CHROM. 7998

GAS CHROMATOGRAPHIC BEHAVIOR OF METAL-TRIS(ETHYLENEDI-AMINE) COMPLEX CATION-EXCHANGED MONTMORILLONITES

VERNON J. THIELMANN and JAMES L. McATEE, Jr.

Baylor University, Chemistry Department, Waco, Texas 76703 (U.S.A.)

(First received July 30th, 1974; revised manuscript received October 1st, 1974)

SUMMARY

Gas chromatographic packing material was prepared from the tris(ethylene-diamine) complexes of Cr(III), Co(III) and Cu(II) exchanged on to Na$^+$-montmorillonite. The retention times of the light hydrocarbons (C$_1$–C$_3$) and oxides of nitrogen showed similar increase as the per cent exchange increased from 0 to 100%. Beyond 100%, however, the behavior was different.

From surface area, X-ray diffraction, differential thermal analysis and thermogravimetric analysis (not included in this paper) it was determined that N$_2$O is involved in an adsorption process on the oxygens of the basal surface of the clay, whereas the light hydrocarbons were most probably involved in a sieving separation.

Good separation on some of the light hydrocarbons (C$_1$–C$_5$) was obtained on very short columns at relatively high temperatures and carrier gas flow-rates.

INTRODUCTION

During the past twenty-five years considerable research has been done in the area of utilization of clays and zeolites as supports and microsieves for use in gas–liquid and gas–solid chromatography. In 1957, White[1] reported the use of organo-montmorillonite for chromatographic separations. Hughes *et al.*[2] reported using dimethyldioctadecylammonium-substituted montmorillonite to effect separation of *o*-, *m*-, and *p*-xylenes.
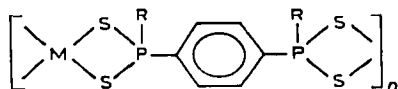
Legate and Johns[3] determined that when using organomontmorillonite systems the separation of polar group compounds was essentially organic–silicate interaction over a range of 40–90°. For non-polar hydrocarbons, however, the best chromatographic separation occurred over the temperature range of 40–70°. This indicated a relationship between the solubility of hydrocarbons and the adsorbed water and their retention times. Above 70° the interaction again appeared to be organic–silicate interaction in nature.

Many others[4–11] reported use of dimethyldioctadecylammonium-substituted clays as gas chromatographic (GC) materials. Taramasso and Veniale[4] carried out the substitution on kaolinite, fire-clay, halloysite, attapulgite, hectorite, nontronites, vermiculites, and montmorillonites. Kiselev *et al.*[10] have also had considerable success

in separation of *o*-, *m*-, and *p*-isomers of terphenyl, phenoxylphenol and nitrophenol when using dimethyldioctadecylammonium montmorillonite as a packing for liquid chromatography.

Moolchandra and Mallik[12] discussed the usage of dimethyldioctadecyl-ammonium attapulgite as a support material for GC. Separation of light hydrocarbons was carried out on the modified attapulgite itself, however most separations were carried out on modified attapulgite with a 10 to 20% (w/w) coating of some other organic material such as Carbowax or squalene.

Another type of complex-substituted clay tried more recently by Delventhal *et al.*[13] contained a coordination polymeric metal complex of Ni(II) and Co(II) with a general formula of

$$\left[\begin{array}{c} \diagup \\ \diagdown \end{array} M \begin{array}{c} S \\ S \end{array} \begin{array}{c} R \\ \mid \\ P \end{array} \bigcirc \begin{array}{c} R \\ \mid \\ P \end{array} \begin{array}{c} S \\ S \end{array} \diagdown \right]_n$$

A 4% (w/w) loading on Chromosorb P was used to give separation on a series of Lewis bases.

The use of zeolite and zeolite-like clays in GC has been studied by several groups[14–19]. Tsitsishvili and Andronikashvili[15] studied the effect of varying the cation on Zeolite X which is a Type III adsorbent. Manara and Taramasso[16,17] studied the GC behavior of hormites (sepiolite and attapulgite) which may be considered Type III adsorbents. They found that O_2, N_2, CO, CH_4 and CO_2 could be separated by running a ballistic type heating program from $-78°$ to $+70°$.

