

THE RELATIONSHIP BETWEEN STRUCTURAL PROPERTIES OF METAL-TRIS (ETHYLENEDIAMINE) MONTMORILLONITE AND THEIR BEHAVIOR AS GAS CHROMATOGRAPHIC PACKING MATERIALS

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(Received 20 September 1974; and in final form 11 February 1975)

Abstract—The tris(ethylenediamine) complex cations of chromium(III), cobalt(III), and copper(II) were exchanged onto sodium montmorillonite. The resulting cation exchanged clays were dried, ground, sieved and the 50/80 mesh size was retained for use as column packing material to be used in gas chromatographic analysis of light hydrocarbons and oxides of nitrogen. Studies indicated that the hydrocarbons were following a sieving action whereas the nitrogen oxides were involved in a surface adsorption process.

The changes in d_{001} -spacing and surface area of tris(ethylenediamine)Cr(III)-montmorillonite were correlated with the changes in gas chromatographic retention time for the light hydrocarbons and the oxides of nitrogen.

Retention time was obtained for the 100 per cent exchanged montmorillonites containing cations of tris(ethylenediamine)Cr(III), tris(ethylenediamine)Co(III), and tris(ethylenediamine)Cu(II). A comparative study of the d_{001} -spacing and surface area of the three clays is shown to be directly related to the retention time.

Heating effects were studied to determine thermal stability. Changes in retention times were compared with various structural changes. DTA and heating-oscillating X-ray powder diffraction analysis were used to help explain the relationship between retention time and structural change.

INTRODUCTION

During the past 25 yr considerable research has been done in the area of utilization of clays and zeolites as supports and microsieves for use in gas-liquid chromatography and gas-solid chromatography. White (1957) and Hughes, White and Roberts (1959) reported using dimethyldioctadecylammonium substituted montmorillonite to effect separation of *o*-, *m*-, and *p*-xylenes. Kiselev *et al.* (1972) had considerable success in using dimethyldioctadecylammonium montmorillonite as a packing for liquid chromatography in separation of *o*-, *m*-, *p*-isomers of terphenyl, phenoxyphenol, and nitrophenol.

Taramasso and Veniale (1969) carried out substitution of dimethyldioctadecylammonium ion on kaolinite, fire-clay, halloysite, attapulgite, hectorite, nontronites, vermiculites and montmorillonites. Their data indicated the influence of surface charge, charge density and location of metal substitution such as tetrahedral vs octahedral of the silicate sheet on the clays' behavior as used in gas chromatography. The clay minerals with tetrahedral substitution seemed to possess the greatest amount of effectiveness as sorbents for gas-chromatographic use which Taramasso and Fuchs (1970) explained as being due to the fact

that in the beidellite type of clay the charge deficit is nearer the basal surface than in the smectite clays.

More recently, Delventhal *et al.* (1972) used coordination polymeric metal complexes of Ni(II) and Co(II) for substitution species. A 4 per cent by weight loading used on Chromosorb P was effective in giving good separation on a series of Lewis bases.

Manara and Taramasso (1972 and 1973) have studied the gas chromatographic behavior of sepiolite and attapulgite which may be considered as Type(III) adsorbents. With a ballistic type heating program from -78°C to $+70^{\circ}\text{C}$ it was possible to get separation of O_2 , N_2 , CO , CH_4 and CO_2 .

The purpose of this investigation was to study the behavior of metal-tris(ethylenediamine) complex substituted montmorillonites when used as gas chromatographic packing materials to determine if they behave primarily as sieves or involve interaction with the basal surfaces. These clays will have basal spacings less than those found in the dimethyldioctadecylammonium substituted montmorillonite (24 Å). However, the porosity size should be greater than that found in the non-substituted hormites (attapulgite = 3.7 by 6.0 Å and sepiolite = 3.7 by 9 Å).

EXPERIMENTAL

Na⁺-ion exchanged, centrifuged, spray-dried Wyoming montmorillonite obtained from the Baroid Division of NL Industries of Houston, Texas was the starting clay for all samples. The salts for exchange were obtained from Ventron and were tris(ethylenediamine)chromium(III)chloride, tris(ethylenediamine)cobalt(III)chloride and tris(ethylenediamine)copper(II)sulfate.

