Determination of the Cation Exchange Capacity in Smectite Clays

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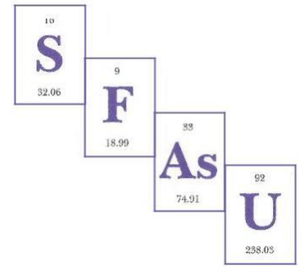

Abstract

The cation exchange capacity (CEC) of a clay is the property that dictates how the clay can be utilized. The CEC is the number of charge sites per gram of clay. There are currently many different methods used in the determination of CEC, but all present a wide margin of error at ±20%. Bomb calorimetry is being explored as a new methodology in hopes to reduce the large error in the determination of CEC. The charge sites in the clay are negatively charged and are exchanged with organic cations. The organic salts that were chosen for this work, tributyl methylammonium bromide (MTBA), tetrapropylammonium iodide (TPA), and octyltrimethylammonium bromide (OTMA) have similar molecular masses but have different structures, thus the effects of steric hinderance can be observed. The exchanged clays are placed in the bomb calorimeter and combustion is performed. The energy that is released from the combustion is solely due to the organic. As there is a 1:1 ratio between the charge sites and the organic cations, the CEC can be calculated based on this energy. Theoretically, the CEC determined using different organics should be the same, as the molecular masses are similar, but differences could be seen due to the structure of the cations. This effect will be examined using x-ray diffraction, XRD.

Discussion

- Different salts of similar carbon count but varied structure were chosen so that the heat of combustion of the pure salt would be similar, however this was not the case
- Due to OTMA having a long carbon chain, it was expected to have larger interlamellar region spacing
  - Instead of paraffin-type, monolayer or bilayer type occurs
- MTBA had the largest spacing, which could be due to one of the arms sticking up
- The heat of combustion for TPA should be much higher due to its carbon count, but experimental data shows a significantly lower value
- The heats of combustion for the salts should be determined using pellets rather than capsules, but the pellets are either too dry or too sticky to be combusted

Acknowledgements

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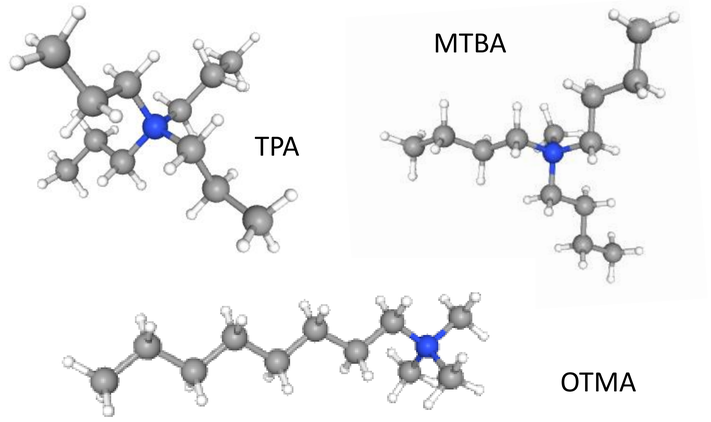
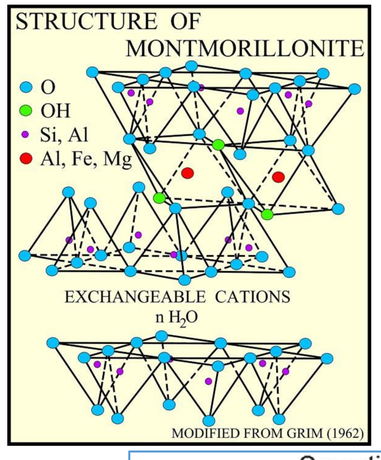
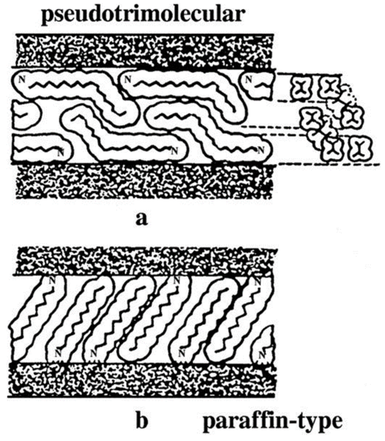
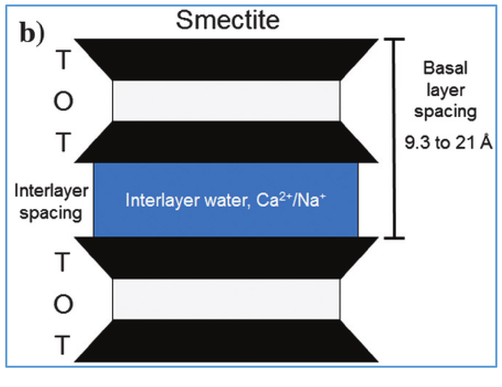
Structure of Clay and Salts



n-Octyltrimethylammonium bromide, PubChem.
Tributylmethylammonium bromide, PubChem.
Tetrabutylammonium iodide, PubChem.







Data

Experimental CEC Data from Bomb Calorimetry
Theoretical CEC of Saz-1: 120 meq/100g

Salt	Avg heat of combustion of salt	Avg. heat of combustion of exchanged clay	Experimental CEC	% Error
MTBA	7450.66 cal/g	1359.08 cal/g	65.1 meq/100g	45.8%
TPA	5733.41 cal/g	903.60 cal/g	50.3 meq/100g	58.1%
OTMA	7008.10 cal/g	1316 cal/g	76.3 meq/100g	36.4%

X-Ray Diffraction Data

Salt	Uncorrected d spacing	Interlamellar region spacing
MTBA	16.098 Å	6.498 Å
TPA	15.391 Å	5.791 Å
OTMA	14.018 Å	4.418 Å

Conclusions

- OTMA (the least hindered salt) had the closest experimental CEC
- Capsules may have caused problems in the determination of heat of combustion of salts
- Incomplete exchange of the clay with salt may not cover all charge sites which would not produce an accurate CEC

Future Work

- Using low CEC types of clay with more hindered salts such as TPA and MTBA
- Using longer chain salts such as ODTMA with SAz-1 and other high CEC clays
- Finding a way to create pellets from each salt to get an accurate heat of combustion via bomb calorimetry

References

1. Moore, D. M.; Reynolds, R. C. *x-ray diffraction and the identification and analysis of clay minerals* , 2nd ed.; Oxford University Press inc.: New York, 1997.
2. U. S. Geological Survey. https://pubs.usgs.gov/of/2001/of01-041/htmldocs/clays/smc.htm (accessed Jun 16, 2021).
3. Busenberg, E.; Clemency, C. V. Determination of the Cation Exchange Capacity of Clays and Soils Using an Ammonia Electrode. *Clays and Clay Miner.* **1973**, *21*, 213–217; DOI: 10.1346/CCMN.1973.0210403.
4. Lagaly, G. Layer charge determination by Alkylammonium Ions. Layer Charge Characteristics of 2:1 Silicate Clay Minerals. 1994, Vol. 6, 2-46.
5. Keith, C. A. Steric Effects of Alkyl Ammonium Salts on the Combustion of Exchanged Smectite Clays. M.S. Thesis, Stephen F. Austin State University, Nacogdoches, TX, 2018
6. Otunola, B. O., Olusola, O, O. A Review on the Application of Clay Minerals as heavy Metal Adsorbents for Remediation Purposes. *Environmental Technology & Innovation* . **2020,** *18.*