

Introduction

- ❖ Silica oxides (SiO₂) come in a variety of forms including silica gel, quartz, opal, diatoms, and phytoliths.
- ❖ Binding of organic chemicals to silica oxides is important for several industries.
 - ❖ Organic catalysts supports bindings of films onto glass
 - ❖ Environmental impacts with contaminant movement and climate change
- ❖ This study will focus on the binding and debinding energetics of sodium benzoate and sodium butyrate on silica gel.

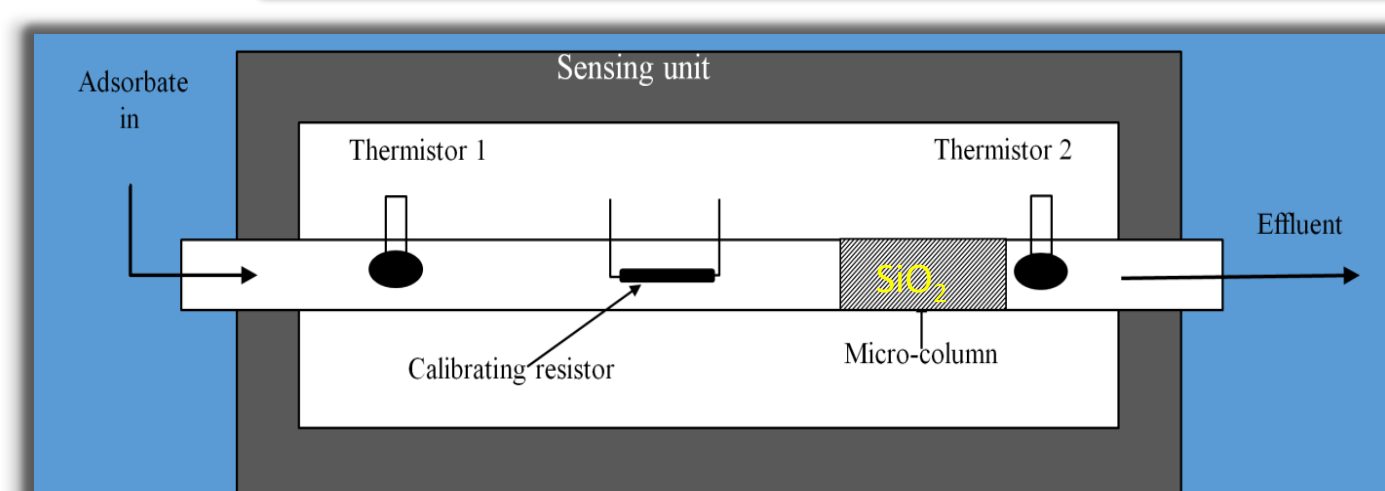
Flow Adsorption Microcalorimetry

Adsorbate:

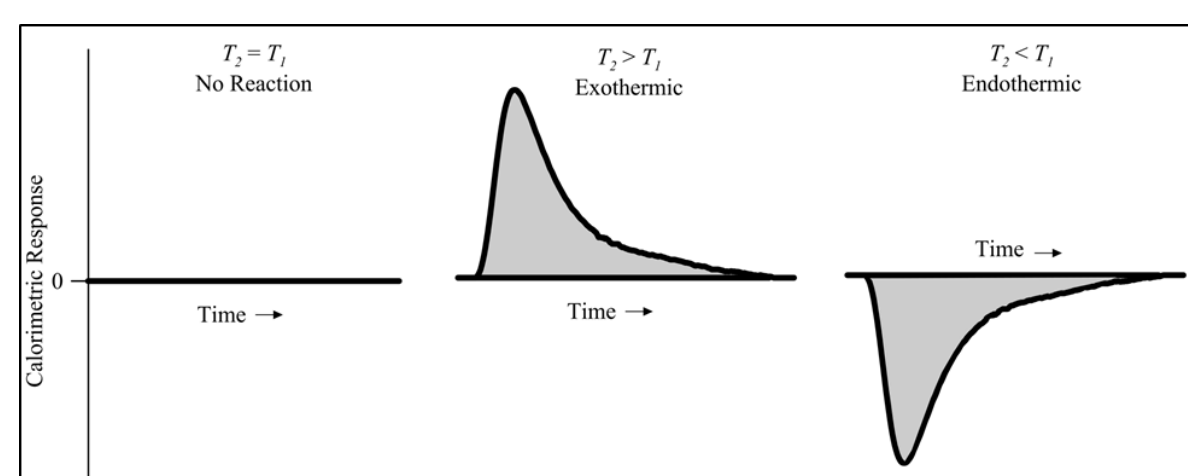
- ❖ 5 mM Na Benzoate in water at pH 3
- ❖ 5 mM Na Butyrate in water at pH 3

