

The Environmental Fate and Transport of Denatonium Benzoate
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A progress report containing Problem and Research Objectives, Research Methodology, and Principal Findings and Significance

Statement of regional or state water problem

H.B. 96 was introduced during the 128th General Assembly of the Ohio legislature. This bill specifies that “engine coolant or antifreeze sold in Ohio that contains more than 10% ethylene glycol and that is manufactured after December 1, 2008 must include a bittering agent to render the engine coolant or antifreeze unpalatable”. This legislation parallels H.R. 615, ‘Antifreeze Bittering Act of 2009’ which, if passed, will amend the Federal Hazardous Substances Act and require that the bittering agent denatonium benzoate (DB) be added to engine coolant and antifreeze to make it undesirable to humans and pets. Although, well-intentioned, no published data exists pertaining to potential negative environmental effects of this highly water-soluble compound. This lack of information, was highlighted by Tom Bonacquisti, director of water quality and production for Fairfax, VA Water and representative of The American Water Works Association who stated that “little is known about the environmental fate and transport of DB...” and who pointed “...out that small amounts of this material could render drinking water supplies bitter and unpalatable” due to the extreme bitterness of DB”. Given the lack of reliable empirical data pertaining to DB environmental behavior and the potential for DB to be released into the environment, a project evaluating DB behavior in the sub-surface environment is timely. At present, there are no known reports of problems associated with DB, however, if Ohio’s legislation and the federal legislation are enacted into law, unintended consequences could arise. A well-known example of unforeseen effects associated with attempts to achieve a greater good was the addition of methyl tert-butyl ether (MTBE) to automobile gasoline formulations to mitigate air pollution; MTBE is now known to have contaminated water bodies around the country rendering them unpalatable at minute concentrations of MTBE. Thus, with the move toward extensive use of DB as an antifreeze additive seemingly imminent, negative environmental impacts associated with DB must be thoroughly investigated *before* widespread introduction. The proposed project will help to articulate the environmental behavior of DB in the sub-surface environment.

Research Objective

The overall focus of this project was to evaluate the hypothesis that the environmental fate and transport of denatonium benzoate (DB) is governed by sorptive interactions with natural surfaces, dissolved aqueous species, and solution conditions. DB is an aversive agent added to many consumer products to discourage intentional use and to minimize (if not prevent) accidental ingestion by animals or humans. The motivation behind this study was the lack of information pertaining to the environmental fate and behavior of this compound. The information is necessary given the fact that certain federal legislators have proposed laws mandating the addition of this agent to anti-freeze sold in the United States.

The specific objectives of the study were to:

- a. Characterize the sorption behavior of the denatonium cation to a variety of clay surfaces
- b. Delineate the role of solution chemistry and temperature in the partitioning of the denatonium cation between aqueous and solid phases.
- c. Determine the sorption mechanism of the denatonium cation to clay surfaces

Research Methodology

Sorption experiments using clay minerals and whole soils will be conducted using specific size fractions for each clay. To evaluate sorption characteristics of clay minerals, the well-established batch test method will be utilized according to Organisation for Economic Co-operation and Development guidelines. In the experiment, a measured amount of sorbent material (solid) is suspended in a sorbate solution and rotated end-over-end. In our batch experiments, initial DB (sorbate) concentrations ranging from 10 ppb to 100 ppm (in 100 mM CaCl₂) from pH = 1 to pH = 10 will be performed. The temporal evolution of aqueous sorbate concentration is evaluated up to equilibrium or near-equilibrium conditions. Following the reaction, the system will be centrifuged and aqueous-phase DB concentrations determined via high-pressure liquid chromatography. The amount sorbed can be directly measured on the sorbent or calculated using mass-balance relationships between the initial aqueous sorbate amount and the final sorbate masses. Based on preliminary measurements, our team determined that significant container adsorption does not occur. Thus, we will measure concentrations using mass-balance relationships.

Principal Findings and Significance

Figure 1 shows room temperature, pH dependent (pH 6.5 and 8.5) denatonium benzoate sorption to kaolinite clay. The data were obtained over an initial aqueous concentration range of 0 – 100 ppm. As initially suspected, the clay exhibited an affinity for denatonium benzoate. The data also suggest that pH has a negligible impact on DB sorption at the values tested. (The values shown were chosen to approximate a slightly acidic to slightly alkaline environment.) Given the fact that silanol and aluminol groups are protonated at the pH values investigated and the structure of denatonium benzoate, it is not surprising that the sorption behavior should be similar under both solution conditions.

