

Thermally-treated clay as a stationary phase in liquid chromatography[☆]

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Abstract

Spray-dried, spherical synthetic hectorite particles have been thermally-treated at 500 °C for 16 h and used as adsorbent materials in reversed-phase liquid chromatography. The retention of a 22 mono and disubstituted aromatic compounds was evaluated to study the retention mechanisms on the clay mineral. The retention of solutes on the thermally-treated clays was markedly different than that measured on octadecylsilica (ODS) columns under identical conditions, but remarkably similar to retention characteristics of the same solutes on porous graphitic carbon columns. The clay columns exhibit an enhanced selectivity over the ODS column in separation of nitroaromatic positional isomers. Under identical mobile phase compositions, a selectivity, α , of 7.15 between *ortho*- and *para*-dinitrobenzene isomers was measured on the clay column compared to a α of 1.04 on the ODS column.

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1. Introduction

Clays and organo-clays have surface properties that make them effective and economical adsorbent materials. Indeed, the interest in using these materials for water treatment processes is a research topic that has received considerable attention over the last few decades [1–7]. Thermally-treated clays have recently been reported as promising adsorbent materials for slow-release pesticides applications and solid-phase extraction material for pollutants from aqueous solutions [8,9]. These initial studies indicate that thermally-treated clays, and associated organo-clay complexes, can be highly effective, and in some cases, highly selective adsorbents for pesticides and nitroaromatic compounds.

Typically, the effectiveness of adsorbent materials is evaluated by traditional batch adsorption experiments that provide valuable adsorption isotherm data. Chromatographic

experiments can provide an alternative way to characterize adsorbent–adsorbate interactions, and thus the effectiveness of adsorbents. Reversed-phase liquid chromatography (RPLC) has been proposed as a method to predict soil adsorption coefficients by various researchers [10–14]. Thus, liquid chromatographic (LC) studies, in principle, should be ideally suited to evaluate the effectiveness of clay and organo-clays as adsorbents used in both analytical applications (solid-phase extraction and stationary phase material) and industrial separation and purification processes.

Earlier work reported using thermally-treated, spray-dried clay materials as stationary phase material in gas, liquid, and supercritical-fluid chromatography [15–22]. In most of these reports, however, the liquid chromatographic separations were either performed in a normal-phase mode [17–20], or the clay surface was further modified for chiral separations [21,22]. Thus, the mechanisms for retention, while important for each application, are not readily applicable to understanding how these adsorbents might be used in such applications as wastewater treatment, where adsorbate–adsorbent interactions are more like RPLC. Recently, researchers reported using spray-dried clay particles as both adsorption media and stationary phase material in the study of the nitro-aromatic compounds in natural waters. They used a predominately aqueous mobile phase

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with a linear gradient, and described the mechanism for a separation of four analytes (2,6-diamino-4-nitrotoluene, 4-amino-2,6-dinitrotoluene, 1,3-dinitrobenzene, and 2,4,6-trinitrotoluene) as being pseudo-reversed phase, governed by electron-donor–electron-acceptor interactions [9]. While these results are intriguing, study of solute–adsorbent interactions from additional compound classes on spray-dried clay particles is needed to better understand the retention mechanism.

In this paper, we present data and a preliminary evaluation of the retention mechanisms in RPLC that govern solute interactions with thermally-treated clay materials. For the studies reported here, the synthetic clay Laponite-RD² is used as the model clay. First, retention studies using substituted benzenes are described on both the clay column and an ODS column to further characterize the retention mechanisms observed on thermally-treated clays. Second, disubstituted benzene solutes were used to evaluate selectivity differences between the clay and ODS columns.