Effluent:

- $\lambda_{\text{abs}} = 300 \text{ nm}$ for Na Benzoate
- $\lambda_{\text{abs}} = 195 \text{ nm}$ for Na Butyrate
- Flow = 0.5 ml/min
- 1 reading/5 sec

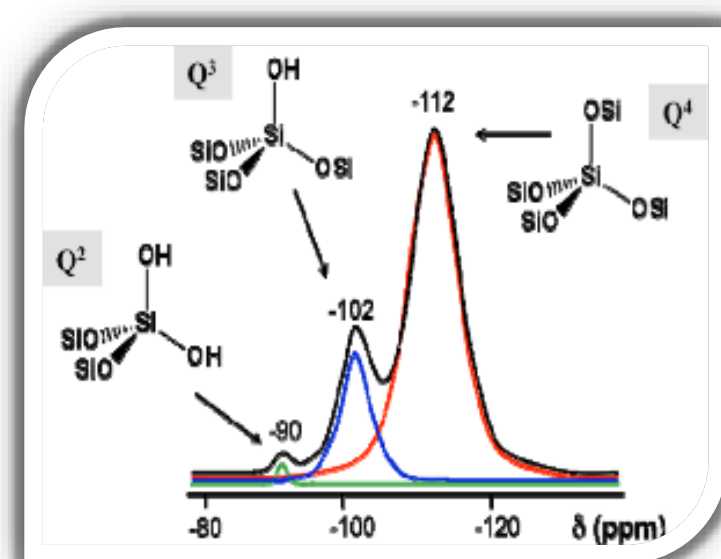


Calorimetric Responses



- ❖ Thermistor 1 is T₁ and Thermistor 2 is T₂
- ❖ An exothermic reaction will give a positive calorimetric response.
- ❖ An endothermic reaction will give a negative calorimetric response.

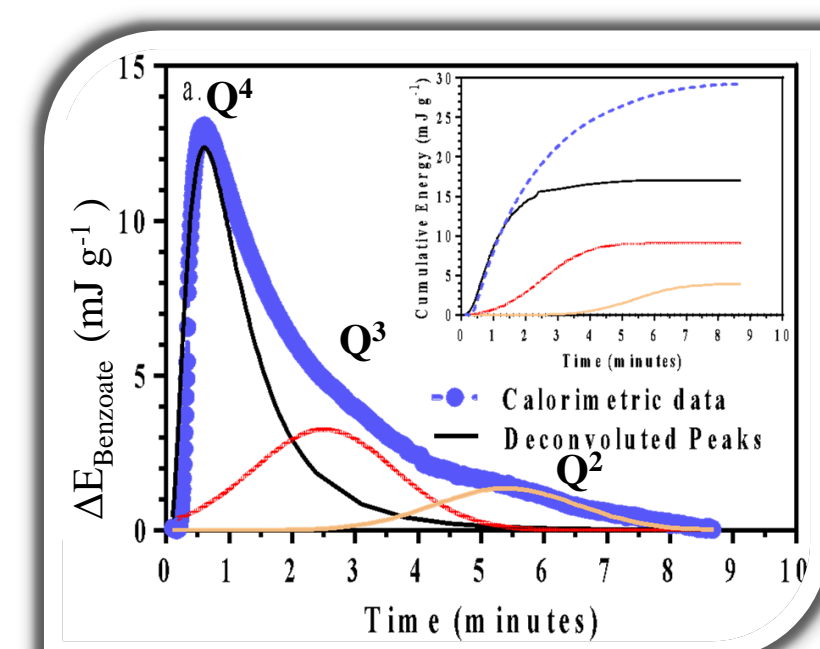
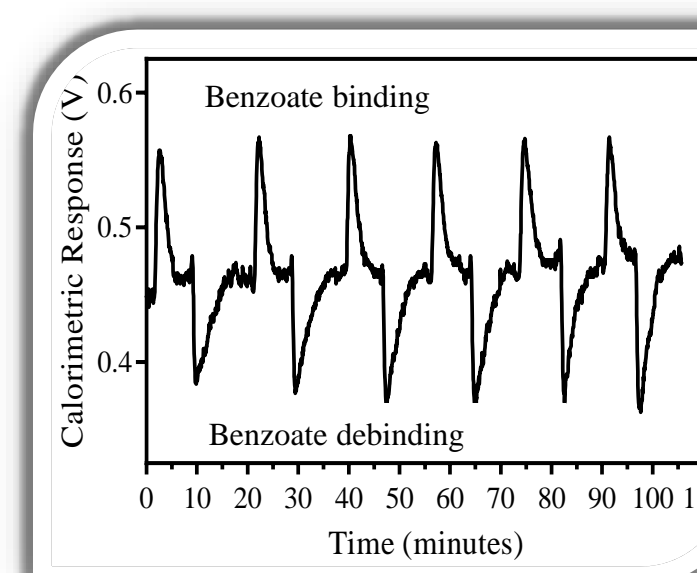
Evolution of Binding Energetics



