University of Victoria | Graduate Studies

Notice of the Final Oral Examination
for the Degree of Doctor of Philosophy

of

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"Mechanistic Diversity in the Guest Binding with Cucurbit[7]uril or Octa Acid Complexes"

Department of Chemistry

Wednesday, June 29, 2016
9:30 A.M.
David Turpin Building
Room A144

Supervisory Committee:
Dr. Cornelia Bohne, Department of Chemistry, University of Victoria (Supervisor)
Dr. Dennis Hore, Department of Chemistry, UVic (Member)
Dr. Frank van Veggel, Department of Chemistry, UVic (Member)
Dr. Stephen Evans, Department of Biochemistry and Microbiology, UVic (Outside Member)

External Examiner:
Dr. Brian D. Wagner, Department of Chemistry, University of Prince Edward Island

Chair of Oral Examination:
Dr. Craig Brown, Department of Biology, UVic

Dr. David Capson, Dean, Faculty of Graduate Studies

Abstract

Supramolecular systems comprised of non-covalent interactions are reversible in nature. This intrinsic reversibility of these systems is essential in achieving several functions, making it crucial to understand the dynamics of supramolecular systems. However, studies on the dynamics of supramolecular systems have always lagged behind structural and thermodynamic characterization of innumerable supramolecular systems developed.

The first objective of this work was to understand the dynamics leading to a shift in the acidity constant (p*K*a) for 2-aminoanthracenium cation (AH+) upon binding with cucurbit[7]uril (CB[7]) host molecule. The adiabatic deprotonation of free AH+ in water was found to be inhibited in the complex with CB[7]. Different spectral characteristics for the protonated and deprotonated form of the guest molecule was used to understand the mechanism of this p*K*a shift associated with the binding to CB[7]. The results suggested that the p*K*a shift upon binding with CB[7] is a result of the slowing down of the deprotonation step in the complex, whereas the association rate constant did not change very much.

The second objective of this work was to understand the role of cations on the binding dynamics of the N-phenyl-2-naphthyl amine (Ph-A-Np) binding to CB[7]. Ph-A Np has two binding sites, which can lead to 1:1 and 2:1 host-guest complexes. The results indicate a switch in the binding mechanism for Ph-A-Np at low and high concentration regimes of sodium ions. Sodium ion was found to reduce the binding affinity of the naphthyl group to CB[7] whereas the complex formed by the phenyl group with CB[7] bound to one sodium ion was found to be stabilized.

The final objective of this work was to study how structural changes to a guest molecule can affect the binding dynamics for the formation of a 2:1 “capsule” like complex with octa acid (OA). The dissociation for the OA capsule with pyrene (Py) as the encapsulated guest was shown to happen in 2.7 s previously. Two pyrene derivatives, 1-methylpyrene (MePy) and 1-pyrenemethanol (PyMeOH) were chosen as guest molecules to study the effect of these substituents on pyrene on the capsule dissociation dynamics. The results show that the residence time for the guests in the OA capsule depends on the substituents. For PyMeOH and MePy a shorter and longer residence time respectively in the capsule was observed when compared to Py.