2. Experimental

2.1. Clay column preparation

A 1% (m/m) suspension of Laponite-RD was prepared with distilled/de-mineralized water. Laponite-RD is a synthetic hectorite with an empirical formula of $\text{Na}_{0.7}^+[(\text{Si}_8\text{Mg}_{5.5}\text{Li}_{0.3})\text{O}_{20}(\text{OH})_4]^{-0.7}$. This suspension was stirred for 24 h prior to creating the particles. To prepare spray-dried clay particles, a commercial, laboratory spray-dryer was used. The inlet and outlet temperatures of the spray-dryer chamber were held at 220 °C and 110 °C, respectively. Filtered, compressed air was used as the aspiration source. The spray-dried particles thus produced were subsequently thermally-treated in air at 500 °C for 16 h. After heat treatment, the particles were separated by sedimentation in distilled water. Before column preparation, the particles were washed with additional distilled water, filtered through a 1.0 μm filter, and dried. The particle size distribution of the clay particles, as determined by scanning electron microscopy (SEM), ranged from 1.0 to 25 μm with 95% of the particles under 15 μm . SEM images of the spray-dried particles are shown in Fig. 1A and B. In early studies, we determined the surface area of the heat-treated (300 °C) Laponite-RD to be 328 m^2/g , which is in agreement with the 300 m^2/g surface area for spray-dried Laponite used in clay-based chiral stationary phases [22]. The surface chemistry of the Laponite-RD is typical of nat-

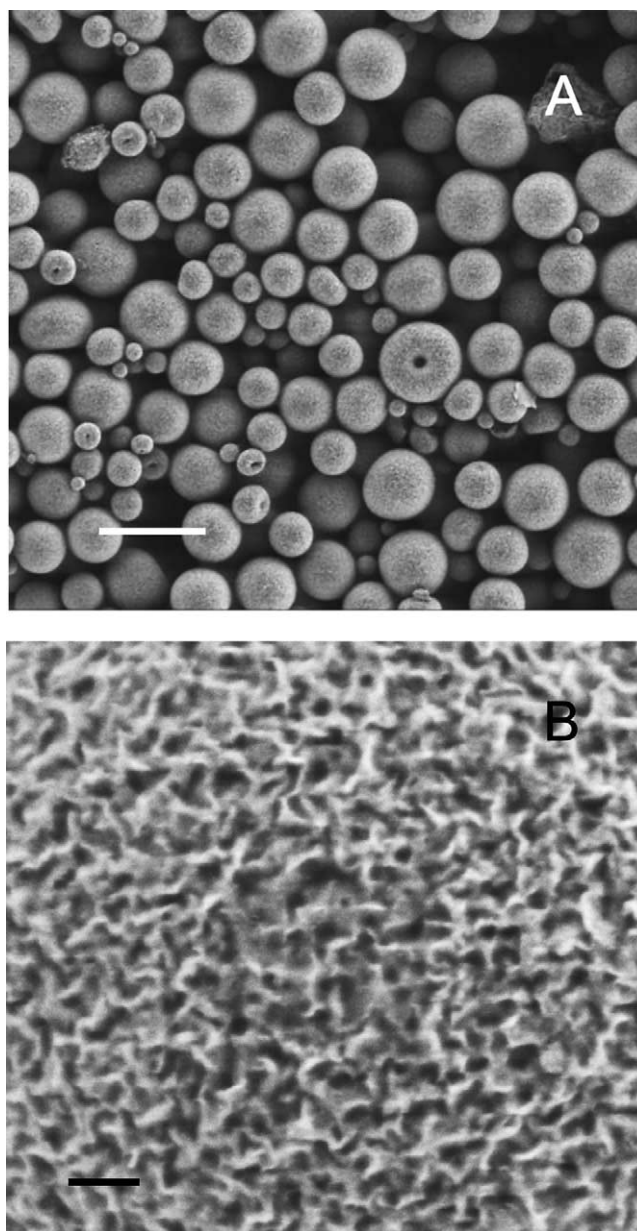


Fig. 1. SEM image of clay particles. (A) The size of 95% of the spray-dried Laponite-RD particles ranged in size from 1.0 to 25 μm . The “donut” morphology present in some particles is a result of steam blistering during particle formation. Scale bar = 10 μm . (B) High resolution image of a single particle showing the “plate-like” morphology on the surface. Scale bar = 200 nm.

ural hectorite clay minerals, and thus is a combination of the silicate layer (including both siloxane and silanol moieties), the adsorbed sodium cation, and the water molecules that hydrate the sodium cation [23].