Rimola et al. 2013

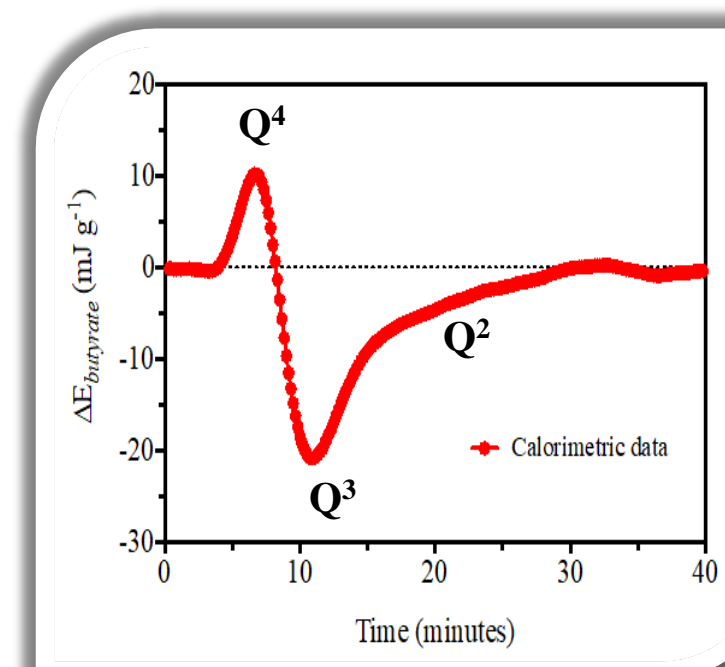
5 mM Na-Benzoate

- ❖ Benzoate binding was a reversible reaction.
- ❖ Benzoate binding was exothermic.
- ❖ Benzoate debinding was endothermic.

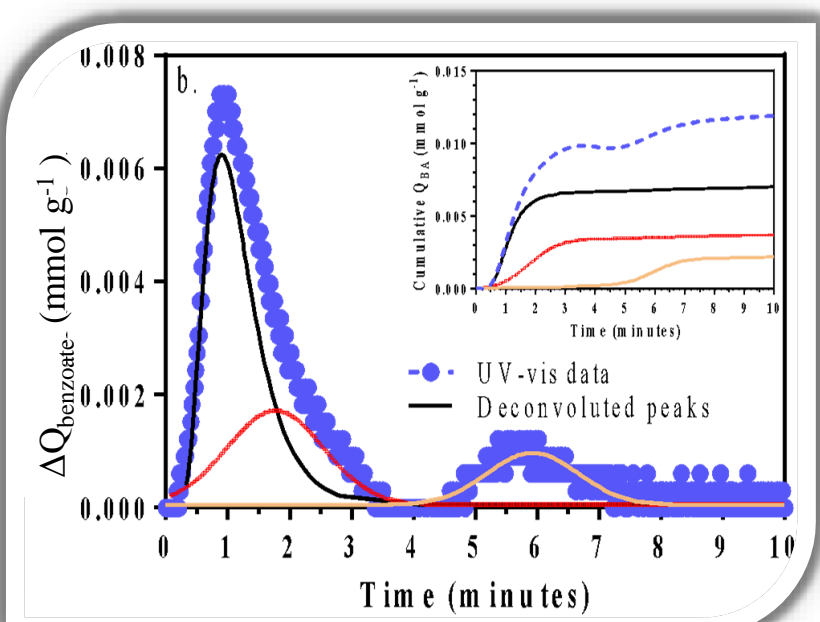


5 mM Na-Butyrate

- ❖ 3 potential sites that are consistent with Q⁴, Q³, & Q².
- ❖ Binding was exothermic on all sites.
- ❖ Exothermic reaction on sites Q⁴.
- ❖ Endothermic reaction on sites Q³ and Q².
- ❖ Butyrate binding was a reversible reaction.