The present paper deals with the development and utilization of cationic exchanged clays which would be intermediate to the dimethyldioctadecylammonium ion substituted clays and the hormite type clays. It was noted in a surface area study carried out by Knudson and McAtee[20] that the d_{001}-spacing of tris(ethylenediamine)-cobalt(III)-montmorillonite had a value of 14.2 Å. This value would be somewhat larger than the hormites (10 Å) but less than the 39 Å for dimethyldioctadecyl-ammonium-montmorillonite. This paper therefore deals with the GC behavior of tris(ethylenediamine) complexes of Co(III), Cr(III) and Cu(II) exchanged on to montmorillonite.

EXPERIMENTAL

The exchanged clays were prepared from Na^+-exchanged, centrifuged, spray-dried Wyoming montmorillonite clay. A 2% suspension in distilled water was prepared in a Waring blender (60°). The appropriate number of milliequivalents of metal-tris(ethylenediamine) exchange salt was dissolved in 250 ml water and then added in small aliquots to the clay suspension with constant stirring. The resulting mixture was then stirred for 15 min and then allowed to stand a minimum of 18 h prior to centrifugation and washing. Each clay was washed a minimum of three times with subsequent centrifugation. The resulting clays were oven dried at 45°. The exchange salts used in this preparation were $Cr(en)_3Cl_3 \cdot 3\frac{1}{2}H_2O$, $Co(en)_3Cl_3 \cdot 3H_2O$ and $Cu(en)_3SO_4$, which were obtained from Ventron (Beverly, Mass., U.S.A.).

The amount of exchange was determined by measuring the amount of cobalt,

chromium or copper (by atomic absorption) remaining in the solution after the initial centrifuging. A Perkin-Elmer Model 403 atomic absorption spectrometer was utilized.

Each clay sample prepared was ground after drying by means of a Weber Bros. Laboratory pulverizing mill. A 0.05-in. screen was used, and to prevent over-pulverizing two-thirds of the beater bars were removed and the speed of the mill was decreased by means of a variable transformer. The grindings were size-fractioned by sieving and the 50–80 mesh fraction was kept for column packing material.

The columns were prepared from Pyrex glass tubing (I.D. 4 mm) bent into a U-shaped tube. The columns were packed by connecting thistle tubes to each side of the column and then slowly pouring the clay into the column as it was being vibrated. An electric vibrating platform (60 cps) was utilized and a high degree of packing reproducibility was obtained. Once filled, the column ends were stoppered with a small piece of glasswool.

The GC data were obtained from a Perkin-Elmer Model 154 vapor fractometer using a thermal conductivity cell. This apparatus was particularly suitable for this investigation as single-bend columns could be utilized with a workable length of 260 cm. Helium was used as carrier gas and flow-rates varied from 10 up to 120 ml/min. Samples were injected with a 1-cc B-D Plastipak Tuberculin syringe with a size 23 stainless-steel needle. Sample sizes varied from 0.05 to 0.40 ml. Reproducibility for injection was $\pm 5\%$. The test samples were air, CH_4, C_2H_6, C_3H_8, N_2O, NO, NO_2, and CO_2. In some of the special short-column work, C_4H_{10} and isobutylene were also utilized.

RESULTS AND DISCUSSION

Study of tris(ethylenediamine)Cr(III)-montmorillonite

The initial and most complete study was carried out on a series of tris(ethylenediamine)Cr(III)-montmorillonites. The difference in the various samples was due to the different amounts of the chromium complex exchanged on to the clay.

Retention times (measured in millimeters on the recorder chart from the point of injection to the maximum peak height) of N_2O versus % $Cr(en)_3^{3+}$ substitution at various column conditions are shown in Fig. 1. It is noted that as the exchange exceeds 100%, the retention times begin to decrease. From surface area, d_{001}-spacing, differential thermal analysis, and thermogravimetric analysis data (not included in this paper), it was determined that the N_2O is involved in an adsorption process on the oxygens of the basal surface of the clay. It is therefore understandable that as excess $Cr(en)_3 \cdot Cl_3$ particles are being adsorbed in the interlamellar clay surface, the clay surface area would thus decrease subsequently, resulting in a lower retention time for N_2O.