Samples were prepared in 21. batches. 40 g (dry weight) clay were added in small increments to 2 l. of distilled water in a three speed Waring blender. The resulting two per cent clay was dispersed over a 15 min period. The appropriate weight of complex ion salt was dissolved in 250 ml of water and then added in small aliquats to the two per cent clay dispersion. The clay dispersion and exchange ion were mixed a total of 15 min. The resulting mixture was allowed to stand a minimum of 18 hr to allow exchange equilibrium to be obtained.

The resulting exchange clay was then centrifuged and washed a minimum of three times. The clays in which greater than one m-equiv. cation/g clay was added were centrifuged only once. The decantant from the initial centrifuging was saved and later analyzed by atomic absorption to determine the amount of metal ion remaining in solution after exchange.

The centrifuged, washed clays were then dried at 45°C. The dried clays were ground in a Weber Bros. Laboratory Pulverizing Mill which was plugged into a variable autotransformer for speed control and had two-thirds of the beater bars removed so as to not overpulverize the clays.

The grindings were size fractionated and the 50/80 mesh fraction was kept for column packing. The 80+ mesh was used for DTA, X-ray and sorptometer studies. Columns were prepared from Pyrex glass tubing and were 110 cm long and an i.d. of four mm. They were bent into a U-shaped tube at midpoint. The columns were packed with the prepared clays by pouring the clays into short thistle tubes attached to the open ends of the column as it was vibrated at 60 cycles/sec.

Gas retention time (measured in mm on the recorder chart from point of injection to maximum peak height) were obtained using a Perkin-Elmer Vapor Fractometer Model 154 with a thermal conductivity cell. Helium was used as the carrier gas. Samples studied included the light hydrocarbons (C₁-C₃) and oxides of nitrogen (N₂O and N₂O₃). Samples were injected with a 1 cm³ B-D Plastipak Tuberculin hypodermic syringe with a size 23 stainless steel needle. Sample sizes varied from 0.05 to 0.40 ml and injection reproducibility was ± 5 per cent.

The DTA apparatus used was built in the Baylor laboratories. It utilized a Model SH-11BR 2 Stone sample holder and a model HX-2A TemPress temperature controller. The heating rate was controlled by a motor driven potentiometer. For low temperature work, aluminum sample pans were used and γ -

Al₂O₃ was used as the reference material. Samples were run under static air conditions.

Surface area studies were carried out on a Perkin-Elmer Model 212C Sorptometer. A special furnace for degassing the samples while they were on the Sorptometer was designed in this laboratory by Dr. M. I. Knudson (presently with Centex Analytical Laboratory, Waco, Texas). Desorption gives sharper peaks and for the reasons discussed by Thomas and Bohor (1968) the desorption peaks were used to determine the adsorption capacities of the clays. To produce the desorption curves the coolant (liquid N₂) was lowered from the sample tube and quickly replaced by a beaker containing warm water (50°C).

A Philips X-ray diffraction unit with a high angle diffractometer was used to obtain X-ray powder diffraction data. The radiation was produced by a copper target and the Cu K α ($\lambda = 1.5418 \text{ \AA}$) radiation was filtered through a Ni foil. The technique of heating-oscillating X-ray diffractometry has been described previously by McAtee and Hawthorne (1964).

RESULTS AND DISCUSSION

An extensive study was carried out on various Cr(en)₃³⁺-montmorillonites to see if a difference could be noted in retention time behavior of the light hydrocarbons and the retention time behavior of the oxides of nitrogen as a function of the per cent exchanged. Figure 1 shows retention time of N₂O vs per cent exchange of Cr(en)₃³⁺. The retention time increases with increased exchange up to 100 per cent after which it decreases fairly rapidly. Retention time for various temperatures and flow rates show that the behavior is not peculiar to one set of conditions. Shown in Fig. 2 are the retention time of C₂H₆ vs per cent exchange. Retention time again increases up to the 100 per cent exchanged clay. However, the