A 50 mm \times 4.6 mm column, fitted with stainless steel frits (mesh size diameter of 0.5 μm), was prepared using a commercial slurry-packing instrument. An aliquot of 1.30 g of the dried clay particles was first suspended in 15 mL of isopropanol and sonicated for 15 min. The column was initially packed in the upward direction for 5 min using degassed

² Certain commercial equipment, instruments, or materials are identified in this paper in order to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the US National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

isopropanol. The column was then rotated 180° and packing was continued in the downward direction for an additional 5 min. To minimize an excess differential pressure across the column bed and flush all isopropanol from the column, a gradual gradient was applied to the column, passing through a pure water phase to the methanol:water mobile phase compositions used in all separations. The void volume of the column was calculated using nitrate ion at multiple flows and mobile phase compositions. The porosity of the column was determined to be 0.22 based on the calculated void volume and the internal dimensions of the stainless steel column.

2.2. Materials and experimental conditions

All 22 solutes (acetophenone, benzaldehyde, benzene, benzyl alcohol, *n*-butylbenzene, chlorobenzene, *p*-cresol, *o,m,p*-dichlorobenzene isomers, *o,m,p*-dinitrobenzene isomers, ethylbenzene, nitrobenzene, 2-phenylethanol, phenol, toluene, *n*-propylbenzene, and *o,m,p*-xylene isomers), methanol, and Laponite-RD were obtained from a commercial source and used as received. Manufacturer specified purities of the solutes ranged from 99 to 99.5% (m/m), and HPLC-grade methanol was used. Individual solutions of the alkyl and substituted benzene solutes were made in methanol. All samples were injected at low enough concentrations to produce symmetric peak shapes. In most cases, this corresponded to solutions ranging in concentration from 10 to 100 ppm (m/m). Distilled/de-mineralized water (de-mineralized to greater than 18 MΩ) was used in the preparation of the aqueous clay solution and the mobile phase.

A commercial liquid chromatographic system with a diode-array ultraviolet-visible absorbance detector was used to perform the analyses. The column was maintained at 50 °C inside the heating compartment of the LC system. An injected sample volume of 1.0 μL was used for all analyses. A flow rate of between 0.50 and 0.70 mL/min was used with the thermally-treated, spray-dried clay column, resulting in a maximum back-pressure of 89 bar. To compare the behavior of the clay phase with a typical reversed-phase packing, separations were also performed on a commercial octadecylsilica (ODS) column (150 mm × 3.2 mm, 5 μm particles). As reported by the manufacturer, column has a surface area of 200 m²/g, pore diameter of 8.0 nm, pore volume of 0.8 mL/g, a carbon load of 10%, and was endcapped to minimize adsorption. The flow rate for these measurements was 1.00 mL/min. All other separation conditions were identical to those of the clay column. An isocratic mobile phase composition of water–methanol (55:45, v/v) was used for the alkyl benzene and reversed-phase test mixture separations, and a composition of water–methanol (50:50, v/v) was used for the study of mono-substituted benzene solutes. The water/methanol mobile phase composition was varied for the retention studies of the disubstituted benzene solutes. All solutes used for retention studies were injected

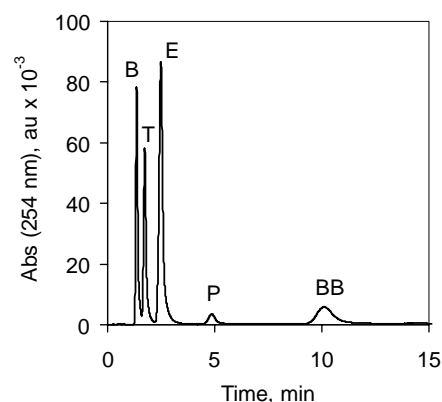


Fig. 2. Alkylbenzene separation on clay column. Flow rate of separation 0.700 mL/min; all other separation conditions specified in Section 2. Analyte identities are benzene (B), toluene (T), ethylbenzene (EB), propylbenzene (PB), and butylbenzene (BB).

in triplicate. Sodium nitrate was used as a void volume marker for both columns.