Fig. 2 shows retention times of C_2H_6 versus % $Cr(en)_3^{3+}$ substitution at various conditions. Somewhat different from the retention times for N_2O, it is noted that a decrease in retention time does not occur until an exchange of over 125% has been reached. Again, studies not included in this paper indicated that the light hydrocarbons were most probably involved in a sieving separation. Thus, one can account for the decrease not occurring until a higher per cent exchange has been reached due to the fact that at low exchange the controlling dimension would be the vertical d_{001}-spacing of the clay complex. At higher levels of exchange, however, the horizontal
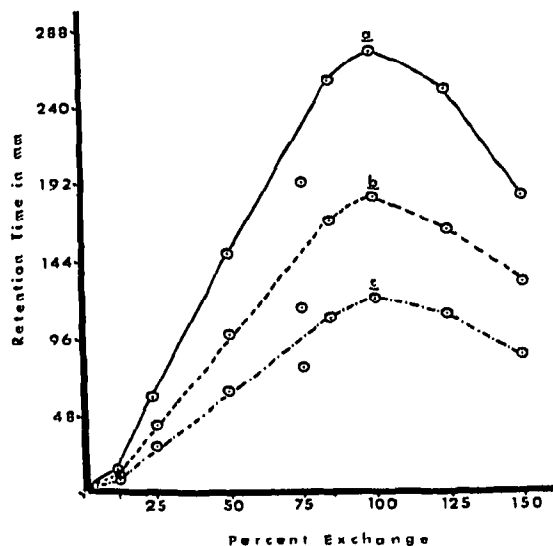
Fig. 1. Retention times of N_2O *versus* % $Cr(en)_3^{3+}$ substitution at (a) 30° and 120 ml/min, (b) 50° and 80 ml/min, and (c) 50° and 120 ml/min obtained with a 110-cm column.
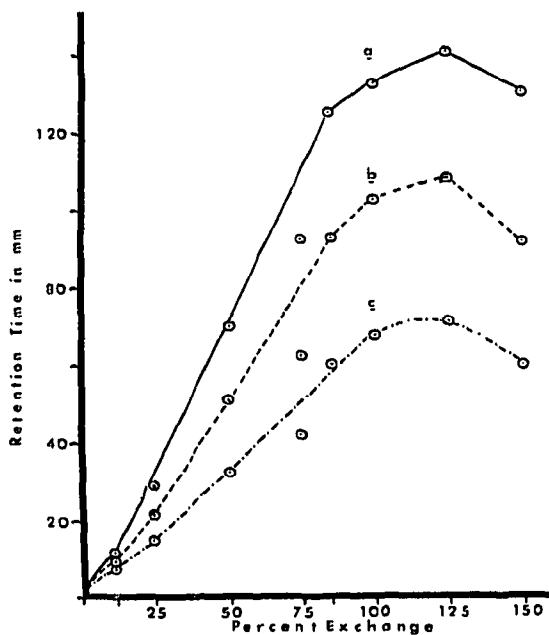

Fig. 2. Retention times of C_2H_6 *versus* % $Cr(en)_3^{3+}$ substitution at (a) 30° and 120 ml/min, (b) 50° and 80 ml/min, and (c) 50° and 120 ml/min obtained with a 110-cm column.

spacing between adsorbed $Cr(en)_3 \cdot Cl_3$ particles may become the controlling factor.