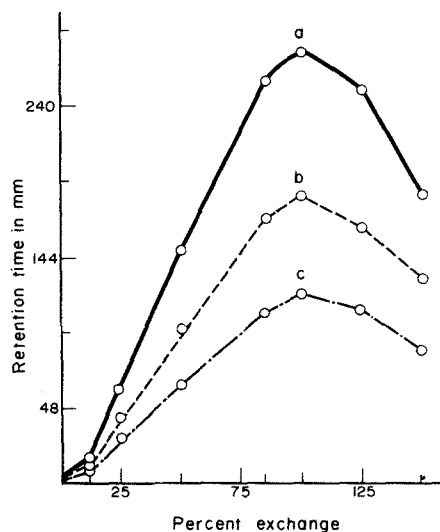


Fig. 1. Retention time of N₂O vs per cent Cr(en)₃³⁺ substitution at (a) 30°C—120 ml/min He flow, (b) 50°C—80 ml/min He flow, and (c) 50°C—120 ml/min He flow obtained with a 110 cm column.

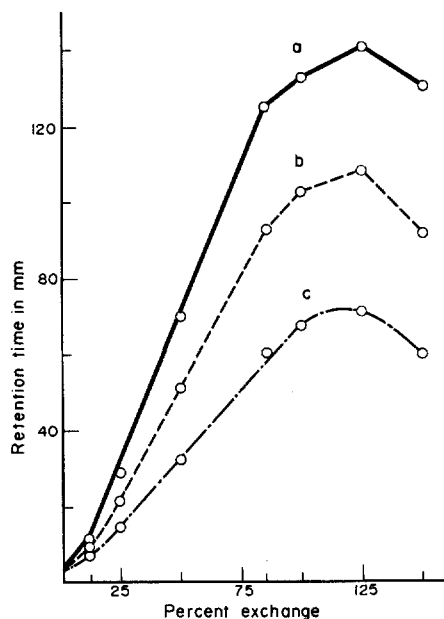


Fig. 2. Retention time of C₂H₆ vs per cent Cr(en)₃³⁺ substitution at (a) 30°C—120 ml/min He flow, (b) 50°C—80 ml/min He flow, and (c) 50°C—120 ml/min He flow obtained with a 110 cm column.

retention time does not drop off rapidly between the 100 and 125 per cent exchanged clay as it did in the case of the N₂O. This difference is again shown in Fig. 3 which shows the retention time of CH₄, N₂O₃, and air. The N₂O₃ shows behavior similar to the N₂O and CH₄ similar to C₂H₆. It was this difference in retention time behavior in this exchange range that led us to investigate further the possibility of different

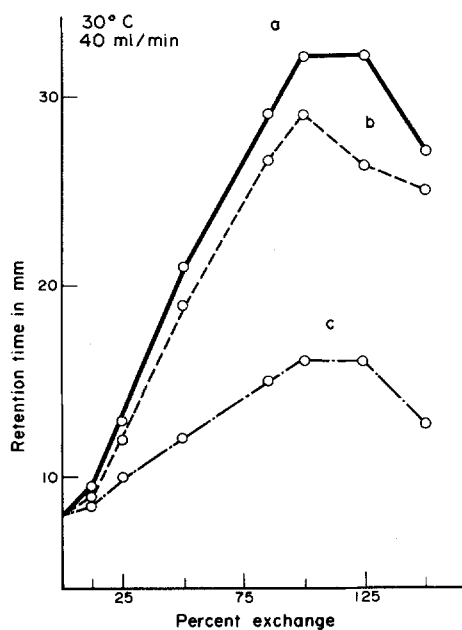


Fig. 3. Retention time of (a) CH₄, (b) N₂O₃ and (c) air vs per cent Cr(en)₃³⁺ substitution obtained with a 110 cm column.

