Sorption Kinetics of Denatonium Benzoate to 2:1 Layered Aluminosilicates

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Kinetics of denatonium benzoate sorption to layered-aluminosilicate clay minerals

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Introduction

The bittering agent denatonium benzoate (DB) is added to many common commercial products, such as antifreeze and rubbing alcohol, to deter ingestion by humans and animals. The intensely bitter taste is detectable by humans at 10 mg/L concentrations while 30 – 50 mg/L concentrations can render drinking water unpalatable. Given the push by US lawmakers to mandate that DB be added to some commercial antifreeze formulations, it is imperative that potential environmental consequences associated with accidental releases of this material be investigated. Accordingly, the main objective of this study was to evaluate the kinetics of denatonium sorption to three types of clay minerals.

Materials and Methods

- Denatonium Benzoate
- Montmorillonite Cl
  - Swy-2
  - Stx-1b
  - Syn-1

  ![Montmorillonite Structure](Figure 2. Montmorillonite Structure)

- 12 samples and two blanks were run in duplicates in 50 ml centrifuge tubes each containing 1/8 g clay used, and 30 ml of a 200 ppm DB and 0.01M CaCl₂ solution.
- Mixed in the hybridization oven for varying periods of time (0-60 minutes) at a constant temperature (either 13 °C, 32 °C, or 65 °C).
- Tubes were centrifuged and 2 ml of the supernatant solution was taken for HPLC analysis.
- The concentration of denatonium remaining in solution was determined (assuming no sorption to centrifuge walls) via difference.

Results and Discussion

Swy-2 at 32 °C

- Results were fit to the Ho-Mckay pseudo-second order kinetic model:
  \[ y = 2.0464x + 0.3906 \]
  \[ R² = 0.9998 \]

Stx-1b at 32 °C

- Results were fit to the Ho-Mckay pseudo-second order kinetic model:
  \[ y = 25.571x + 1.5515 \]
  \[ R² = 0.9996 \]

Syn-1 at 13 °C, 32 °C, and 65 °C

- Results were fit to the Ho-Mckay pseudo-second order kinetic model:
  \[ y = 24.859x + 9.9776 \]
  \[ R² = 0.9998 \]

Syn-1 Arrhenius Plot

Conclusions

- Pseudo-second order sorption process for each clay.
- \( E_s \) for sorption to Syn-1 is 25.89 kJ/mol
- The magnitude of \( E_s \) is consistent with previous studies of organic cation sorption where the sorption mechanism was physisorptive.
- Surface-area normalized sorption capacities showed that sorption was greatest for SWY-2 and least for Syn-1.
- A possible treatment method for water-impacted DB could include SWY-2 clay as an absorbent.

Further Studies

- Denatonium desorption studies at various temperatures.
- Collect constant-temperature isotherms to evaluate the thermodynamics of sorption.
- Evaluate the impact of pH, background electrolyte and ionic strength on sorption (and desorption) kinetics.