

Gas chromatographic retention properties of organoammonium exchanged montmorillonites

II. $\text{CH}_3\text{N}^+\text{H}_3$, $(\text{CH}_3)_4\text{N}^+$, $(\text{CH}_3)_3\text{N}^+\text{CH}_2\text{C}_6\text{H}_5$ and 1,4-diazabicyclo[2.2.2]octane $\cdot 2\text{H}^+$

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ABSTRACT

The gas chromatographic retention properties of four organoammonium tailored montmorillonites were characterized using 68 probe molecules. The retention patterns favored a steric model in which retention was governed by three parameters: adsorbate dimensions and orientation, interlamellar plate separation distance, and inter-cation volumes in the interlamellar region. Tailored montmorillonites are limited in steric selectivity at large interlamellar plate distances by swelling and acceptance of oversized molecules.

INTRODUCTION

Tetramethylammonium exchanged montmorillonite showed gas chromatographic selectivity implicative of steric mechanisms in retention and excellent thermal stability from ambient to 200°C. In contrast, the tetraethyl- to tetrabutylammonium montmorillonites were thermally unstable [1]. When heated to temperatures above 100°C, these packings decomposed to corresponding free amines and halogenated alkanes. A central factor believed responsible for this thermal instability was acidic hydrogens located β to the nitrogen rendering the cation susceptible to an elimination reaction. Thus, attempts to probe retention properties of and construct retention models for organoammonium tailored montmorillonites were thwarted. In this report, organoammonium cations *without β -hydrogens* were evaluated in order to examine an anticipated relationship between interlamellar distance in modified montmorillonite and retention in gas chromatography (GC). This was accomplished using 68 probe compounds comprising six chemical classes and four tailoring agents. A preliminary model of retention in tailored montmorillonites includes interlamellar distance and cation volumes within the interlamellar region.

EXPERIMENTAL

Details of preparation of columns, retention measurements, and data reduction were given in the preceding article [1]. The tailoring agents used in the current work were methylamine · HCl (MA), tetramethylammonium chloride (TMA), benzyltrimethylammonium iodide (BTMA) and 1,4-diazabicyclo[2.2.2]octane · 2 HCl (DABCO) and the probe compounds are listed in Table I. All compounds were obtained in the highest quality readily available and generally were reagent or analytical grade.

Retention was expressed in terms of capacity factor (k') or corrected retention time (t'_r) as conventionally defined since retention in the tailored montmorillonite compounds was a mixture of partition, adsorption, and steric sieving. However, control columns were used to delineate trends in retention to determine relative importance of the steric component. A column temperature program was used to simplify data collection since small differences in structures caused large differences in elution

TABLE I
RETENTION TIMES FOR PROBE COMPOUNDS ON TAILORED CLAY COLUMNS

| Compound | Column | | | |
|--------------------------------------|--------|--------|--------|--------|
| | MA | TMA | BTMA | DABCO |
| <i>Alkanes</i> | | | | |
| Pentane | 0.758 | 0.591 | 0.740 | 0.676 |
| Hexane | 7.404 | 13.070 | 7.821 | 0.894 |
| Heptane | 11.895 | 18.041 | 13.551 | 1.356 |
| Octane | 16.646 | 22.323 | 17.014 | 2.438 |
| Nonane | 20.843 | 26.680 | 20.549 | 10.035 |
| Dodecane | 30.923 | | | 18.167 |
| 2,2-Dimethylbutane | 0.592 | 0.550 | 0.746 | 0.719 |
| 2,3-Dimethylbutane | 0.599 | 0.594 | 0.741 | 0.799 |
| 2-Methylpentane | 0.604 | 0.646 | 0.767 | 0.806 |
| 3-Methylpentane | 0.604 | 0.636 | 0.816 | 0.839 |
| Isooctane | 1.701 | 1.048 | 10.005 | 1.255 |
| <i>Alkenes and alkynes</i> | | | | |
| 1-Hexene | 6.400 | 14.588 | 10.870 | 0.878 |
| <i>cis</i> -2-Hexene | 5.213 | 8.548 | 9.448 | 0.966 |
| <i>trans</i> -2-Hexene | 6.988 | 15.059 | 11.233 | 1.046 |
| 1-Hexyne | 9.577 | 13.371 | 12.626 | 1.151 |
| <i>Cycloalkanes and cycloalkenes</i> | | | | |
| Cyclopentane | 0.601 | 4.029 | 0.749 | 0.782 |
| Cyclohexane | 1.377 | 4.162 | 7.201 | 1.103 |
| Cyclohexene | 2.727 | 2.556 | 9.681 | 1.224 |
| Methylcyclopentane | 1.818 | 6.209 | 5.600 | 0.968 |
| Methylcyclohexane | 3.956 | 7.545 | 9.760 | 1.466 |
| 1,3-Cyclohexadiene | 4.459 | 2.464 | 13.306 | 6.600 |
| 1,4-Cyclohexadiene | 5.383 | 3.799 | 16.545 | 12.011 |
| 1-Methyl-1,4-cyclo-hexadiene | 10.534 | 6.864 | 14.299 | 11.924 |
| <i>cis</i> -Decalin | 10.600 | 11.689 | 21.230 | 13.538 |
| <i>trans</i> -Decalin | 14.600 | 20.625 | 21.614 | 13.780 |
| Dicyclohexyl | 21.178 | 26.778 | 28.087 | 19.167 |