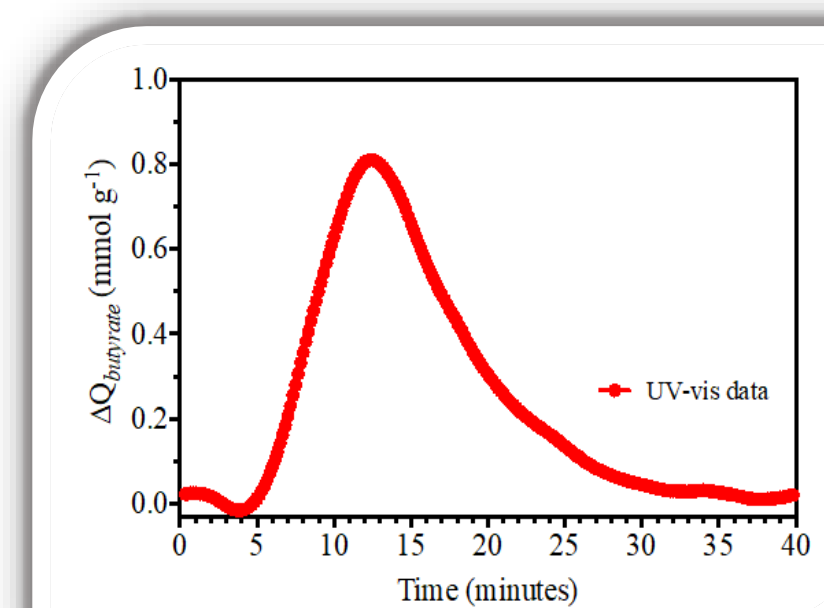


Sorption Data



Benzoate

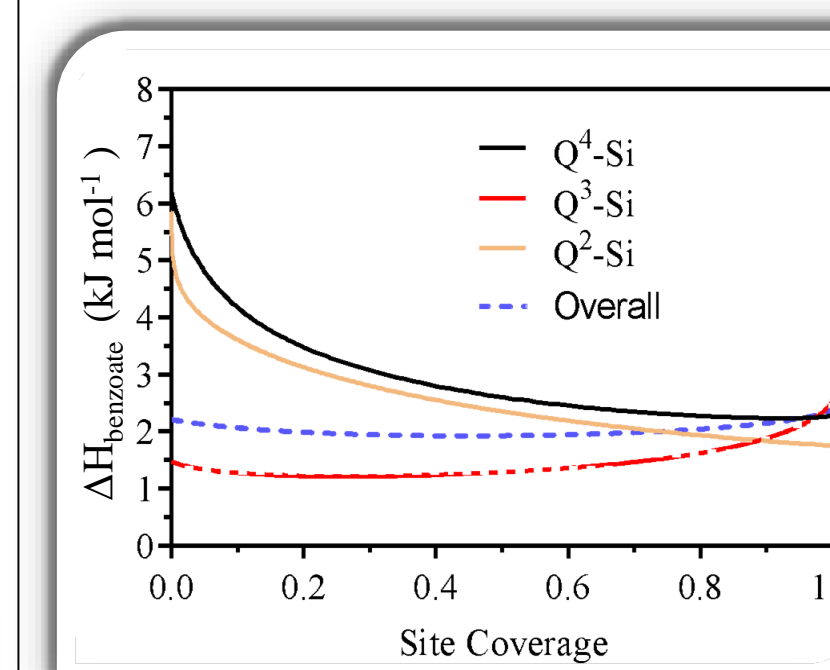
- ❖ UV Vis data has been deconvoluted and shows 3 potential sites that are consistent with Q⁴, Q³, & Q².