3. Results and discussion

The isocratic separation of a series of alkylbenzenes on thermally-treated clay (hereafter referred to as only clay) is shown in Fig. 2. From this separation, it is apparent that retention of the solutes is governed by the hydrophobicity of the stationary phase since the addition of each methylene group results in an increase in retention [24]. Since an increase in the concentration of organic modifier in the mobile phase (not shown here for brevity) decreases the retention of the alkyl-benzene homologues, the separation is reversed-phase in nature [25]. In Fig. 3, the separation of a reversed-phase test mixture, with solutes of varying polarity, is shown for both the clay and ODS stationary phases. The retention for each separation is expressed in the form of

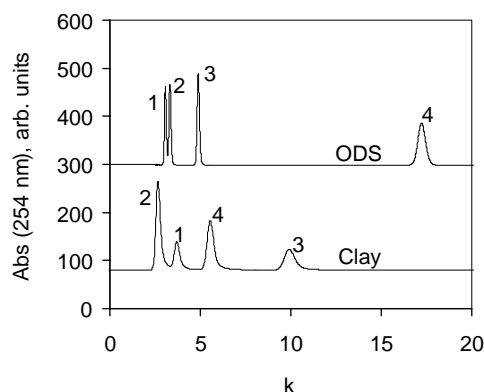


Fig. 3. Reversed-phase test mixture comparison. The separation of 2-phenylethanol (1), *p*-cresol (2), nitrobenzene (3), and toluene (4) on ODS and thermally-treated clay columns. Flow rate of separation 0.700 mL/min on clay column and 1.000 mL/min on ODS column; all other separation conditions for each column specified in Section 2.

the retention factor, k , for comparison. Under the reversed-phase conditions, the solutes elute in the order shown on the chromatogram from the ODS separation, with the more polar compounds eluting first. While the separation on the clay column occurs under the same conditions, it is clear from Fig. 3 that solute retention, and thus selectivity on the clay stationary phase is quite different from that observed with the ODS stationary phase. This is not surprising since the clay–solute interaction is an adsorption process, while the ODS–solute interaction is governed by partitioning behavior. To further our understanding of the retention behavior of the solutes on clay under reversed-phase conditions, an approach or model to explain the observed retention is needed.

The interpretation and prediction of retention behavior in reversed-phase high-performance liquid chromatography is generally accomplished by one of two approaches. One approach correlates retention characteristics of analytes with their molecular physical and structural properties (i.e., dipole moment, molecular connectivity, size, planarity, pK_a , partition coefficients, etc.) through either direct or multivariate correlations [26,27]. The second approach correlates collective structural and functional group properties of compound classes to retention characteristics [28]. By examining functional group contributions with respect to a reference compound, solute–adsorbent interactions of various compounds with stationary phase materials can be evaluated. This technique has provided insight in describing retention mechanisms on porousgraphitic carbon [24] and carbon coated zirconia stationary phases [29]. We have therefore chosen this approach as a preliminary step in the evaluation of retention data from thermally-treated clay columns.

Functional group contributions are calculated by evaluating the difference in retention of two analytes that differ only by the presence or absence of the functional group. Using benzene as a reference compound, the functional group contributions, τ_X , are calculated by:

$$\tau_X = \ln \left(\frac{k_{R-X}}{k_{R-H}} \right) = \ln k_{R-X} - \ln k_{R-H} \quad (1)$$

where k is the retention factor of the analyte, R the reference compound, X the functional group, and H represents the hydrogen in the reference compound. Thus, τ_X values are retention factors normalized to a standard, which in this study has been selected as benzene.

The functional group contributions, τ_X , for a series of mono-substituted benzene compounds, were calculated for both clay and ODS columns, and are presented in Fig. 4. A maximum uncertainty of 2% for τ_X values was calculated with standard error propagation techniques (based on propagation of an uncertainty of two standard deviations for each measured value). Therefore, error bars are not shown in Fig. 4 since they would not be visible on the scale of the figure. As shown in Fig. 4, retention characteristics differ dramatically between the clay and ODS columns. It is clear from Fig. 4 that the same solute–stationary phase interactions that govern retention of the mono-substituted aro-

