Gas chromatographic properties of organoammonium exchanged montmorillonites

I. Tetraalkylammonium cations

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(First received June 28th, 1990; revised manuscript received January 28th, 1991)

ABSTRACT

The retention of aliphatic hydrocarbons, benzene, and substituted benzenes was determined by gas chromatography with R_4N^+ treated montmorillonite in a OV-101 film. Columns were modified with four R_4N^+ cations for R = CH_3, C_2H_5, n-C_3H_7 and n-C_4H_9; Na^+ and NH_4^+ exchanged montmorillonites were used in control columns. The $(CH_3)_4N^+$ tailored montmorillonite showed thermal stability and enhanced retentive properties *versus* control columns. Relative retention of substitutional isomers of benzene suggested a steric component in separations. Analyses by gas chromatography–mass spectrometry of decomposition products of other, thermally instable, R_4N^+ montmorillonites was consistent with a base promoted elimination reaction. Organoammonium tailoring agents with β-hydrogens including Bentone-34 should all exhibit thermal instability in treated montmorillonites.

INTRODUCTION

Montmorillonite is a 2:1 layered type of phyllosilicate with negative charges of 0.25–0.6/unit cell from isomorphic substitution of Mg^{2+} for Al^{3+} in octahedral layers of the aluminosilicate. Sodium is the natively abundant counterion in the interlamellar region and exchange by organic ammonium cations may impart characteristic adsorptive properties to montmorillonite. In most investigations, alkyl- or arylamine cations based on $R_{(4-x)}NH_x^+$ for x = 0–3 have been utilized to alter clay properties. While coulombic forces promote cation exchange, the alkyl substituents are attracted to the basal plane and other alkyl chains (if sufficiently long) through Van der Waals interactions. Presumably, the alkyl groups affect adsorption or retention of compounds by these tailored clays [1–4].

In the mid-1950s, stationary phases based upon natural solids including zeolites, clays, silicas, and others received attention as packings for gas-solid chromatography (GSC). A few organoammonium montmorillonites of the form $R_2N^+R'_2$ (R = CH_3 and R' = $C_{18}H_{37}$) or $RN^+R'_3$ (R = CH_3 and R' = $C_{16}H_{35}$) were examined between 1957–1968 [5–8] and the octadecyl form was deemed useful in separating

substituted benzene isomers. A commercial product, Bentone-34, eventually became available and a steric component to separation was tacitly suggested but not explored.

In 1971, Tarramasso [9] demonstrated that montmorillonite could be tailored to impart specific chromatographic properties and proposed that basal spacings of 24–26 Å would allow compounds to enter the interlamellar region. The elution order via partition or adsorption mechanisms for isomers of trimethylbenzene was 1,3,5-1,2,4- and 1,2,3-trimethylbenzene. This order was reversed with tailored montmorillonite [9,10] and steric models were invoked to explain the reversal in retention order. The interlamellar distances for montmorillonite with the following tailoring agents are [11,12]: TMA [$(CH_3)_4N^+$], 4.3 Å; TEA [$(C_2H_5)_4N^+$], 4.5 Å; TPA [$(C_3H_7)_4N^+$], 5.0 Å; and TBA [$(C_4H_9)_4N^+$], 6.7 Å. Thus, the interlamellar region is sufficient to accept and retain small molecules and possibly allow some separation based upon adsorbate geometry or size. Specific interactions should be weak and retention should be governed by adsorbate size and geometry for non-polar molecules. Thus, retention might be anticipated in the order of increasing R from CH_3 to C_4H_9 where the basal space is incrementally enlarged and the interlamellar region is available for adsorption.

An objective of this and a following investigation was to systematically examine the retention properties of several organoammonium tailored montmorillonites. A model for retention with tailored clays in gas chromatography (GC) will be proposed and could provide a basis for predicting tailoring agents for improved GSC performance. The simplest organoammonium cation family to initiate this investigation was the R_4N^+ for carbon numbers of 1–4 for the alkyl group, R.

EXPERIMENTAL

Instrumentation

A Hewlett-Packard Model 5890A gas chromatograph was equipped with a flame ionization detector, heated injector port, and HP Model 3392A integrating recorder. The inlet was modified with a 0–100 p.s.i. pressure gauge (Ashcroft–Dura-gauge) which permitted continuous inspection and measurement of inlet pressures (0.5 p.s.i. precision). Column flows were measured at the detector with a soap-bubble meter.

