Detection of Sodium Halides in Aqueous Systems Using Ultra-Thin Hydrogel Layers on a Quartz Crystal Microbalance

Jackie A. Shepard, Venkat R. Bhethanabotla, and Ryan G. Toomey

Sensors Research Laboratory, Clean Energy Research Center - University of South Florida Department of Chemical Engineering, Tampa, FL 33620-5350

ChE. 9

Stimuli-Responsive Hydrogel Networks

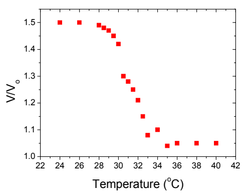
Motivation

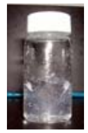
- Stimuli-responsive hydrogel networks carry a potential role in biological systems, foods, cosmetics, pharmaceuticals, and other industries, and are not fully understood.
- The effect of salts on hydrogel networks that expand and contract in one-dimension has never been demonstrated.
- Our goal is to develop a set of "intelligent" hydrogel materials that *recognize* and *communicate* ion binding to demonstrate the effect of salt stimuli on one-dimensional transition networks.

Concept

- *What is an LCST network?* It is a polymer network that undergoes a reversible phase transition at a well-defined temperature. The temperature is determined by the sum of hydrogen bonding, ionic, and van der Waals interactions in the network.

Swelling Behavior:

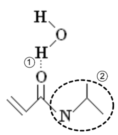




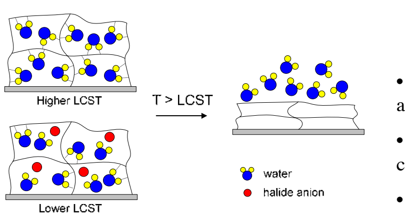
T = 24 ºC
Swollen State
(hydrophilic)

T = 35 ºC
Collapsed State
(hydrophobic)

- *Why use an LCST network?* The transition temperature is an effective gauge of the "nanoscale" environment.



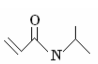
NIPAAm



- Ions destroy the water structure around polymers.
- Ions interact with polymer chains.
- LCST is strongly dependent on anions: $I^- < Br^- < Cl^- < F^-$

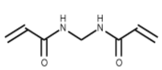
Hydrogel Preparation

- The hydrogel networks are fabricated through UV illumination using free radical polymerization *in situ*:



N-Isopropylacrylamide (NIPAAm)

Monomer

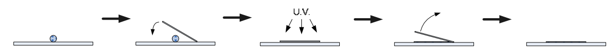


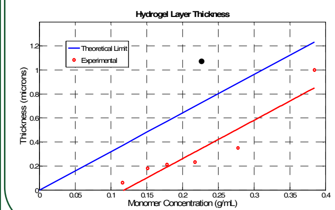
N,N'-Methylenebisacrylamide

Cross-linker

Thickness Information

- Dry hydrogel thickness is controlled through the concentration of monomer added prior to polymerization.
- Polymerization process carried out in an inert gas atmosphere:





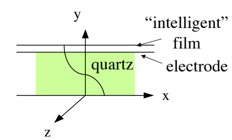
- Theoretical thickness calculation:

$$Thickness = \frac{concentration \times amount\ deposited}{density \times area\ of\ deposition}$$

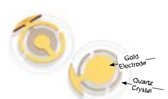
- The hydrogel thickness provides different levels of ion sensitivity.

Quartz Crystal Microbalance (QCM) Principles

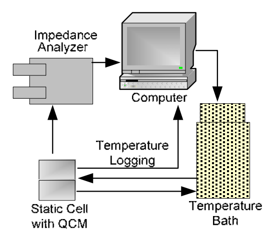
- *Principle*: The quartz crystal vibrates at its fundamental resonance frequency.
- Changes in the mechanical stress at the quartz surface induces a measurable shift in its fundamental resonance frequency.



- The targeted analyte will be "sensed" based on the temperature at which the hydrogel collapses.



- *Experimental Setup*: water with the target sodium halide is contained within the static cell. The temperature bath provides heat for hydrogel collapse.

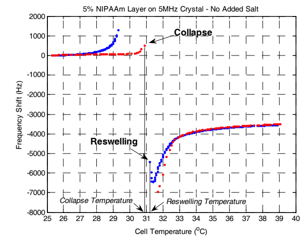


Acknowledgements

Funding is provided by NASA-Glenn via Florida Solar Energy Center (FSEC) and University of South Florida Division of Sponsored Research. Jackie Shepard is partially supported by the Research Experience for Undergraduates program as funded by the College of Engineering at the University of South Florida. Funding is also provided by the USF Office of Undergraduate Research.

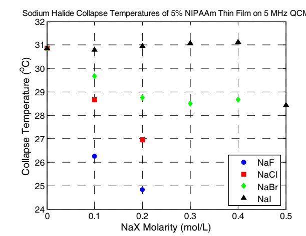
Results

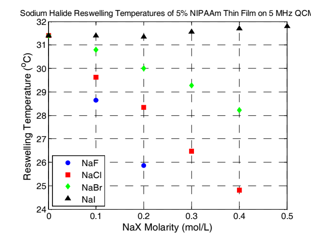
- Frequency response of collapse and reswelling of NIPAAm thin film with no added salt:



- Continuous transition
- Transition marked by a highly ordered system to a disordered one
- Transition is distinguishable by a frequency shift of 3 to 4 kHz
- Three runs per NaX per concentration were averaged to find the transition temperatures
- Average transition temperatures varied by 0.1 to 0.2 °C in most cases

- Transition temperatures of NIPAAm thin film with various concentrations of different sodium halides:





Future Directions

- Turbidity measurements to compare one-dimensional transitions to three-dimensional swelling transitions.
- Investigation of the LCST behavior of the NIPAAm in conjunction with metallopeptides for heavy metal ion detection in potable water.
- Antibody/Antigen incorporation into the NIPAAm network for earlier detection of specific diseases.

Conclusions

- Detection of sodium halides is based on the signal response of the QCM to a change in swelling and viscoelastic properties of the hydrogel network upon ion interaction. The fabrication of ultra-thin pNIPAAm hydrogel matrices has been demonstrated.
- Detection would offer reusability and reproducibility as shown by its frequency response recovery upon heating to its LCST.
- Sodium halide concentration within the hydrogel matrix can be "transduced" by the QCM into a readable signal.

UNIVERSITY OF SOUTH FLORIDA

CERC Clean Energy Research Center

SRL Sensors Research Laboratory