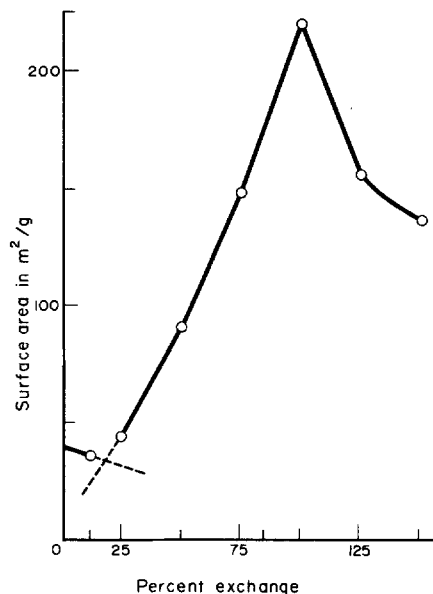


Fig. 4. Surface area vs per cent exchange for Cr(en)₃³⁺-montmorillonite.

gas-chromatographic separation pathways for the light hydrocarbons vs the oxides of nitrogen.

Surface area studies were carried out on the various per cent exchanged clays and are shown in Fig. 4. The surface area shows a fairly linear increase from 25 to 100 per cent exchange. The two areas of special interest are the areas between 0 and 25 per cent and beyond the 100 per cent exchange.

In studying the surface area between 0 and 25 per cent exchange one notes that there is a decrease in surface area which, on extrapolation of the data, appears to reach a minimum between 17 and 18 per cent exchange. Several factors must be considered here to postulate an answer. The X-ray data, Fig. 5, shows that as Cr(en)₃³⁺ ion is added, even in small

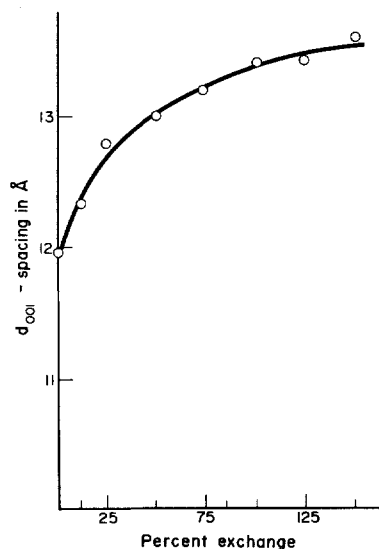


Fig. 5. d₀₀₁-spacing vs per cent exchange for Cr(en)₃³⁺-montmorillonite.

amounts, the d_{001} -spacing begins to increase indicating some degree of interlamellar exchange. However, it is possible that rather than an exchange into an interlamellar space available in a clay aggregate, the multivalent cation may be initially exchanged onto an external surface. Then this may be followed by subsequent attraction to and exchange onto a second aggregate surface above it. The new denser aggregate then would contain an interlamellar space containing $\text{Cr}(\text{en})_3^{3+}$ ions which would be available to nitrogen penetration and sorption. For this the average d_{001} -spacing would be greater than that found in the Na^+ -montmorillonite which is indicated to be the case from the X-ray data (Fig. 5). The net result of this type of aggregate thickening would, however, be a decrease in measured surface area. This is due to the fact that prior to aggregate stacking, caused by the multivalent $\text{Cr}(\text{en})_3^{3+}$ -ion, two facial surfaces were available for nitrogen sorption. After the stacking occurs, however, the two facial surfaces which now make up the newly formed interlamellar space are able to accommodate only a monolayer of nitrogen between them because of the dimensions of the interlamellar space. This, of course, results in a decrease of surface area.

There is another factor which could be involved in this decrease in surface area. Studies have indicated that in the case of montmorillonite, approximately 20 per cent of the exchange occurs on the fractured bonds such as Al-O^- and SiO^- on the edge of the silica-alumina units (Grim 1968). This type of exchange could result in a decrease in the surface area due to the covering of the edge area and/or due to increasing aggregate size.