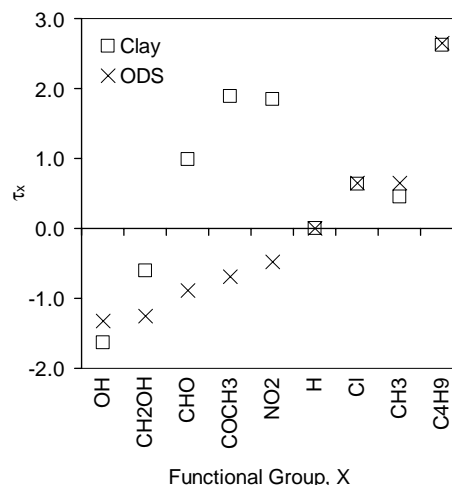


Fig. 4. Lot of functional group substitution vs. τ_X . Clay column (\square) and ODS column (\times). Mobile phase composition used on both columns was methanol–water (50:50, v/v).

matic compounds on the ODS column do not apply to the clay column. In general, as functional groups are added to the benzene ring, retention time increases relative to benzene on the clay phase. The exceptions are compounds with highly polar functional groups (phenol and benzyl alcohol). The behavior of retention of ODS is quite different, with an increase in retention relative to benzene occurring only for the chloro and alkyl substitutions. This observed trend in retention and selectivity on the clay is remarkably similar to that observed on porous graphitic carbon (PGC) and carbon coated zirconia (C/ZrO_2) stationary phases [29,30]. Studies of similar solutes on PGC and C/ZrO_2 suggest that the addition of functional groups increases the retention of the substituted benzenes both from dipolarity and/or dipole-induced dipole interactions, and strong dispersive forces.

Retention data (i.e., k) collected from both columns were of different magnitudes. Thus, it is preferable to compare these data on a similar scale to assure comparisons being made between the retention interactions are valid. A range scaling transformation was used that scales the retention time of each solute with respect to the longest retained solute on a particular stationary phase. This approach to range scaling has been particularly useful in evaluating the orthogonality of separation components (i.e., stationary and mobile phases) used in multidimensional chromatography, and has been described in detail elsewhere [31,32]. Specifically, a fractional correction is performed for each solute by:

$$X_a = \frac{t_i - t_o}{t_f - t_o} \quad (2)$$

where X_a is the scaled retention factor for stationary phase a , t_i the retention time of solute i , t_o the retention time of a non-retained solute, and t_f is the retention time of the longest retained solute. The X_a for all solutes measured on the clay and ODS columns (methanol–water, 50:50, v/v, mobile phase composition) are shown in Fig. 5. If each

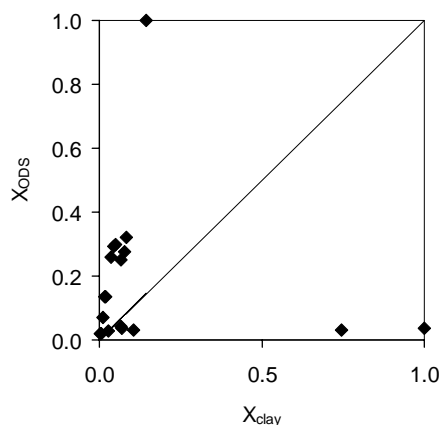


Fig. 5. Lot of X_{CLAY} vs. X_{ODS} . Mobile phase composition used on both columns was methanol–water (50:50, v/v).

stationary phase exhibited similar retention characteristics, X_{CLAY} and X_{ODS} would be highly correlated. A hypothetically perfect correlation between the two phases is indicated by the solid line in Fig. 5. As in Fig. 4, it is clear that the retention mechanism occurring between the solutes and each of the two phases is different.

It is not surprising that the clay columns exhibit similar behavior to the carbon surfaces. Since the retention on all three surfaces (PGC, C/ZrO₂ or clay) is purely adsorption (i.e., no partitioning mechanisms are responsible for retention on these surfaces), the dominant retention mechanism or mechanisms between the solutes and the substrates are very likely the same. Dispersive forces alone, which contribute to the retention of solutes on all phases, cannot explain this similarity between the phases. Thus, these observations suggest that the electron-rich clay surface is contributing to the retention behavior.