Materials and reagents

Montmorillonite was obtained in sodium form from a commercially available clay, Aquagel, also known as Wyoming Bentonite, through purification and isolation as summarized in Table I. Tailored montmorillonites were prepared from purified sodium montmorillonite and aqueous solutions of appropriate ammonium salts. Typically, tailoring agent was added to 1 g of sodium montmorillonite in 1000-fold excess of the estimated cation-exchange capacity, stirred with paddles at 30 rpm for 8–10 h, and isolated by decanting after a 2 h period for settling. The clay was air-dried at ambient temperature for 24 h and then heated at 100°C for 2 h. A 115-mesh fraction was added to a solution of OV-101 and packings were prepared through rotary evaporation of solvent. Ratios of packing, liquid phase and clay are given in Table II.

TABLE I

PURIFICATION OF WYOMING BENTONITE (AQUAGEL) TO SODIUM MONTMORILLONITE (25 g)

Step	Treatment
1	Add 250 ml of a sodium acetate buffer, pH 5, 70°C; stir gently for 1 h
2	Centrifuge, decant and mechanically remove black grit
3	Add in order: 200 ml solution of 0.3 M sodium citrate, 25 ml of 1 M NaHCO$_3$, 5 g of sodium dithionite; then stir for 1 h
4	Centrifuge, decant and remove grit
5	Add 100 ml of 30% H$_2$O$_2$ and stir 1 h
6	Centrifuge and decant
7	Resuspend with 250 ml of water and floc with sodium chloride
8	Filter solid and dry at 90°C for 48 h

Procedures

Since retention was particularly sensitive to compound and column temperature, a temperature gradient of 5°C/min from 50°C was regarded as a reasonable vehicle to characterize retention for a large number of compounds. The retention times, t_r and retention time for an unretained solute, t_m, in this instance methane, were obtained under identical conditions for all columns and compounds. Sufficient ambiguities existed in the exact mechanism of retention, *i.e.* partition, adsorption, or steric exclusion, that use of more elementary terms such as specific retention volumes or partition coefficients was considered premature and experimentally intractable. Consequently, reliance was made on daily reproducibility of column flows and inlet pressures to facilitate comparisons of retention. An aliquot of 1 μl of 0.01 M solutions of compounds in carbon disulfide was introduced into the GC apparatus simultaneously with the start of the temperature program.

TABLE II

CHARACTERISTICS OF PACKINGS FOR TAILORED MONTMORILLONITES

Column	Form of tailoring agent	Column packing mass (g)	Clay adsorbent mass (g)
Composition of individual columns			
TMA	Cl⁻ salt	2.5082	0.0502
TEA	Br⁻ salt	2.4851	0.0497
TPA	Br⁻ salt	2.6226	0.0525
TBA	Br⁻ salt	2.7488	0.0550
Composition of packing (w/w):			
96% solid support: Chromosorb W-AW			
2% liquid phase: OV-101			
2% tailored montmorillonite			

Vapors from thermal decomposition of tailored montmorillonite solids were analyzed using a Hewlett-Packard 5995A gas chromatography–mass spectrometer with a 30-m SuperOx II capillary column. An inlet liner was packed with 0.3–0.8 mg of solid and inserted in the GC–mass spectrometric (MS) injection port. The capillary column had previously been set to $-10°C$ in order to cryogenically focus highly volatile decomposition products. The inlet (250°C) was operated in splitless mode for *ca.* 10 s and reset to split mode with the start of the oven temperature program. This program consisted of initial temperature, $-10°C$; initial time, 5 min; program rate, 6°C/min; and final temperature, 200°C or lower. The mass spectrometer was started after 1 min to allow the venting of air and then was operated from m/z of 35 to 600 at 600 a.m.u./s.

