



Bomb Calorimetry: A New Method of CEC Determination

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Abstract

A new method of determining the cation exchange capacity (CEC) of clay minerals was examined.¹ This method involved exchanging the smectite clay with organic cations and using bomb calorimetry to measure the energy of combustion of the material. Because the clay is noncombustible, the energy is completely dependent on the amount of organic present, which is dependent on the CEC of the clay. Two organic cations, tetrapentylammonium and octadecyltrimethylammonium, with similar size but much different shape were used. For clays with lower CECs, using the more symmetric ion yielded better accuracy (4.24%), while for clays with higher CEC, using the straight chain organic yielded better accuracy (1.16%). Overall, the results indicate that using bomb calorimetry presents a viable option in the determination of cation exchange capacity.

Introduction

Clays are phylloaluminosilicates with a multi sheet-like structure. During formation, isomorphous substitution can occur causing the clay to have a net negative charge. The general structure of a clay can be seen in Figure 1. These sites are filled with cations, generally sodium or calcium, but can be exchanged with any cationic species. The number of these sites per unit mass of clay is referred to as the cation exchange capacity (CEC) of the clay. It dictates how the clay can be used. Because of this, it is important to know the CEC as accurately as possible. One of the most prolific methods to determine CEC is the ammonia probe method.² While it is a fairly easy method to perform, there is an acceptable $\pm 20\%$ error. Bomb calorimetry was investigated as a possible technique used in the determination of CEC. The layer structure of the clay is not actually combustible, so the charge sites were exchanged with the organic cations shown in Figures 2 and 3. The combustion of the organo-clays results in the generation of a gross heat, which is dependent on organic ions present. By knowing the standard gross heat of combustion of each organic and organo-clay, the CEC was calculated.

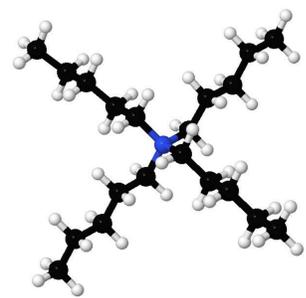


Figure 2. Tetrapentylammonium cation (TPentA).

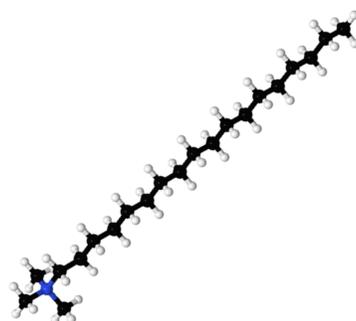


Figure 3. Octadecyltrimethylammonium cation (ODTMA).

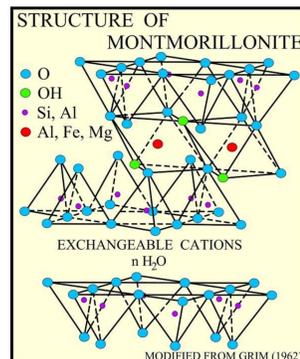


Figure 1. The basic structure of a montmorillonite clay.⁴ A layer is formed from two silicon tetrahedral sheets sandwiching an aluminum octahedral sheet. During formation, isomorphous substitution can occur, leaving a net negative charge, giving rise to the CEC of the clay. The spacing between the layers is the interlamellar region and is where the organic cations will reside.

Results

Table 1. Gross heats of combustion for the organics and exchanged clays. These values are used in the calculation of the CEC of each clay. TPentA is tetrapentylammonium and ODTMA is octadecyltrimethyl ammonium.

| Compound | TPentA | ODTMA |
|--------------------|-----------------------------|-----------------------------|
| Salt | 7709.1576 cal/g \pm 43.67 | 7979.0391 cal/g \pm 14.01 |
| S _{HCa-1} | 1338.2213 cal/g \pm 66.70 | 918.8567 cal/g \pm 22.38 |
| S _{Az-1} | 1140.3888 cal/g | 3802.0359 cal/g \pm 13.77 |
| S _{Wy-2} | 1766.1853 cal/g | 4007.640 cal/g \pm 11.98 |