TABLE I (continued)

| Compound | Column | | | |
|---|--------|--------|--------|--------|
| | MA | TMA | BTMA | DABCO |
| <i>Aromatics</i> | | | | |
| Benzene | 6.266 | 6.301 | 19.495 | 12.600 |
| Toluene | 10.196 | 6.138 | 17.381 | 11.384 |
| <i>o</i> -Xylene | 13.758 | 8.003 | 11.731 | 6.592 |
| <i>m</i> -Xylene | 15.013 | 8.931 | 16.754 | 12.281 |
| <i>p</i> -Xylene | 16.225 | 17.257 | 20.445 | 14.952 |
| Ethylbenzene | 14.399 | 9.745 | 20.528 | 14.284 |
| <i>n</i> -Propylbenzene | 18.201 | 14.406 | 24.919 | 17.019 |
| Isopropylbenzene | 16.721 | 11.980 | 22.180 | 14.276 |
| <i>n</i> -Butylbenzene | 22.732 | 18.956 | 28.401 | 19.454 |
| Isobutylbenzene | 20.716 | 16.551 | 26.659 | 18.154 |
| <i>sec</i> -Butylbenzene | 20.403 | 15.701 | 25.141 | 16.938 |
| <i>tert</i> -Butylbenzene | 12.400 | 11.578 | 22.463 | 14.056 |
| Di- <i>tert</i> -butylbenzene | 21.000 | 23.768 | | 18.950 |
| 1,3,5-Trimethylbenzene | 22.443 | 14.522 | 11.970 | 6.882 |
| 1,2,3-Trimethylbenzene | 21.711 | 14.756 | 13.496 | 8.351 |
| 1,2,4-Trimethylbenzene | 21.804 | 14.753 | 15.781 | 11.474 |
| <i>Polycyclic aromatic hydrocarbons</i> | | | | |
| Biphenyl | 31.765 | 30.233 | | |
| Naphthalene | 23.416 | 18.885 | 24.513 | |
| Fluorene | 34.128 | 30.049 | 26.786 | |
| <i>Halogenated alkanes</i> | | | | |
| Methylene chloride | 6.400 | 8.200 | 0.763 | 0.739 |
| Chloroform | 7.894 | 10.788 | 0.751 | 1.055 |
| Carbon tetrachloride | 0.796 | 3.400 | 0.768 | 1.134 |
| 1-Chlorobutane | 11.453 | 15.070 | 11.885 | 1.242 |
| 2-Chlorobutane | 7.698 | 9.967 | 8.989 | 0.988 |
| 1-Bromobutane | 13.356 | 17.523 | 14.458 | 2.518 |
| 2-Bromobutane | 8.000 | 11.597 | 11.309 | 1.449 |
| <i>Halogenated benzenes</i> | | | | |
| Chlorobenzene | 12.239 | 9.276 | 21.400 | 18.528 |
| <i>o</i> -Dichlorobenzene | 21.474 | 12.193 | 15.832 | 12.768 |
| <i>m</i> -Dichlorobenzene | 20.888 | 13.228 | 22.064 | 18.981 |
| <i>p</i> -Dichlorobenzene | 21.912 | 17.050 | 27.523 | |
| Fluorobenzene | 6.901 | 6.797 | 20.848 | 14.268 |
| <i>o</i> -Difluorobenzene | 14.143 | 6.134 | 17.162 | 9.893 |
| <i>m</i> -Difluorobenzene | 11.896 | 5.278 | 16.759 | 9.842 |
| <i>p</i> -Difluorobenzene | 14.264 | 10.926 | 24.934 | 17.800 |
| 1,2,4-Trifluorobenzene | 21.202 | 10.471 | 18.200 | 10.148 |
| 1,2,4,5-Tetrafluorobenzene | 28.144 | 15.655 | 16.900 | 7.723 |
| 1,2,3,5-Tetrafluorobenzene | 26.499 | 14.084 | 7.800 | 1.076 |
| 1,2,3,4-Tetrafluorobenzene | 28.394 | 15.879 | 10.906 | 1.501 |
| Perfluorobenzene | 40.000 | 25.400 | 15.000 | 0.940 |
| a,a,a-Trifluorotoluene | 7.562 | 6.810 | 17.591 | 10.974 |
| Bromobenzene | 14.509 | 11.214 | 23.673 | 20.063 |
| <i>Solvent</i> | | | | |
| Carbon disulfide | 0.617 | 0.623 | 0.799 | 0.746 |

at fixed temperatures on the montmorillonite columns. The large number of probe compounds necessitated the simplicity offered by a temperature program.

RESULTS AND DISCUSSION

Thermal stability and reproducibility

The four quaternary ammonium cations including MA, TMA, BTMA, and DABCO exhibited thermal stability with upper temperature limits of 220°C (MA and TMA); 180°C (BTMA); and 140–150°C (DABCO). Unfortunately, this upper temperature limit effectively restricted studies to molecules no larger than *ca.* 150 a.m.u. Nonetheless, columns could be made reproducibly from fresh batches of sodium montmorillonite to within 10% relative standard deviation on relative retentions. The columns exhibited low chromatographic efficiency [1] in current mechanical configurations. Finally, the tailored montmorillonites showed chromatographic retention patterns diametrically opposed to those observed with general (non-specific partition) interactions and with gas–solid adsorption in control columns [1].