Butyrate

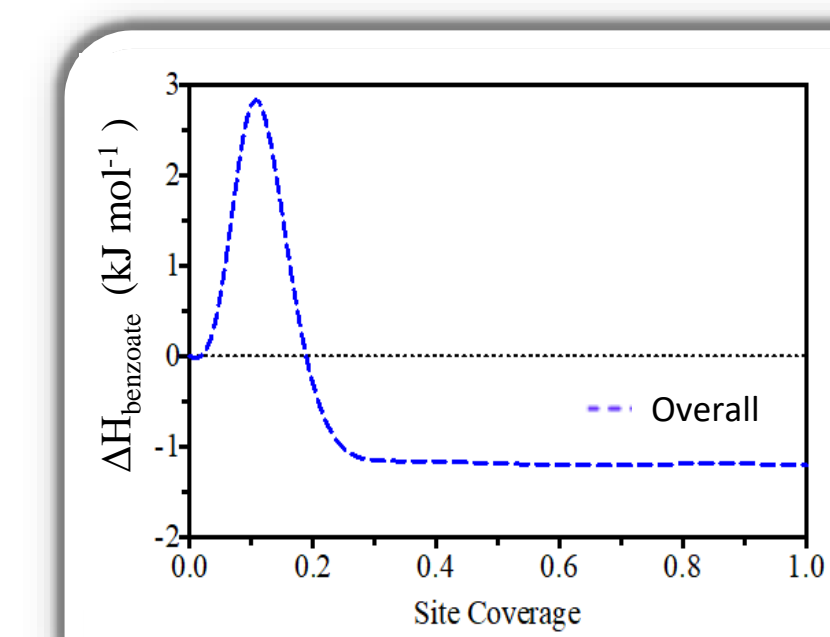
- ❖ UV Vis data has not been deconvoluted.

Surface Binding and Binding Energetics



Benzoate

- ❖ Bond strength ($\Delta H_{\text{binding}}$) is stable with no peaks overall.
- ❖ Peaks have been deconvoluted with respect to site bonding

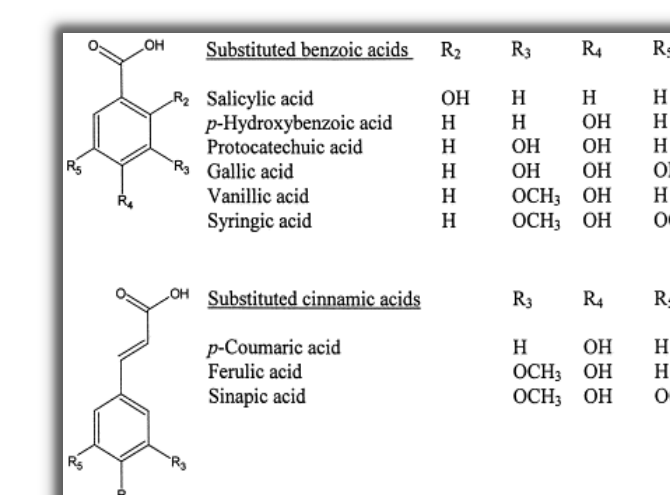
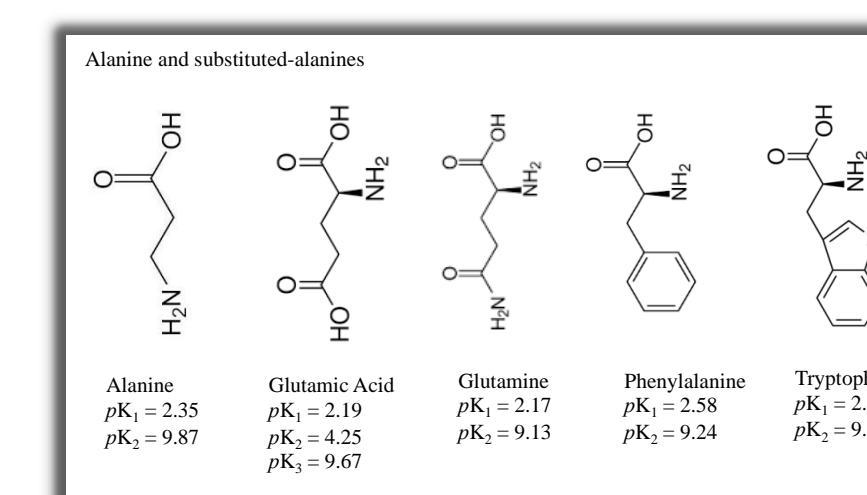


Butyrate

- ❖ Positive peaks indicate bond strength is higher.
- ❖ Positive integrals indicate exothermic reactions.
- ❖ Peaks have not been deconvoluted for sites.

Ongoing and Future Work

- ❖ Examine sorption of other silica surfaces
 - ❖ Quartz, opal, bamboo phytoliths, and diatoms
- ❖ Examine sorption of different organic chemicals with increasing complexity



References

- ❖ "Phosphate Alteration of Chloride Behavior at the Boehmite–Water Interface: New Insights from Ion-Probe Flow Adsorption Microcalorimetry." *Journal of Colloid and Interface Science*, Academic Press, 26 May 2015.
- ❖ "Silica Surface Features and Their Role in the Adsorption of Biomolecules: Computational Modeling and Experiments". Rimola et al. *Chemical Reviews*, 2013, 113 (6), 4216-4313.