Temperature dependent sorption experiments (not shown) at two initial DB concentrations (25 ppm and 50 ppm) did not indicate that temperature significantly impacted the sorptive behavior of the kaolinite over the temperature range chosen (25, 45, and 55°C) but did indicate an endothermic sorption process at initial concentrations of 25 and 50 ppm at pH 6.5 as shown in figure 2.

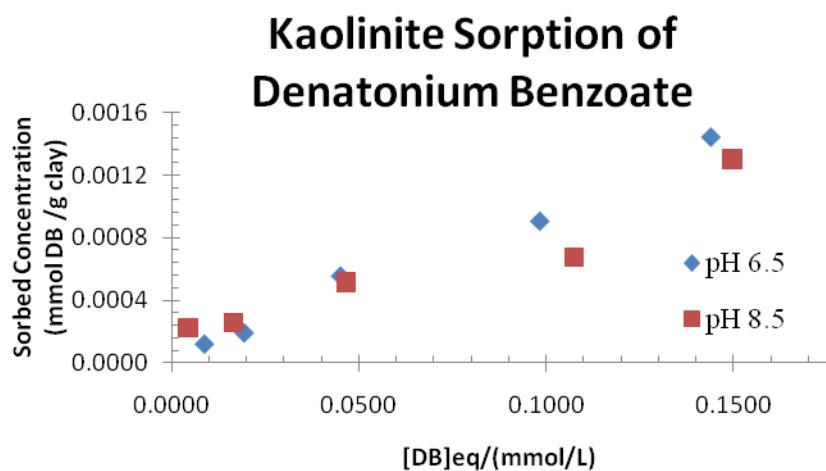


Figure 1. Room temperature (25°C) sorption isotherms for DB sorbing to kaolinite at pH 6.5 and 8.5

The results taken with data room temperature (25°C) data (not shown) for hectorite and montmorillonite clay minerals (at various pH values) suggest that the clay identity could impact the transport of denatonium benzoate in the subsurface environment. The results from varied pH experiments with hectorite and montmorillonite clays also indicate that the solution chemistry impact the ability of denatonium benzoate to sorb to clay mineral surfaces.

The partitioning of denatonium benzoate between clay mineral surfaces and water was evaluated using multiple types of clay sorbents (components of natural soils). Generally, one can expect intentional (or unintentional) releases of this aversive agent to result in sorption to mineral components of natural soils. pH-dependent sorption isotherms showed that solution chemistry plays a role in the sorption behavior of denatonium benzoate to each mineral studied. Finally, the sorption process for kaolinite was endothermic at 25 ppm and 50 ppm initial concentrations of DB. The implications of the observed behavior in clay minerals are that the mobility of this bittering agent in the subsurface environment is likely to be controlled in soils by interactions with these clay minerals. Thus, more detailed knowledge on the interactions with whole soils should be undertaken in an effort to more accurately characterize the ability of this material to migrate through soil environments. This work is currently being undertaken in this laboratory.

Publications

None at this time.

Students Supported

Yun Yun Zhou, (M.S. Student, Department of Chemistry), Taylor Pair (B.S. Student, Department of Chemistry)

Notable Awards or Achievements

None at this time.

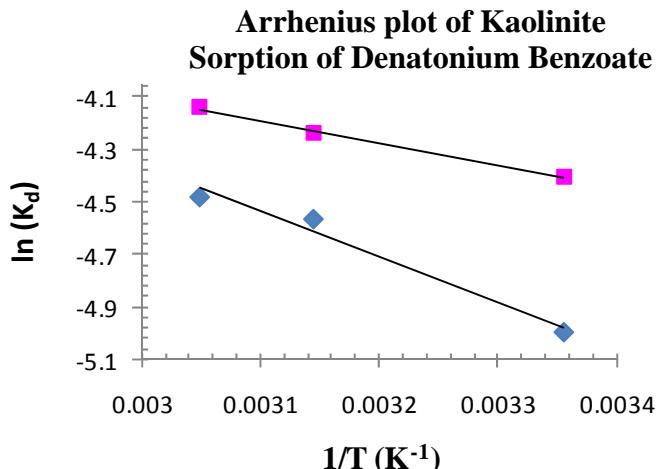


Figure 2. Arrhenius plots for kaolinite sorption at 25 ppm and 50 ppm initial concentrations of denatonium benzoate.

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