TABLE II

ln *k'* FOR PROBE COMPOUNDS ON MODIFIED CLAY PHASES AND CONTROL COLUMNS

The largest value for ln *k'* is given in italics in each compound series and for each column. Values are emphasized where isomers exhibit identical retention within a series.

| Compound | Column ^a | | | | | | | | |
|---------------------------------------|---------------------|---------|-----|-----|-----|-----|-----|------|----------------|
| | OV-101 | Na-Clay | TBA | TPA | TEA | MA | TMA | BTMA | DABCO |
| <i>Dimethylbenzenes</i> | | | | | | | | | |
| <i>o</i> -Xylene | 5.6 | 4.4 | 5.3 | 5.5 | 5.9 | 6.2 | 5.9 | 6.2 | 5.6 |
| <i>m</i> -Xylene | 5.4 | 4.3 | 5.2 | 5.4 | 5.8 | 6.3 | 6.1 | 6.6 | 6.3 |
| <i>p</i> -Xylene | 5.4 | 4.3 | 5.2 | 5.4 | 5.9 | 6.4 | 6.7 | 6.8 | 6.5 |
| <i>Dichlorobenzenes</i> | | | | | | | | | |
| <i>o</i> -Dichlorobenzene | 6.1 | 5.0 | 6.1 | 6.3 | 6.2 | 6.7 | 6.4 | 6.6 | 6.4 |
| <i>m</i> -Dichlorobenzene | 6.0 | 4.9 | 5.9 | 6.1 | 6.2 | 6.6 | 6.5 | 6.9 | 6.8 |
| <i>p</i> -Dichlorobenzene | 6.0 | 4.9 | 6.1 | 5.8 | 6.4 | 6.7 | 6.7 | 7.1 | + ^d |
| <i>Trimethylbenzenes</i> ^b | | | | | | | | | |
| 1,3,5-Trimethylbenzene | 5.9 | 4.8 | 5.6 | 5.8 | 5.9 | 6.7 | 6.6 | 6.3 | 5.7 |
| 1,2,3-Trimethylbenzene | | | | | | 6.7 | 6.6 | 6.4 | 5.9 |
| 1,2,4-Trimethylbenzene | | | | | | 6.7 | 6.6 | 6.6 | 6.2 |
| <i>Decalins</i> ^c | | | | | | | | | |
| <i>cis</i> -Decalin | | | | | | 5.9 | 6.3 | 6.9 | 6.4 |
| <i>trans</i> -Decalin | | | | | | 6.3 | 6.9 | 6.9 | 6.4 |

^a Findings for columns of ammonium, piperazine, pyrazine, and hexamethylenediamine were comparable to the sodium clay and OV-101 in magnitude and order of elution.

^b 1,2,3-Isomer yielded greatest ln *k'* values on columns of RSL-150, piperazine, pyrazine, and hexamethylenediamine.

^c *cis*-Decalin yielded greatest ln *k'* values on columns of RSL-150, piperazine, pyrazine, and hexamethylenediamine.

^d Indicates a peak that was strongly retained and flattened in shape so that a retention time measurement was problematic.

TABLE III

ln k' FOR FLUORINATED BENZENES AND NON-AROMATIC RING COMPOUNDS ON TAILORED CLAY COLUMNS

The elution order is ranked in bold numbers adjacent to the ln k' values.

| Compound | Column | | | | |
|------------------------------------|---------------|---------------|---------------|---------------|---------------|
| | RSL-150 | MA | TMA | BTMA | DABCO |
| <i>Fluorinated benzenes</i> | | | | | |
| Fluorobenzene | 1.43 6 | 5.5 1 | 5.8 3 | 6.8 6 | 6.5 6 |
| <i>m</i> -Difluorobenzene | 1.40 4 | 6.1 2 | 5.5 1 | 6.6 4 | 6.1 5 |
| <i>o</i> -Difluorobenzene | 1.58 9 | 6.2 3 | 5.7 2 | 6.6 4 | 6.1 5 |
| <i>p</i> -Difluorobenzene | 1.46 7 | 6.3 4 | 6.3 5 | 7.0 7 | 6.7 7 |
| 1,2,4-Trifluorobenzene | 1.42 5 | 6.7 5 | 6.2 4 | 6.7 5 | 6.1 5 |
| 1,2,3,5-Tetrafluorobenzene | 1.30 2 | 6.9 6 | 6.5 6 | 5.8 1 | 3.3 2 |
| 1,2,4,5-Tetrafluorobenzene | 1.38 3 | 7.0 7 | 6.6 7 | 6.6 4 | 5.8 4 |
| 1,2,3,4-Tetrafluorobenzene | 1.48 8 | 7.0 8 | 6.6 8 | 6.2 2 | 3.8 3 |
| Perfluorobenzene | 1.20 1 | 7.3 9 | 7.1 9 | 6.5 3 | 3.0 1 |
| <i>Non-aromatic ring compounds</i> | | | | | |
| Cyclopentane | 0.13 1 | 1.44 1 | 5.20 4 | 2.43 1 | 2.56 1 |
| Cyclohexane | 0.33 3 | 3.52 2 | 5.24 5 | 5.73 3 | 3.33 3 |
| Methylcyclopentane | 0.24 2 | 3.93 3 | 5.67 6 | 5.46 2 | 3.08 2 |
| Methylcyclohexane | 0.55 7 | 4.89 5 | 5.88 8 | 6.06 5 | 3.81 5 |
| Cyclohexene | 0.38 5 | 4.45 4 | 4.68 2 | 6.05 4 | 3.52 4 |
| 1,3-Cyclohexadiene | 0.35 4 | 5.02 6 | 4.64 1 | 6.38 6 | 5.65 6 |
| 1,4-Cyclohexadiene | 0.49 6 | 5.23 7 | 5.14 3 | 6.61 8 | 6.29 8 |
| 1-Methyl-1,4-cyclohexadiene | 0.84 8 | 5.95 8 | 5.78 7 | 6.46 7 | 6.28 7 |

