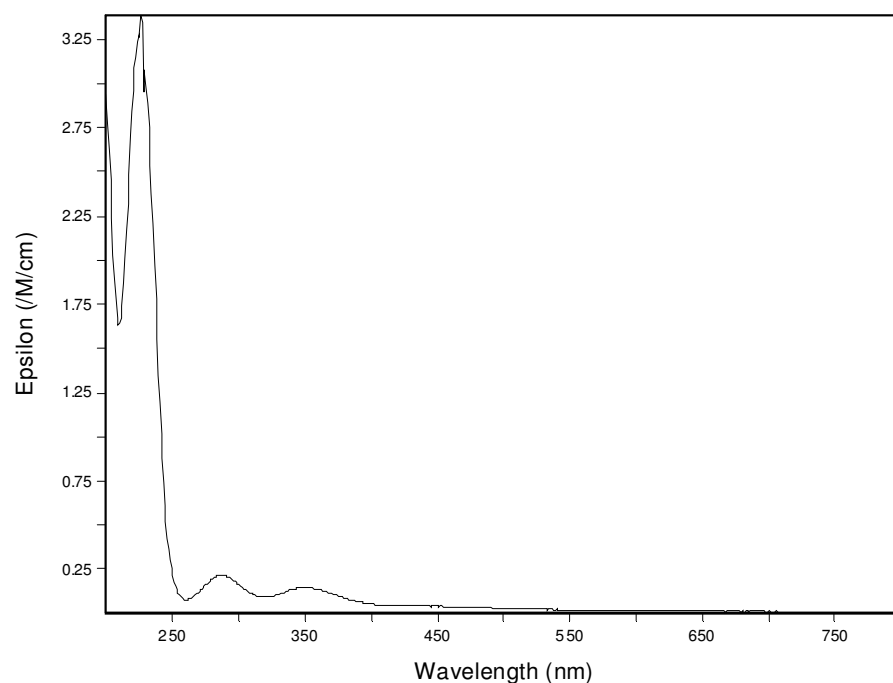
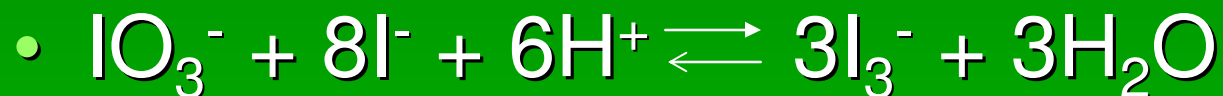
- Spectrum of complex as a function of I_2/I_3^- concentration ratio
- Hydrolysis studies – acid vs. enzymic
 - Targeting of linkages
- Charged starches – cationic, anionic, and bi-ionic

Humble Beginnings

- Aqueous iodine chemistry is extremely complicated!!!
- Experimental Methods (UV-Vis Spectroscopy)
- Analysis Methods (curve fitting)
- Results to Date