The plot of surface area versus per cent exchange (Fig. 4) indicates that only a small decrease in surface area occurred from 0 to 25 per cent exchange for the $\text{Cr}(\text{en})_3^{3+}$ -montmorillonites. This decrease is much smaller than one might predict from the previous discussion and is considerably less than that found by Knudson (1973) for a comparable exchanged $\text{Co}(\text{en})_3^{3+}$ -montmorillonite. It would, therefore, appear that the amount of aggregate stacking, etc. is either quite small or partially offset by true interlamellar exchange within the clay platelets even at low exchange values. A more thorough discussion on this area of cation exchange and its surface area effects carried out on a similar cation ($\text{Co}(\text{en})_3^{3+}$) has been published recently by Knudson (1974).

Although of interest, the surface area behavior between 0 and 25 per cent is not of considerable help in solving the problem of this report which involved the determination of gas chromatographic behavior of light hydrocarbons and oxides of nitrogen on $\text{Cr}(\text{en})_3^{3+}$ -montmorillonite. The area of much greater interest is from 100 to 150 per cent exchange. In Fig. 4 the surface area drops off rapidly as one exceeds the exchange capacity of the clay. This occurs as the excess $\text{Cr}(\text{en})_3^{3+}$ is adsorbed on the clay surface in the form of an association molecule $\text{Cr}(\text{en})_3 \cdot \text{Cl}_3$, Grim (1968). In the preparation of these clays only one cen-

trifuging was carried out so that the excess adsorbed complex would not be washed away.

A comparison of surface area (Fig. 4) to retention time of N_2O (Fig. 1) shows that there is a very close correlation between the two. The surface area for the 125 per cent exchanged clay is approximately equal that of the 80 per cent exchanged clay and the retention time of the 125 per cent clay is also approximately equal that of the 80 per cent exchanged clay. Likewise, the 150 per cent exchanged clay has a surface area approximately equal to 65 per cent exchanged clay and retention time is also close to the 65 per cent exchanged clay. A similar relationship is noted in Fig. 3 for the N_2O_3 . It is, therefore, quite evident that the gas chromatographic separation of the N_2O and N_2O_3 on $\text{Cr}(\text{en})_3^{3+}$ -montmorillonite involves a surface adsorption process.

In contrast, if one compares the trend in retention time of C_2H_6 and CH_4 above the 100 per cent exchange vs the surface area, it is noticed that the retention time of the two increase as the surface area is decreasing between 100 per cent and 125 per cent exchange. Between the 125 and 150 per cent, a small decrease in retention time has occurred whereas the surface area has decreased to a value approximately equal to a 60 per cent exchanged clay. It would appear that the light hydrocarbons are involved in a separation process which is not greatly dependent upon surface area.

The other parameter to be considered is the d_{001} -spacing. It is this factor which would affect the microsieving abilities of the clay. As mentioned earlier, Manara and Taramasso (1972 and 1973) had found that the hormites had micropore sizes (attapulgite = $3.7 \times 6.0 \text{ \AA}$ and sepiolite = $3.7 \times 9 \text{ \AA}$) which are of adequate dimension to be involved in microsieving behavior. The $\text{Cr}(\text{en})_3^{3+}$ -montmorillonite which has an interlamellar vertical spacing of 4 \AA should also be involved in sieving processes. If one assumes that the light hydrocarbons are following a sieving gas chromatographic separation process, the retention time trend between 100 and 150 per cent exchanged clay can be explained.

Atomic absorption measurements on the clay prepared by the addition of 1 m-equiv. $\text{Cr}(\text{en})_3^{3+}$ cation/g montmorillonite indicated that nearly 100 per cent of the cation was exchanged onto the clay. However, only 0.93 ± 0.02 m-equiv. Na^+ ion were released. This probably occurs due to the exchange of some $\text{Cr}(\text{en})_3 \cdot \text{Cl}_2^{2+}$ and $\text{Cr}(\text{en})_3 \cdot \text{Cl}_2^+$ cations due to possible orientation problems at the higher exchange level. Therefore, there would still be approximately 6 per cent of the interlamellar spaces totally occupied by Na^+ ions and these particles would not have vertical spacing sufficient to allow sieving to occur.