Retention properties

Retention times for the probe analytes on the four columns are tabulated in Table I and selected results for k' from all columns including controls are shown in Tables II and III. Both k' and elution orders for disubstituted benzenes on tailored montmorillonite *versus* control columns (Table II) suggested that retention was due not only to non-specific partitioning. For example, the *para* isomer of disubstituted benzenes ($C_6H_4X_2$, where X = Cl and CH_3) showed retention times longer than the *ortho*- and *meta*-isomers on those clay columns which were thermally stable. In contrast, the *para*-isomer eluted first from non-polar OV-101 and sodium or ammonium control columns and on clay columns believed to decompose to ammonium forms [1]. Inversions of trends were also observed with the trimethylbenzenes (Table II) and comparisons within clay phases is suggestive of subtle effects (*vide infra*). A final example of retention inversion was the geometric isomers of decalin. *cis*-Decalin was retained longer than *trans*-decalin on non-polar and control columns while the reverse was observed for MA and TMA (Table II). These isomers had comparable retention times on BTMA and DABCO columns indicating an absence of steric selectivity.

Specific patterns in retention and energetics of intercalation

Plots of t'_r for 68 probe compounds and four tailored clays are shown in Fig. 1 and can be compared to the retention of *n*-alkanes and *n*-alkylbenzenes on control