To further substantiate the different mode of separation between the hydrocarbons and oxides of nitrogen. Fig. 3 gives retention times of air, CH_4, and N_2O_3 versus % $Cr(en)_3^{3+}$ substitution. Retention times for hydrocarbons greater than C_2 were quite long and very broad.
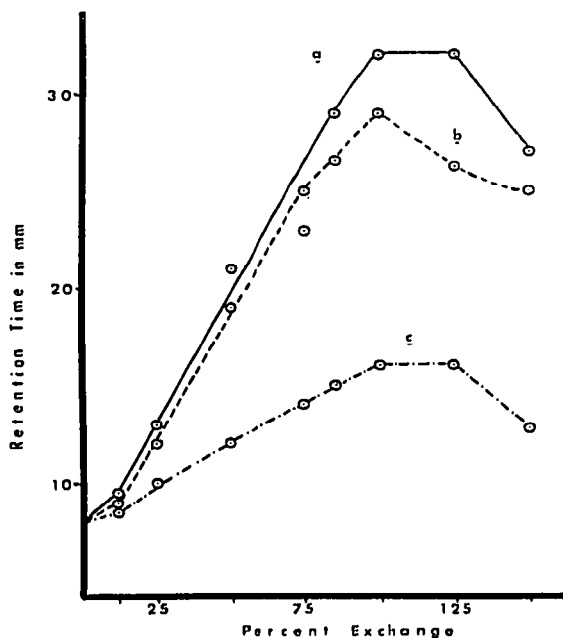

Fig. 3. Retention times of (a) CH_4, (b) N_2O_3 and (c) air versus % $Cr(en)_3^{3+}$ substitution obtained with a 110-cm column at a temperature of 30° and a flow-rate of 40 ml/min.

To determine the thermal stability of the $Cr(en)_3^{3+}$ clays, the 100% exchanged clay was used. The column was heated for various lengths of time at a variety of temperatures. A flow-rate of helium through the column was maintained at 80 ml/min during all heating periods. After each heating period the column was cooled back to 50° and retention times were measured at 120 and 80 ml/min helium flow-rate.

Plots of the retention times versus the hours of heating are shown in Fig. 4 for ethane and nitrous oxide. The increase in retention time over the first 6 h of heating at 100° is apparently due to the additional loss of adsorbed water and water of hydration associated with the cation. The column was initially conditioned at 50° and 80 ml/min helium flow-rate for 8 h. Continued heating at 100° had little or no further effect upon retention time.

After 2 h of heating at 150° the retention time for N_2O greatly decreases whereas that for C_2H_6 has a slight increase. Pfeiffer and co-workers[21] reported that heating tris(ethylenediamine)Cr(III) salts gives a loss of water of hydration at 130° and loss of one-third of their ethylenediamine at 160° resulting in the formation of a bis(ethylenediamine)Cr(III) species. Several other workers[22-25] have found that this
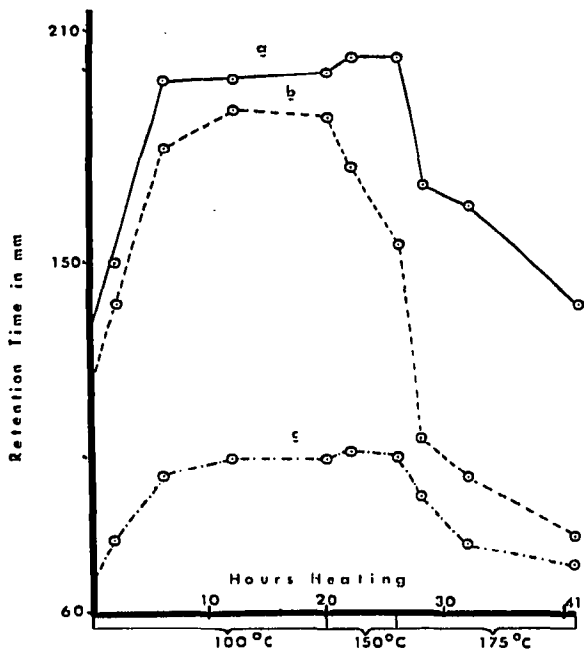
Fig. 4. Retention time *versus* hours of heating for (a) C_2H_6 at 30° and 120 ml/min, (b) N_2O at 50° and 120 ml/min, and (c) C_2H_6 at 50° and 120 ml/min obtained on a 110-cm column of 100% $Cr(en)_3^{3+}$-montmorillonite.