Table 2. Experimental CEC values calculated using the gross heats of combustion. These are compared to the theoretical CEC values for the standard clays used.³

| ODTMA-Clay | Experimental CEC | Theoretical CEC ³ | Percent Error |
|--------------------|---------------------------|------------------------------|---------------|
| S _{HCa-1} | 29.34 $\frac{meq}{100g}$ | 44 $\frac{meq}{100g}$ | 33.3% |
| S _{Wy-2} | 127.97 $\frac{meq}{100g}$ | 80 $\frac{meq}{100g}$ | 60.0% |
| S _{Az-1} | 121.40 $\frac{meq}{100g}$ | 120 $\frac{meq}{100g}$ | 1.16% |
| TPentA-Clay | Experimental CEC | Theoretical CEC ³ | Percent Error |
| S _{HCa-1} | 45.87 $\frac{meq}{100g}$ | 44 $\frac{meq}{100g}$ | 4.24% |
| S _{Wy-2} | 60.53 $\frac{meq}{100g}$ | 80 $\frac{meq}{100g}$ | 24.3% |
| S _{Az-1} | 39.09 $\frac{meq}{100g}$ | 120 $\frac{meq}{100g}$ | 67.4% |

Table 3. Experimental d-spacing values obtained from XRD. All values are given in Angstroms. The width of a clay layer (9.6 Å) was subtracted out to obtain the adjusted d-spacing.

| Compound | Na-S _{Az-1} | ODTMA-S _{Az-1} | Na-S _{HCa-1} | ODTMA-S _{HCa-1} | TPentA-S _{HCa-1} |
|----------------------|----------------------|-------------------------|-----------------------|--------------------------|---------------------------|
| Unadjusted d-spacing | 12.7891 | 20.0686 | 14.0165 | 14.9675 | 17.5990 |
| Adjusted d-spacing | 3.1891 | 10.4690 | 4.4165 | 5.3675 | 7.9990 |

Objectives

- Purify and exchange 3 well characterized, standard clays
- Combust organics for baseline energies and combust organo-clays
- Determine CEC of clays.
- Analyze organo-clays with XRD.

Methods and Materials

Standard clays from the Source Clays Repository³ will be purified via a standard procedure. These clays will be modified with organic cations of various sizes and shapes, producing organo-clays. These organo-clays will be characterized using x-ray diffraction (XRD) to determine how the cation is oriented in the clay. To determine the CEC of the clay, a bomb calorimeter will be used. The calorimeter will first be calibrated and standardized using benzoic acid, following the instrumentation guidelines. Samples of the organic cations will be combusted to determine the quantity of energy they produce. Then, samples of the organo-clays will be combusted. When the clay is modified with the organic, a single organic cation occupies each charge site on the clay, so using the two energies measured, we are able to calculate the CEC of the clay. Since the energy depends only on the organic, and there is one cation per site, this will be a direct measure of the CEC. The clays used have been very well characterized so the results can be verified. The effect of the size and shape of the organic cation will be evaluated using the XRD.

Discussion

All the standard clays were purified and exchanged with the two different organic cations. The samples were put through two different analyses, bomb calorimetry and XRD. The values for the gross heats of combustion are shown in Table 1 with the calculated CEC values in Table 2. The results of XRD are given in Table 3. The XRD results indicate that the organic cations were successfully exchanged and give some indication as to the orientation of the cation. For ODTMA-SAz-1, the large spacing value indicates that the cation is arranged at a slight angle to the clay layer whereas for ODTMA-SHCa-1, the small value indicates the organic is laying flat between the layers. There were difficulties taking the XRD of the samples and further work needs to be done, changing the sample prep for analysis. For the CEC determination, the results show that using the ODTMA worked well for the high CEC clay (1.16%) but not for the low CEC clay (33.3%). The TPentA worked well for the low CEC clay (4.24%) but not for the high CEC clay (67.4%). This can be attributed to the arrangement of the cation in the clay. Neither cation worked well for the intermediate clay.

Conclusions

The results that were obtained during this research are very encouraging. The low percent errors indicate that using bomb calorimetry is a viable option in determining CEC. However, there is also indication that the structure of the cation used when exchanging the clay does matter. Future work will involve in depth XRD studies of the organo-clays, working to determine a better sample prep for analysis. In addition, the number of cations used will be expanded to see if there is one cation that can be used for all clays.

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References

1. Keith, Celeste A. Steric Effects of Alkyl Ammonium Salts on the Combustion of Exchanged Smectite Clays. Master's Thesis, Stephen F. Austin State University, Nacogdoches, Texas 2018
2. Busenberg, E.; Clemency, C. V. Determination of the Cation Exchange Capacity of Clays and Soils Using an Ammonia Electrode. *Clays and Clay Minerals*. **1973**, Vol. 21, 213-217.
3. Mermut, A., Baseline Studies of the Clay Mineral Society Source Clays: Layer-Charge Determination and Characteristics of Those Minerals Containing 2:1 Layers. *Clays and Clay Minerals*. **2001**, Vol. 49, 5, 393-397.
4. Grim, R. E. *Clay Mineralogy*; McGraw-Hill: New York, 1968.