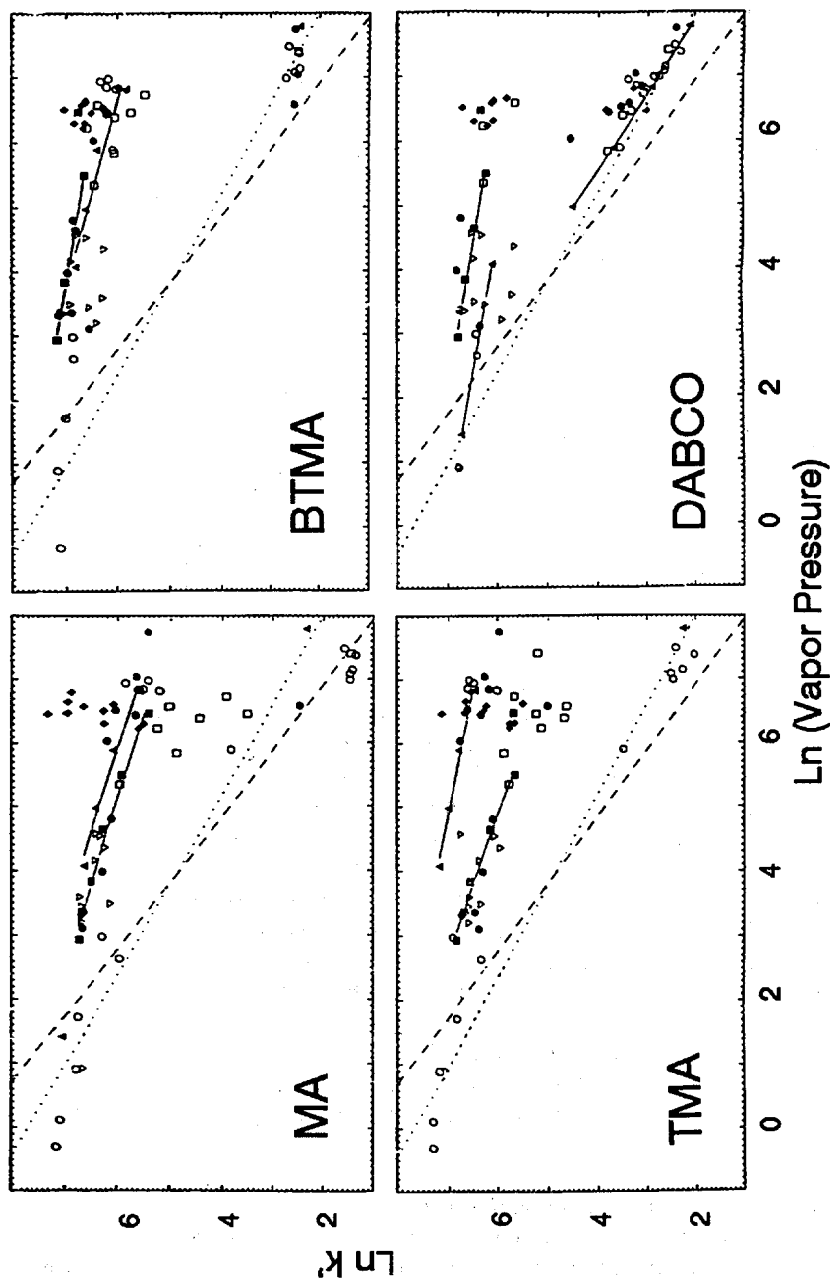


Fig. 1. Plots of $\ln k'$ versus \ln vapor pressure (at 75°C) for organic compounds on MA, TMA, BTMA, and DABCO tailored montmorillonite. The dashed line depicts the retention of *n*-alkylbenzenes on control columns. The dotted line depicts the retention of *n*-alkanes on control columns. Legend: \blacktriangle = *n*-alkanes, \blacksquare = *n*-alkylbenzenes, \blacklozenge = fluorobenzenes, \square = non-aromatics, \bullet = halogenated hydrocarbons, ∇ = polysubstituted benzenes.

columns. Adsorbate retention was generally greater with the tailored clays than on the control columns and the *n*-alkanes and *n*-alkylbenzenes were particularly affected. Since this increase could not be attributed to dipole-induced dipole interactions, hydrogen bonding, or liquid phase partitioning on the coated clay surface, adsorbates evidently were migrating into the interlamellar plate region created by the cations where known distances are [2]: NH_4 , 1.0–1.2 Å; MA, 2.1–2.6 Å; TMA, 4.1 Å; DABCO, 5.4 Å. These distances represent plates at low potential energy and the distances can be increased, if justified by energies, through imbibing compounds. For example, a benzene ring and an alkane group are 3.7 Å and 4.0 Å thick, respectively and MA must expand the interlamellar region if a molecule is to enter this region and undergo retention. The TMA tailored clay could accept, without expansion, the *n*-alkanes, *n*-alkylbenzenes, and cyclopentane. Nearly all other compounds, in particular the branched methylalkanes and neo-alkanes, necessitate expansion to 5.9 Å. Ammonium and sodium forms with interlamellar distances of 1.0–1.2 Å and *ca.* 0 Å respectively showed no retention while the MA and TMA forms did exhibit retention. Thus, plate distances of 1.2–2.1 Å represent a region of transition from no expansion to partial expansion of the clay layers or plates.

Binding energies between clay plates arise from dispersion and electrostatic cohesion and dispersion forces may be substantially due to the large surface areas of adjacent sheets. Electrostatic cohesion forces exist due to the Coulombic interactions between positive charged counterions and negative charged clay sheets. When sheets are in close proximity (Na^+ and NH_4^+ forms) these energies are comparatively large. However, when sheets or plates are separated by 5.5 Å (DABCO) or 4.1 Å (TMA), the electrostatic forces are relatively weak. In order to retain adsorbate molecules which are larger than the dimensions of the interlamellar region, the plates must be separated and seemingly occurred with TMA and DABCO. Adsorption of comparable compounds on Na^+ and NH_4^+ forms with strong plate interactions might be anticipated as unlikely. Thus, space in sodium and ammonium forms of the clay should be unavailable to probe molecules and experimentally these inorganic montmorillonite showed low retention. In instances where the tailoring agent was suspected of thermal degradation to ammonium forms, comparable behavior was observed. In contrast, oversized molecules were retained by the MA and TMA organoammonium tailored clays indicating lessened inter-plate strengths of attraction.

These dynamic GC measurements have static sorption precedent [3] where the sorption/desorption curves with MA and TMA were observed as hysteresis loops and the extent of separation between loops was indicative of further swelling that the clay experiences in intercalating a molecule. Except for water, all analytes created hysteresis in sorption–desorption lines with MA and this was pronounced with bulky compounds such as cyclohexane and isoalkanes. This remarkable agreement supports the interpretation of these GC measurements and the conclusion that intercalation of guest molecules by the tailored clays was occurring.

Comparisons of tailored montmorillonites

Of the four tailored clays that showed chromatographic retention, the MA and TMA had permanent plate separations less than DABCO and BTMA. Correspondingly, the MA and TMA columns displayed behavior different from that for DABCO and BTMA columns and this difference was not simply an augmentation of the trends

seen with MA and TMA columns. For example, the MA and TMA columns retained *n*-alkanes to a larger extent than the aromatic hydrocarbons while this trend was reversed with DABCO and BTMA columns (Fig. 1). A reversal was also observed with the two sets of chromatographic adsorbents (MA and TMA *versus* BTMA and DABCO) in the elution order for *cis*- and *trans*-isomers of decalin.