When the chromium complex added to a clay is in an amount greater than 1 m-equiv./g, such as in the 125 per cent exchanged clay, these remaining sodium spaces probably would be exchanged with the larger $\text{Cr}(\text{en})_3^{3+}$ cation. This exchange would increase the total amount of available sieving space and thus

would give an increase in retention time for a sample following a sieving pathway. In the case of C_2H_6 and CH_4 , this is observed experimentally. The d_{001} -spacings shown in Fig. 5 have a fairly linear increase from the 25 per cent to the 100 per cent exchange and then level off with only a slight increase between 100 per cent and 150 per cent exchange.

The fact that the retention time decreases between 125 and 150 per cent exchanged clay even though the d_{001} -spacing remains constant may at first make the sieving theory for the light hydrocarbons questionable. However, the decrease is quite easily explained. The controlling dimension on the sieving process initially is the vertical interlamellar space. At low exchange amounts there would be fairly large horizontal distances between the large $Cr(en)_3^{3+}$, but as the percentage increases beyond the 100 per cent exchange capacity, adsorption of excess $Cr(en)_3^{3+} \cdot Cl_3$ association molecules would tend to bring about a considerable decrease in the horizontal dimension of the sieving pathway. When a sufficient number of these molecules have been adsorbed, the retention time should then begin to decrease as the number of sieving pathways is greatly reduced.

To further verify the conclusions reached from the study of $Cr(en)_3^{3+}$ -montmorillonite, a comparative study was made involving the 100 per cent exchanged clays containing $Cr(en)_3^{3+}$, $Co(en)_3^{3+}$ and $Cu(en)_3^{3+}$ ions. Surface area, d_{001} -spacing and retention time were measured for the three clays. Figure 6 gives a comparison of the retention time for N_2O and the surface area for the three different clays. It is readily seen that $Cu(en)_3^{3+}$ -montmorillonite*, which has the largest measured surface area, shows the longest retention of N_2O , and $Co(en)_3^{3+}$ -montmorillonite,

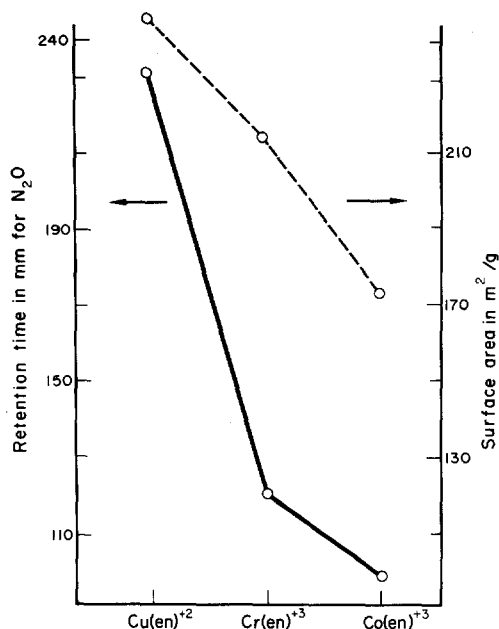


Fig. 6. Comparison of surface area and retention time ($50^\circ C$ —120 ml/min He flow) to type of exchanged cation.

which has the lowest measured area, has the shortest retention time for N_2O .

A comparison of d_{001} -spacing and retention time for C_2H_6 of the three different cation clays is shown in Fig. 7. It can be seen that there is a close correlation between the d_{001} -spacing and retention time of C_2H_6 , $Co(en)_3^{3+}$ -montmorillonite, which has the largest d_{001} -spacing, also shows the longest retention of C_2H_6 , and $Cu(en)_3^{3+}$ -montmorillonite, which has the smallest d_{001} -spacing, has the shortest retention of C_2H_6 .