Iodine and Triiodide Spectra

1. Triiodide – produced by reaction between I^- and IO_3^-



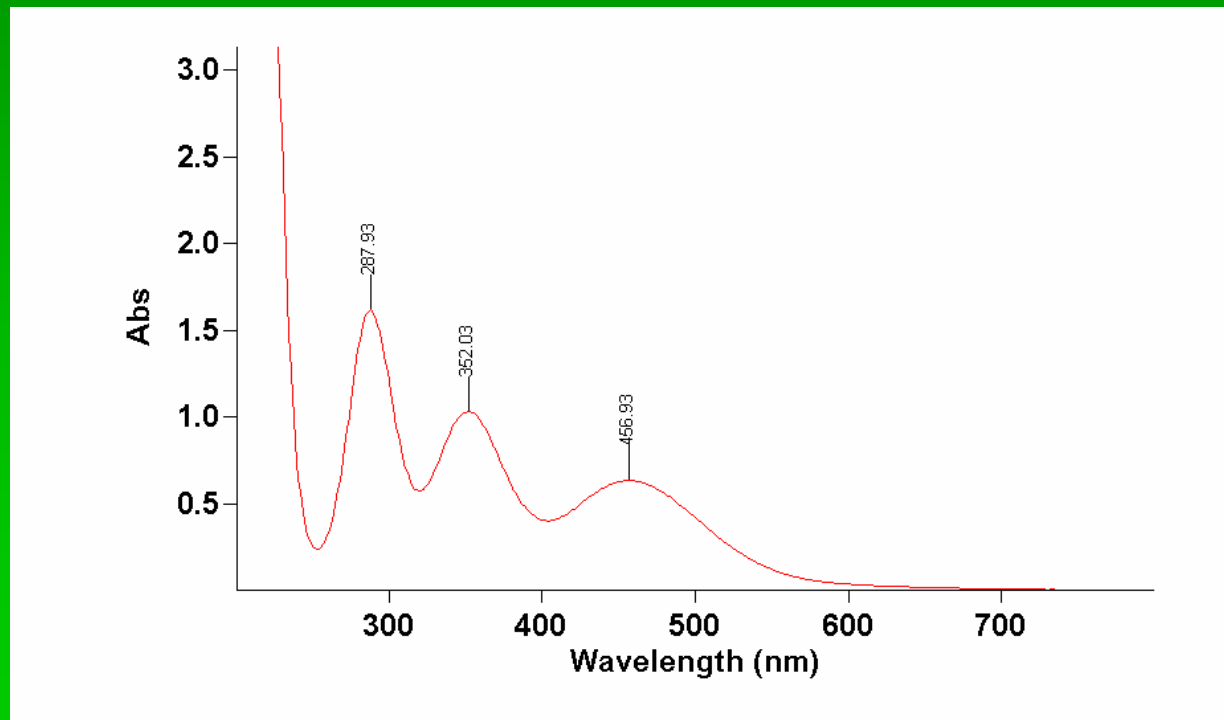
Triiodide spectrum

$\lambda_{max} \sim 350\text{nm}$ &
 280nm

Iodine and Triiodide Spectra

2. Iodine – sublimed elemental iodine in H₂O

- Expect to see a $\lambda_{\max} \sim 460\text{nm}$



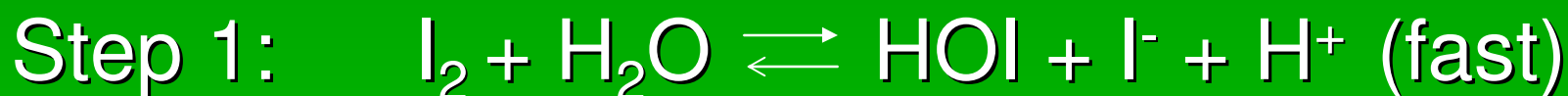
Chromasolv Spectra

Complex Aqueous Equilibria

I₂ disproportionates in aqueous solutions



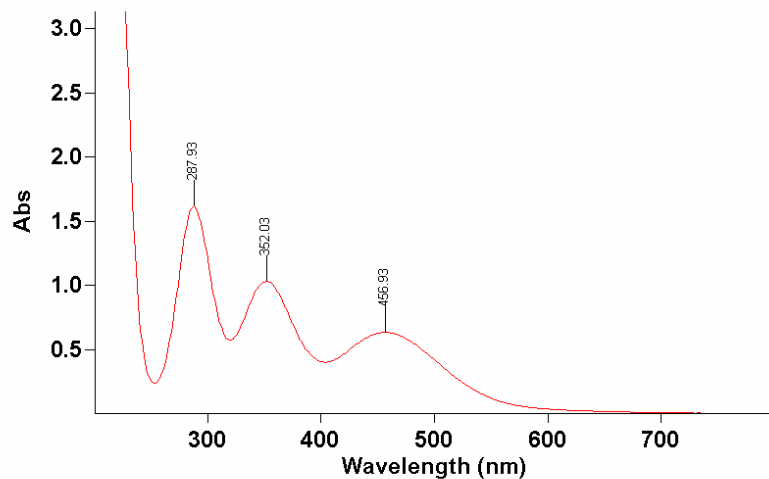
- Disproportionation occurs in two steps



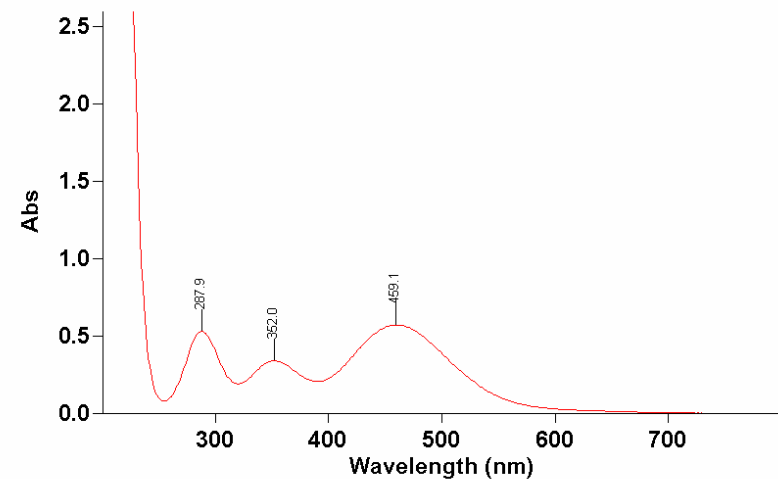
- pH dependence ?
 - [H⁺] will affect the reaction rate
 - Promoted by basic solution

Aqueous Equilibria and pH

- pH dependence
 - Relative peak heights change
 - More I_2 present in the acidic solution