The differences in elution orders for the two pairs (MA and TMA *versus* DABCO and BTMA) can be rationalized using models for the interlamellar pillars. The original consideration was expansion of the distance vertical to the plates through large and rigid molecules. However, charge densities of the clay affect cation exchange and the extent and quantity of pillar formation. Cation-exchange capacities (CEC) and charge densities for batches of montmorillonites are unique within a range. In tailored clays, the charge density directly governs the average area per cation permitted in the interlamellar region and thus will control the average lateral free or available distance between cation sites. Depending on the lateral size of a fixed pillar cation, a lateral distance between ions will be empty and will be unique to a clay and a cation. Montmorillonites, with DABCO as the exchanged cation, have average free distances of *ca.* 6 Å [2]. In contrast, for the same clay, MA and TMA must have lateral distances > 6 Å. Thus, for the retention of cyclopentane, benzene, cyclohexane, and cyclopentane on DABCO clay, the molecules had to assume an orientation normal to the plate surface (Fig. 2) and these dimensions favored retention of the aromatic molecules. These aromatic compounds could also be accommodated with MA and TMA at the expense of energy to swell the interlamellar distance. The cyclic guest analytes assumed a flat position which is reasonable considering charge densities. Since BTMA showed retention properties much like DABCO, the expectation is that BTMA should have an interlamellar region much like DABCO.

The *n*-alkanes were retained on all columns except DABCO. Some swelling in MA was needed to physically allow penetration of alkanes into the region in a zigzag manner with the chain parallel to the plate. Swelling with TMA is not needed for alkanes to enter the interlamellar region and once the alkanes are intercalated in MA and TMA columns, close contact between the adsorbate and the clay surfaces should promote maximum interactions via Van der Waals forces. The BTMA column also retained the alkanes significantly and molecular dimensions suggest that perpendicular slots were just large enough to accept the adsorbate for intercalation. This close contact promoted Van der Waals attractions. In contrast to the trends for MA, TMA, and BTMA, alkanes of all sizes until nonane were not appreciably retained on DABCO. Presumably, the distances between cations in DABCO were large enough that the alkanes were capable of entering and leaving the interlamellar region without geometric constraints promoting strong Van der Waal interactions.

Support for this model of combined lateral and vertical parameters in tailored montmorillonites arises from the retention behavior of branched alkanes. All four structural isomers of *n*-hexane eluted early on every column indicating little or no retention and correspondingly, no penetration into the interlamellar space. The MA and TMA columns exhibited low retention for all branched alkanes *versus* that for DABCO and BTMA columns. Isooctane was not retained by MA and TMA but was retained by BTMA and may be a gauge of a certain critical size. Certainly the cavity in DABCO is large enough to intercalate a *tert.*-butyl group and perhaps large enough not to experience significant interactions between guest and tailoring agent.

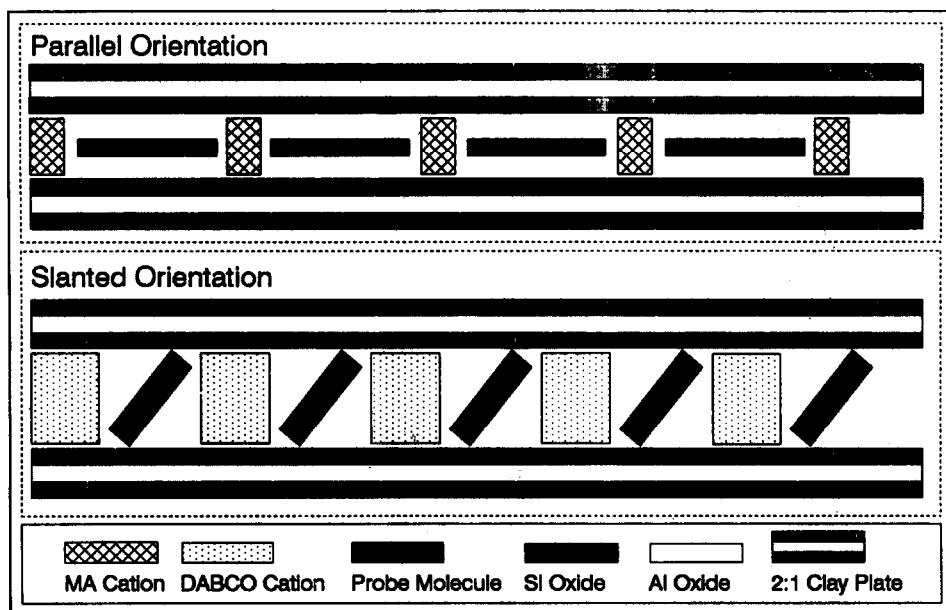


Fig. 2. Schematic of insertion of molecules into interlamellar region of tailored montmorillonite for a small (MA) and large (DABCO) cation.

The *tert.*-butyl group was active in selective retention for the alkylaromatic hydrocarbons. Retention of *tert.*-butylbenzene was low for MA and TMA but was comparable in retention to the corresponding *n*-alkylbenzenes for DABCO and BTMA. Olefins were retained much like their *n*-alkane counterparts in all columns.