thermal deamination was catalytically affected by certain salts. The outlet gases from the vapor fractometer were bubbled through a solution of phenolphthalein to test for the presence of ethylenediamine. The presence of ethylenediamine in the outlet gas was not noticed until a temperature of 175° had been reached. No color change
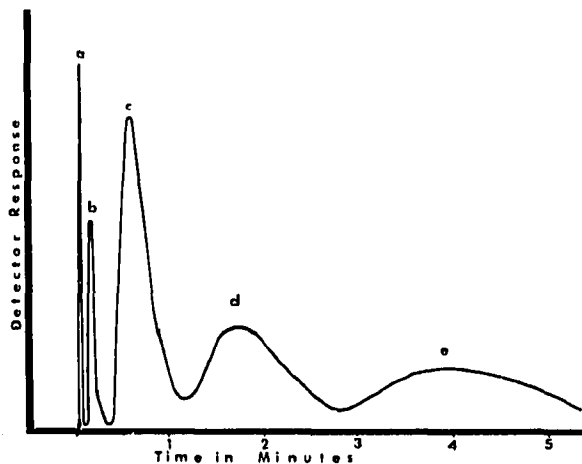

Fig. 5. GC separation of (a) CH_4, (b) C_2H_6, (c) C_3H_8, (d) isobutylene and (e) n-C_4H_{10} carried out on a 20-cm column of 75% $Cr(en)_3^{3+}$-montmorillonite at a temperature of 100° and a flow-rate of 120 ml/min.

was noted in the phenolphthalein solution during the 6 h of heating at 150°. DTA data indicated that an endothermic dissociation occurred about 130°. However, apparently the released ethylenediamine is immediately adsorbed on the basal surface, thus decreasing the surface area of the complex and subsequently lowering the retention time of the N_2O. In contrast, the C_2H_6 which is involved in a sieving separation is not affected initially by this phase transition. However, as the temperature is increased the ethylenediamine begins to move through the column and thus affects the sieving paths of the clay. A similar study carried out on the 85% exchanged clay gave the same results.

Due to the fact that the high per cent exchange $Cr(en)_3^{3+}$-montmorillonites have such high retention times for the hydrocarbons, it is possible to obtain quite good separation of the light hydrocarbons (C_1–C_5) on very short columns. Because elevated temperatures and high flow-rates can be utilized, the analysis time is very short. Typical chromatograms are shown in Figs. 5 and 6.
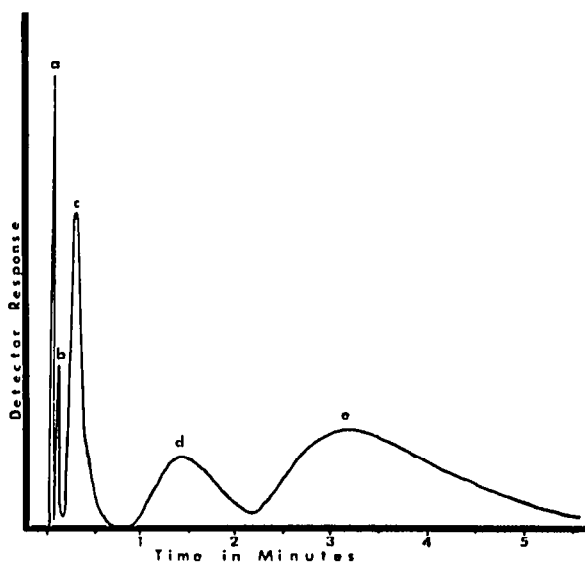

Fig. 6. GC separation of (a) CH_4, (b) C_2H_6, (c) C_3H_8, (d) n-C_4H_{10}, and (e) 2-pentene carried out on a 20-cm column of 75% $Cr(en)_3^{3+}$-montmorillonite at a temperature of 125° and a flow-rate of 120 ml/min.