Chromasolv Spectra
pH 8.91



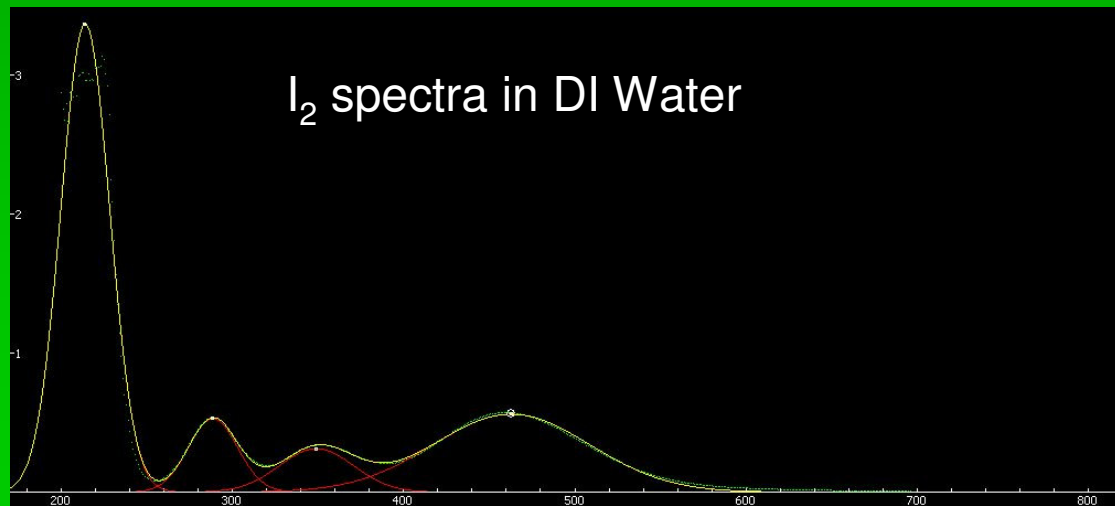
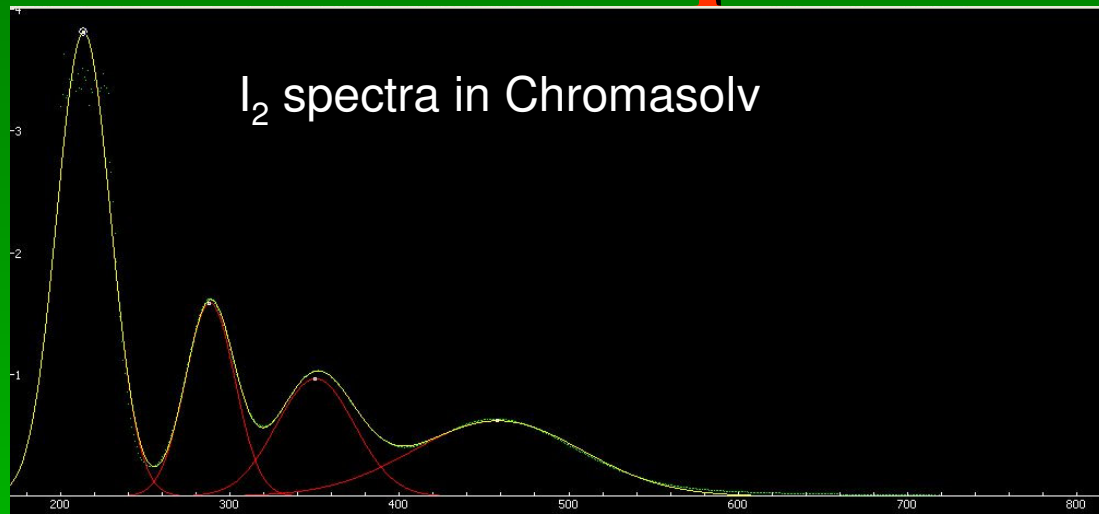
DI water spectra
pH 5.23

Characterization of I₂ Solutions

- Comparison with recent equilibrium and kinetic data (Nagy et al., 2004)
- Analysis of Spectra – Fityk
 - Fitting of experimental spectra to generic lineshapes (Gaussian, Lorentzian, Voigt, ...)
 - Simultaneous fitting of multiple peaks
 - Levenberg-Marquardt Algorithm

Fit Iodine Spectra

I_2	I_3^-
2.23×10^{-3} M	8.67×10^{-3} M
2.01×10^{-3} M	2.81×10^{-3} M



Conclusions and Next Steps

- More Data on pH dependence
- Compare results with kinetic and equilibrium parameters of Nagy et al.
- Stability of solutions
 - Nagy et al. saw fast kinetics, pre-equilibria, and slow kinetics
 - In our solutions, the fast kinetics occur during mixing; the solutions are stable for several hours.
 - Starch studies can begin after completion of this characterization.