RESULTS AND DISCUSSION

GC retention properties for R_4N^+-montmorillonites

Retention behavior of montmorillonite tailored with TMA, TEA, TPA, and TBA for alkanes from pentane to nonane is shown in Fig. 1. In comparison, control columns (Na^+ or NH_4^+ tailored montmorillonite in 2% OV-101) exhibited retention
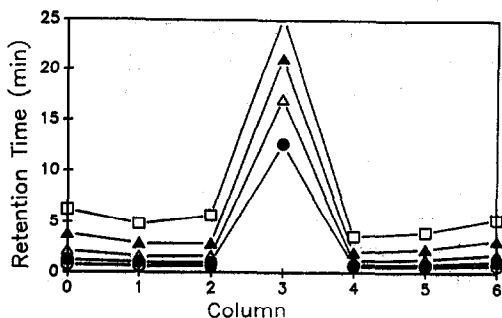
Fig. 1. Retention times and trends for *n*-alkanes on controls and tetraalkylammonium exchanged montmorillonite. Columns: 0 = No clay; 1 = Na^+; 2 = NH_4^+; 3 = TMA; 4 = TEA; 5 = TPA; 6 = TBA. *n*-Alkanes: O = pentane; $\bullet$ = hexane; $\triangle$ = heptane; $\blacktriangle$ = octane and $\square$ = nonane.

Fig. 2. Retention times and trends for monosubstituted benzenes on controls and tetraalkylammonium exchanged montmorillonite. Columns as in Fig. 1. Monosubstituted benzenes: O = benzene; $\bullet$ = toluene; $\triangle$ = ethylbenzene; $\blacktriangle$ = propylbenzene; $\square$ = butylbenzene.
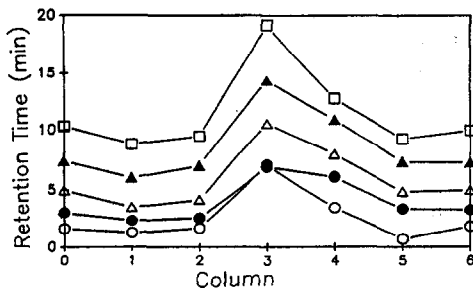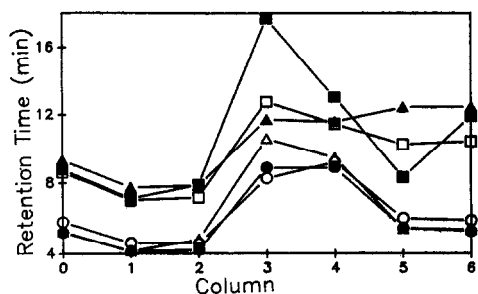
Fig. 3. Retention times and trends for disubstituted benzenes on controls and tetraalkylammonium exchanged montmorillonite. Columns as in Fig. 1. Disubstituted benzenes: $\bigcirc$ = *o*-xylene; $\bullet$ = *m*-xylene; $\triangle$ = *p*-xylene; $\blacktriangle$ = *o*-dichlorobenzene; $\square$ = *m*-dichlorobenzene; $\blacksquare$ = *p*-dichlorobenzene.

times of 0.8 to 6 min for pentane and nonane, respectively. Thus, only the TMA montmorillonite exhibited retention significantly larger than that for controls and was inconsistent with an expected trend of TBA > TPA > TEA > TMA. Similarly, monosubstituted benzenes (Fig. 2) were retained better on TMA than on controls, TEA, TPA, and TBA packings. In the retention times for xylenes and dichlorobenzenes (Fig. 3), the TMA column showed enhanced retention over all other phases where retention times were inversely proportional to vapor pressures. Thus, retention in controls and packings, except TMA, occurred through general dispersion interactions with no obvious steric component. The retention order for disubstituted benzenes with non-specific liquid phases has been determined [9] as *ortho > meta > para*. However, this trend was inverted with both dichlorobenzenes and xylenes on TMA suggesting some control over retention through a steric mechanism.

Column efficiencies for various analytes ranged from acceptable to poor for packed columns. For example, an average number of theoretical plates was *ca.* 400 or height equivalent for a theoretical plate of 0.5 cm for a 2-m column. While this performance cannot be regarded as analytical grade behavior, the emphasis in this work was the coverage of active sites and mechanical integrity of the column. Thus, the use of thin films of montmorillonite not in a supporting liquid phase might be expected to impart column efficiency better than that observed here.