The *cis*- and *trans*-isomers of decalin also seemed to be sensitive indicators of the differences in lateral and vertical spaces in the interlamellar region (Table II). Retention times for *cis*-decalin were 10.6, 11.7, 21.2, and 13.5 min for MA, TMA, BTMA, and DABCO, respectively. In contrast and under identical conditions, respective times for *trans*-decalin were 14.6, 20.6, 21.6, and 13.7 min. Greater expansion of the plates was required for the *cis*-isomer than for the *trans*-isomer and was evident in the retention times with MA and TMA where plate expansion would be costly in electrostatic energy. The difference in retention times was fully 9 min on TMA relative to MA despite similar physical properties for the isomers. On a non-polar column based on solubility but non-specific, dispersion interactions, the retention order was reversed to *trans* before *cis* and retention times showed minor differences. The retention of the decalins on BTMA and DABCO was significant compared to MA and TMA but no selectivity for the geometric isomers was exhibited. The dimensions of cavities for the interlamellar region in BTMA and DABCO tailored clays were sufficiently large to permit unobstructed access by each isomer with the ring intercalated perpendicular to the plates. Moreover, in this orientation, the limiting dimensions of the isomers were identical (Table II).

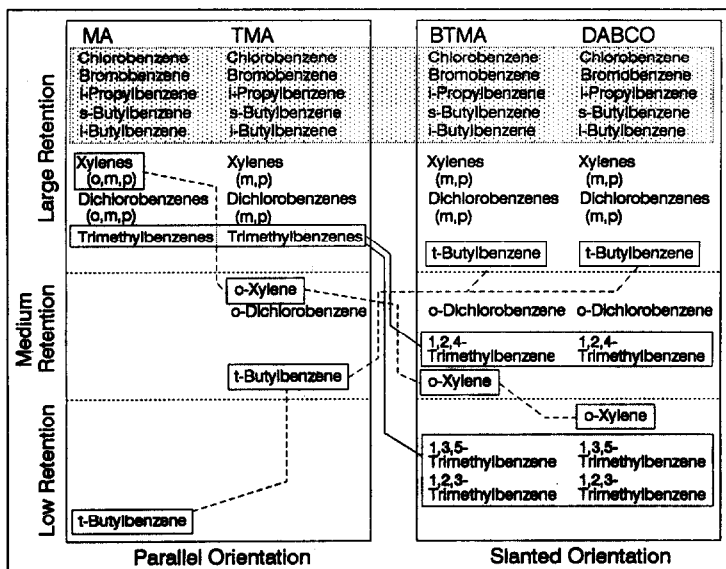


Fig. 3. Trends in retention for four columns of tailored montmorillonites. The compounds in the shaded box were unaffected by changes in cation. The trends suggest differences in orientation of intercalation or orientation as designated.

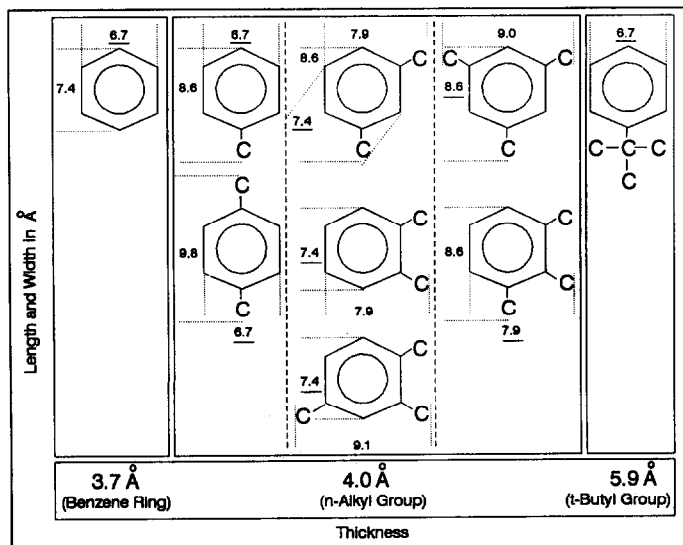


Fig. 4. Calculated molecular length, width and thickness for substituted benzenes from Barrer [5]. The underlined dimension represents the smallest and controlling dimensions for intercalation.

Retention for alkyl and fluorine substituted benzenes

Originally, the substituted benzenes were considered molecular probes of the steric requirements associated with the substituent group. Retention can be divided into three rows or zones per Fig. 3. The top row was for the substituted benzenes that were retained as well as corresponding *n*-alkylbenzenes. The bottom row was for those substituted benzenes that did not show intercalation or retention. Intermediate behavior is shown in a middle row. These results can be discussed through an evaluation of calculated dimensions of the various guest molecules as shown in Fig. 4.

The only molecule of the alkylated and fluorinated benzenes not retained by the MA and TMA columns was *tert.*-butylbenzene which has a thickness of *ca.* 5.9 Å from the butyl group *versus ca.* 4.2–4.5 Å for an alkane in either zigzag orientation ($\alpha //$ or $\alpha \perp$). The cumene substituent, an isobutyl moiety, and a *sec.*-butyl moiety were of comparable thickness when they underwent intercalation with the chain lengthened and parallel to the montmorillonite surface. The xylenes, dichlorobenzenes, and trimethylbenzenes were intermediate sizes and were all only 4 Å or less in thickness. The MA column behaved ideally in that all of the compounds except *tert.*-butylbenzene were intercalated and retained according to Van der Waals interactions. The TMA column showed retention trends identical to those for MA with slightly improved resolution in xylene and dichlorobenzene isomers. Slightly smaller unoccupied lateral distances in TMA than in MA may have contributed to enhanced interactions and slightly improved resolution.