In addition to the mechanistic study presented above, retention studies of positional isomers of three disubstituted aromatic compounds were evaluated on both the clay and ODS columns. Mobile phase composition was varied to de-

termine optimum selectivity on each column that could be accomplished in a reasonable elution period for all isomer sets. Selectivity between position isomers is defined here as:

$$\alpha = \frac{k_X}{k_Y} \quad (3)$$

where k_X is the retention factor of the more retained isomer and k_Y is the retention factor of the least retained isomer. To evaluate selectivity between the columns under reasonable retention conditions (a guideline set here to be a maximum analysis time of 60 min), a mobile phase composition of water–methanol (50:50, v/v) was selected for comparison. The retention results, in the form of k , along with selectivity ratios, are summarized in Table 1. Measurement uncertainties are included in Table 1 with a coverage factor of $k = 2$ (that is, two standard deviations). While there is no selectivity increase between the xylene and dichlorobenzene isomers, the selectivity increase between the dinitrobenzene isomers from the ODS to clay stationary phases is dramatic and warrants additional discussion.

The pronounced increase in retention of, and selectivity between the dinitrobenzene isomers is very similar to that observed on C/ZrO₂ when compared to ODS [29]. In addition, the results also are in agreement with adsorption isotherm data on natural clay minerals [33,34]. In pure aqueous solutions, sorption processes on clay are dominated by electronic and steric substituent effects. In the case of the *ortho*-substituted dinitrobenzene, the proximity of the two nitro-groups prevents the solute from forming a planar configuration. This prevents the optimal resonance of the nitro-substitution groups with the benzene ring. As a result, the electron-rich surface of the clay minerals is less likely to donate to an electron-deficient aromatic ring. This results in a large difference in the retention time of the *ortho*-substituted isomer over the *meta*- and *para*-substituted isomers.

Like the retention behavior on PGC, the retention mechanism on thermally-treated clay is complex. A direct comparison between the phases, however, is not appropriate

Table 1
Selectivity of positional isomers measured on clay and ODS columns^{a,b}

Compound	Retention factor, k		α (k/k)	
	ODS	Clay	ODS	Clay
<i>o</i> -Xylene	22.36 ± 0.15	2.18 ± 0.02	1.13 ± 0.01	1.20 ± 0.01
<i>m</i> -Xylene	25.27 ± 0.25	2.63 ± 0.02	1.02 ± 0.02	1.17 ± 0.01
<i>p</i> -Xylene	25.77 ± 0.31	3.07 ± 0.02		
<i>o</i> -Dichlorobenzene	21.50 ± 0.05	4.04 ± 0.01	1.10 ± 0.01	1.17 ± 0.01
<i>p</i> -Dichlorobenzene	23.68 ± 0.07	4.73 ± 0.02	1.17 ± 0.01	1.07 ± 0.01
<i>m</i> -Dichlorobenzene	27.71 ± 0.05	5.04 ± 0.01		
<i>o</i> -Dinitrobenzene	2.62 ± 0.01	6.34 ± 0.10	1.04 ± 0.01	7.15 ± 0.16
<i>p</i> -Dinitrobenzene	2.73 ± 0.01	45.33 ± 0.68	1.13 ± 0.01	1.34 ± 0.03
<i>m</i> -Dinitrobenzene	3.09 ± 0.02	60.87 ± 0.99		

Uncertainty value set as 0.01; calculated uncertainty would round to 0.00.

^a Mobile phase composition methanol–water (50:50) for all analyses.

^b Uncertainty values correspond to a coverage factor of $k = 2$ (i.e., two standard deviations).

with this limited data set since simple theories and models have failed in the prediction of retention on PGC stationary phases [35,36]. Thus, future work will involve analysis of multiple isomers, homologous series, and various ionizable compounds under various pH conditions to further our understanding of the retention mechanism.

4. Conclusion

We have presented a preliminary assessment of adsorbate interactions with thermally-treated clay materials using liquid chromatography. These retention characteristics are analogous to those observed and reported in PGC and C/ZrO₂ columns used in RPLC. Many polar compounds exhibit increased retention when compared to ODS, suggesting thermally-treated clays might be useful as adsorbent material for the separation of polar analytes. Future work, however, is needed to further understand the complex retention mechanisms of these unique adsorbents.

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