Thermal stabilities of tailored montmorillonites

The failure of TEA, TPA, and TBA packing to exhibit comparable, if not better, retention than TMA might originate with thermal decomposition of the R_4N^+ pillars and collapse of the montmorillonite layers to a H^+ or NH_4^+ exchanged form. Thermal instability of tailored montmorillonite was seen as excessive column bleed for TEA, TPA, and TBA packings and corresponded with decreases in retention times. In contrast, retention behavior for the TMA phase was unaffected by conditioning at temperatures up to 200°C. Estimated upper temperature limits for conditioning columns without degradation were: TEA, 180°C; TPA, 160°C; and TBA, 130°C. Previously, comparably tailored montmorillonites were shown to undergo decomposition to alkenes, olefins, and alkanes [13] lending credence to the concept of a collapsed interlamellar region for TEA, TPA, and TBA.
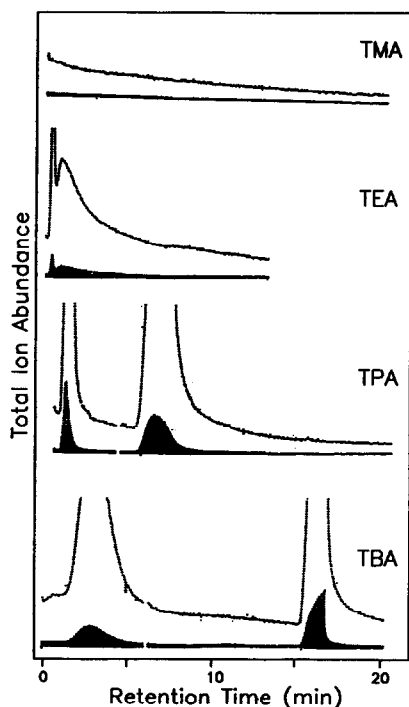
Fig. 4. Total ion chromatograms from GC–MS analysis of thermal decomposition products from tetraalkylammonium exchanged montmorillonites.

The total ion chromatograms (TIC) from GC–MS analysis of gases from heated TMA, TEA, TPA, and TBA packings are shown in Fig. 4. Thermal decomposition of TMA was not observed in the TIC which was essentially free of any detectable components. In contrast, TICs for TEA, TPA, and TBA showed large amounts of components in simple chromatograms. In every instance, the peak eluting second in the TIC (retention times of 2.64, 7.16, and 16.96 min for TEA, TPA, and TBA, respectively) was identified as R_3N, presumably derived from R_4N^+. The first peak in each TIC was identified as a bromine substituted hydrocarbon from the R branch of the particular ammonium cation R_4N^+, namely RBr. Mass spectra were matched favorably to catalogued mass spectra [14] and retention times were checked with authentic standards.

Reactions of tetraalkylammonium cations have been reported [11,12,15,16] and could occur via a halide substitution reaction (eqn. 1) or through a Hofmann elimination (eqn. 2):

$$\overset{\ominus}{X}\diagdown\underset{|}{\overset{\overset{R'}{|}}{C}}-\overset{\oplus}{N}R_3 \longrightarrow R'CH_2-X + :NR_3 \tag{1}$$

$$(2)$$

A substitution in the interlamellar region would require a halide anion, the nucleophile, to substitute for the leaving group, the free amine (II), as shown in eqn. 3:

$$(3)$$

The products of this reaction, I and II, were consistent with the GC–MS findings (Fig. 4) and could originate with treatment of clays with bromide and iodide salts (*i.e.* $R_4N^+Br^-$). The exception, TMA, was introduced as the chloride salt and differences may be associated with a lower nucleophilic strength of Cl^- *versus* Br^-. This possibility was examined with GC–MS studies on decomposition of TMA^+Br^- and TMA^+I^- salts. Small levels of methylhalides were observed and trimethylamine was not detected. This suggested that an elimination mechanism and not nucleophilic attack caused decomposition of the tailoring agent. A reservoir of X^- in the interlamellar region was unexpected and could arise from excess tailoring salt not washed from the montmorillonite.

　　Consequences from thermal degradation of tailoring agent will leave the clay with H^+ in place of R_4H^+ and adsorbate molecules would be sterically blocked from entering the interlamellar region. Thus, the chromatographic properties of the decomposed tailored montmorillonites should resemble those for untailored material as was observed in Figs. 1–3. The findings suggest that tailored montmorillonites undergo degradation through an adaptation of a Hofmann elimination [17–19]; an exact proof is presently impossible since products from a halide substitution and an elimination reaction will be the same.