Comparison of Cr(III)-, Co(III)- and Cu(II)-tris(ethylenediamine) complex exchanged montmorillonites

A comparison of the GC properties of the three different clay complexes was carried out on the 100% exchanged montmorillonites. The retention times for N_2O were directly related to the surface area (Fig. 7) and are greatest for the $Cu(en)_3^{2+}$-montmorillonite and least for the $Co(en)_3^{3+}$-montmorillonite. The C_2H_6 retention times were directly related to the d_{001}-spacing of the clay and, as can be seen from Fig. 8, are greatest for $Co(en)_3^{3+}$-montmorillonite and least for $Cu(en)_3^{2+}$-montmorillonite.
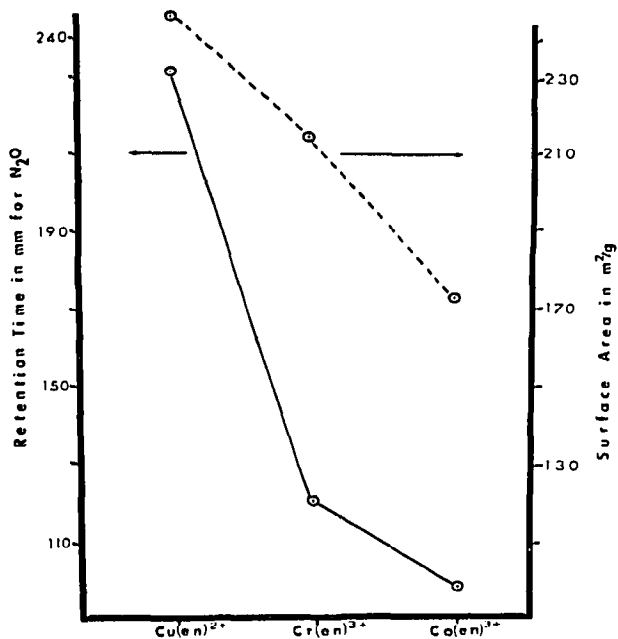
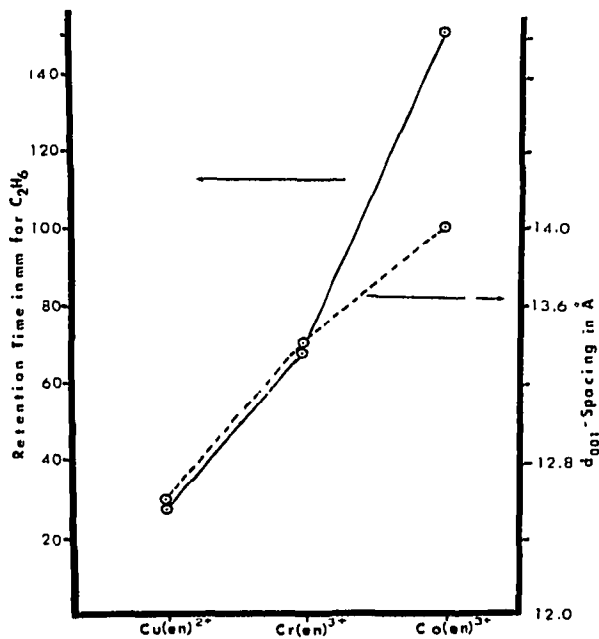Fig. 7. Comparison of surface area and retention time (at 50° and 120 ml/min) to type of exchanged cation.

Fig. 8. Comparison of d_{001}-spacing and retention time (at 50° and 120 ml/min) to type of exchanged cation.

There is considerable difference in the thermal stability of the three clays. The temperatures (T_d) where decomposition was noted as indicated by a change in the color of phenolphthalein solution through which the outlet gas was being bubbled are given in Table I.

TABLE I

TEMPERATURES OF DECOMPOSITION OF THE CLAYS

Type of cation on clay	Temperature of decomposition, T_d ($^\circ C$)
$Cr(en)_3^{3+}$	$150 < T_d < 175$
$Co(en)_3^{3+}$	$135 < T_d < 150$
$Cu(en)_3^{2+}$	$75 < T_d < 100$

Several factors make the $Cr(en)_3^{3+}$-montmorillonite the most practical of the three clays, such as its greater degree of thermal stability. Two other factors are that the $Cr(en)_3^{3+}$-montmorillonite has an intermediate surface area and d_{001}-spacing, thus providing for good retention times for both the light hydrocarbons and oxides of nitrogen.

ACKNOWLEDGEMENTS

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