In contrast to the generally unselective MA and TMA, BTMA and DABCO were selective to size with respect to length and breadth of molecules if not so much to the thickness of compounds. Consequently, *tert.*-butylbenzene was highly retained in comparison to other butylbenzene isomers and cumene. These molecules were essentially benzenes with single substituents and thicknesses of 4.6 Å or less. Trimethylbenzene isomers were remarkably excluded from intercalating on BTMA and DABCO and showed low retention times. The ring width for the 1,2,4-isomer was slightly smaller (7.4 Å) than the other two isomers (7.9 and 8.6 Å) and insertion of molecules into the interlamellar space, with rings perpendicular to the clay plates, was shown to be sensitive to this dimension (Table II). One of the distinguishing features between the adsorbent pairs of MA/TMA and BTMA/DABCO was the overall inversion of retention times between alkanes and aromatic compounds (Fig. 1). For MA and TMA, both classes of molecules can enter the interlamellar region parallel to the stacked layer planes. In this manner, alkanes can undergo favorable Van der Waals interactions and show strong retention on MA and TMA.

Fluorinated aromatic and non-aromatic controls

A series of fluorinated benzenes were used to refine this chromatographic model and the discussion below can be referenced to the relative retention of these compounds on a non-polar RSL-150 capillary column (Table III). The retention of these compounds on the MA columns did not parallel the non-polar column pattern and trends were unequivocal. The highly fluorinated benzenes were highly retained and this was especially evident with the TMA column. The simplest possibility was that the fluorine atoms inductively reduced the π electron density of the aromatic ring and thus allowed the fluorinated benzenes to intercalate in a flat orientation on the MA and TMA columns.

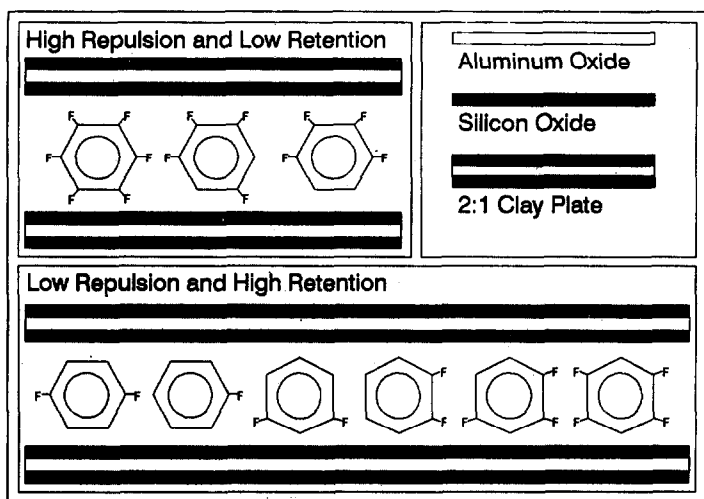


Fig. 5. Model for electrostatic repulsions for fluorinated aromatics in interlamellar layers.

The retention order of these compounds on DABCO columns also did not parallel trends seen in the RSL-150 column or on MA/TMA. In particular, the retention of 1,2,3,4-tetrafluorobenzene, 1,2,3,5-tetrafluorobenzenes, and perfluorobenzene were moderated presumably by vapor pressure and the concept of vertical slots. Fluorinated benzenes that exhibited extremely low retention times *versus* those that were well retained on BTMA or DABCO are depicted in Fig. 5. Those compounds that were retained could intercalate into vertical slots without locating a fluorine atom toward the clay surface. Moreover, those fluorobenzenes that were not retained and likely did not intercalate, were not able to squeeze into a vertical slot without forcing a fluorine atom toward or against the montmorillonite surface. The overall negative charge on the plate surfaces presumably caused Coulombic repulsions and forced an exclusion of those fluorinated benzenes with structures as shown in Fig. 5.

Another analyte series for consideration was the five and six-carbon, non-aromatic rings and retention times for these are shown in Table III. All columns except TMA exhibited trends like those in the non-polar RSL-150 column. That is, non-specific dispersion forces were the effective mechanism of retention and this paralleled simple vapor pressure trends.

The retention behavior of non-aromatic unsaturated rings and halogenated alkanes suggest that the steric model is not complete and a second moderating factor may exist. For example, on MA and TMA, 2-bromobutane, 2-chlorobutane, 1-bromobutane and 1-chlorobutane were retained strongly whereas the four isomers of saturated hexane were not retained. From a strictly steric exclusion perspective, this behavior should not have occurred. The halogenated analytes and the unsaturated rings were the only test compounds with some degree of polarity or high electron density and these aberrations were noted for a limited test set of compounds. Thus, the concept of another controlling parameter for highly polar organic compounds seemed reasonable though not highly developed from these limited results and should be anticipated. The main source of adsorption for non-polar compounds should be attributed to steric considerations with organoammonium tailored montmorillonites.

CONCLUSIONS

The core concept in this model is that of two-dimensional intercalating cavities. Vertical dimensions in the interlamellar region do not suffice alone as a predictor of chromatographic retention or of resolution with tailored montmorillonites in agreement with static models [4]. Retention of non-polar molecules on montmorillonite tailored with organoammonium cations was due to three parameters including the interlamellar distance, the lateral free-volume or distance between exchanged cations, and the CEC and surface area.

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