　　A point that supports a Hofmann elimination is the availability of basic reactant sites on clays. The Al–O octahedrally coordinated layer framework contains two coordinated hydroxyl groups for each Al–O octahedron. These hydroxyl groups protrude into the hexagonal holes created by the Si–O tetrahedra of the outermost layer. The hydrogens on these Al–OH groups vary in acidity due to uneven distribution of charge density, degree of isomorphic substitution of metal cations, and the ratio of dioctahedral to trioctahedral sites in the Al–O layer. Consequently, protons from the OH group become delocalized and migrate to neighboring OH groups forming OH_2^+ and loss of water occurs. The remaining oxide, O^-, then coordinates with a vacant Al site [20] as shown (eqn. 4):

$$(4)$$

Dehydroxylation has been recognized for inorganic cation clays [21,22] and is promoted by low humidities and high temperatures as would be experienced in a purified nitrogen stream of a GC column. The temperatures needed to promote dehydroxylation are large (250–700°C) relative to GC elution temperatures with the organic ammonium pillars. Another factor that promotes dehydroxylation is interlamellar dimensions and in general, dehydration rates increase with increases in the interlamellar distance. Organoammonium ions may be expected to dehydroxylate and decompose at relatively low temperatures (130–180°C) since escape routes for water molecules will be enhanced with organoammonium montmorillonites.

The basic nature of the clay interlamellar region was probed with the thermal instability of two tailoring agents each without β-hydrogens. A column prepared with a tailoring agent of high pK_a, 1,4-diazabicyclo[2.2.2]octane · 2H$^+$ (DABCO) with a first pK_a of 8.6 exhibited stable retention properties. However, a column prepared with pyrazines (pK_a = 0.65) was very unstable. Neither could decompose through a β-elimination indicating the presence of a reasonably basic site on the clay surface.

The last consideration for bimolecular eliminations is the generation of alkenes rather than RBr as observed in the GC–MS analyses; a subsequent hydrobromination addition to the alkene would have to occur with Hofmann eliminations. Hydrobromination of alkenes in montmorillonites or related materials is unreported and this final step of the thermal decomposition must be regarded as problematic; however, proton additions to alkenes to produce carbocations are known [23] for DABCO-montmorillonite.

In summary, a principle argument against a substitution mechanism is that despite the availability of a halide ion and the similarity of :N(CH$_3$)$_3$ and :N(CH$_2$CH$_3$)$_3$ as leaving groups, decomposition of TMA did not occur under these conditions. If substitution was the degradation mechanism, then the TMA clay should have undergone a thermal decomposition to free amine and halogenated alkane.

Significance for GSC stationary phases

Few reports on chromatographic properties of alkylamine salts as modifying agents for montmorillonite could be found with the exception of the early chromatographic studies with long chained amines from the 1950s and early 1960s. A commercial material based on dimethyldioctadecylammonium clay is available as a packing under the trade name Bentone-34 and has a recommended upper temperature limit of 150°C. Since Bentone-34 has hydrogens on two β-carbons, decomposition reactions as observed with TEA, TPA and TBA should be observed chromatographically as a declining drift in retention times with prolonged exposure to high temperatures and as elution of free amines in decomposition vapors released from packing at 200°C. Instability in retention times was noted but not systematically documented. However, the GC–MS analysis of decomposition vapors for Bentone-34 produced six major and *ca.* seven minor constituents that were detected and were identified with mass spectra as alkanes and alkenes with carbon numbers greater than 16. Identifications based upon manual interpretation and comparisons to data bases included: hexadecene, heptadecane, octadecane, dodecene, and tetradecene. This supported the general concept that instability in such packings is related to the tailoring agent and is consistent with a Hofmann elimination via a proton on a β-carbon with base promotion from the clay surface.

CONCLUSIONS

No comparable reports on chromatographic retention of alkylammonium modified montmorillonites exist with the exception of the early chromatographic studies with long-chained amines from the 1950s and early 1960s. Findings here are helpful in rationalizing the upper temperature limit and column instability of a commercially available dimethyldioctadecyl-ammonium clay, Bentone-34. Evidently the Bentone 34 also experienced thermal degradation consistent with the findings from R_4N^+-montmorillonites. Should elimination reactions dominate the cause for thermal instability in such tailoring agents, the existence of β-hydrogens portends poor thermal properties for all such tailoring agents. Only agents in which there are no β-hydrogens should be viewed as viable tailoring agents with packings at elevated temperatures.

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