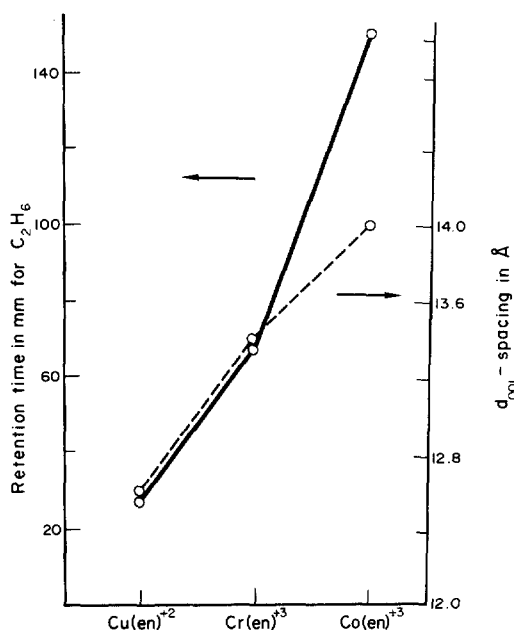


Fig. 7. Comparison of surface area and retention time ($50^\circ C$ —120 ml/min He flow) to type of exchanged cation.

* Because the measured surface area was so large for the $Cu(en)_3^{3+}$ -montmorillonite it was decided to calculate the total actual surface area of this clay. A model was made of the metal-tris(ethylenediamine) cation using a Fisher-Hirschfelder-Taylor Metal-Coordination Atom Model Kit. Volume dimensions of the cation were $9 \text{ \AA} \times 9 \text{ \AA} \times 7 \text{ \AA}$. In the 100 per cent exchanged clay, there would be 1 m-equiv./g clay of cation present of which approximately 20 per cent would be exchanged on external surfaces and 80 per cent internal surfaces (Grim, 1968). The 20 per cent external material would account for a surface area of $32 \text{ m}^2/g$. There would be two possible orientations of the internal cation, one of which would give a surface area coverage of $202 \text{ m}^2/g$ and the other $256 \text{ m}^2/g$. Each internal cation would have two faces in contact with the clay basal surfaces. (The total measured surface area was $246 \text{ m}^2/g$). Assuming monolayer adsorption by the N_2 molecule, Knudson (1973) found a surface area of $34 \text{ m}^2/g$ for Na^+ -montmorillonite. The total measured surface area for the $Cu(en)_3^{3+}$ -montmorillonite was $246 \text{ m}^2/g$. By subtracting the $34 \text{ m}^2/g$ from the total, a value of $212 \text{ m}^2/g$ is obtained for the interlamellar monolayer of adsorbed N_2 . Because two basal surfaces are in contact with the internal adsorbed N_2 , the actual clay facial surface would be $424 \text{ m}^2/g$. The two total values obtained, therefore, depending on cation orientation, are $692 \text{ m}^2/g$ and $746 \text{ m}^2/g$. The second of these two values which involves the more probable cation orientation approaches very close to the theoretical values of $750 \text{ m}^2/g$ calculated by van Olphen, (1966).

These two comparisons of retention time of N_2O vs surface area and retention time of C_2H_6 vs d_{001} -spacing again indicate the high probability of N_2O being involved in a surface adsorption whereas C_2H_6 is involved in a sieving process. This will be substantiated again in the heating studies discussed in the following section.

HEATING EFFECTS

To determine the effect of heating upon retention time and the thermal stability of the $Cr(en)_3^{3+}$ clays, a column of 100 per cent $Cr(en)_3^{3+}$ -montmorillonite was used. The column was placed in the Vapor Fractometer and heated for various lengths of time at a variety of temperatures. A flow of helium through the column was maintained at 80 ml/min during all heating periods. After the heating period, the column was cooled back to 50°C and retention time measured at 120 ml/min and 80 ml/min helium flow. The column was then cooled to 30°C and retention time measured at 120 ml/min.

Plots of the retention time vs the hours of heating are shown in Fig. 8. The retention time of both N_2O and C_2H_6 begin to rise fairly sharply in the first six hours of heating at 100°C. Upon comparing this data to DTA and TGA data, it was concluded that additional water loss was occurring at this temperature. The column had been initially conditioned for eight hr at 50°C and 80 ml/min helium flow. A DTA pattern typical of the results obtained is shown in Fig. 9 for the 85 per cent $Cr(en)_3^{3+}$ -montmorillonite. The DTA pattern obtained for the 100 per cent $Cr(en)_3^{3+}$

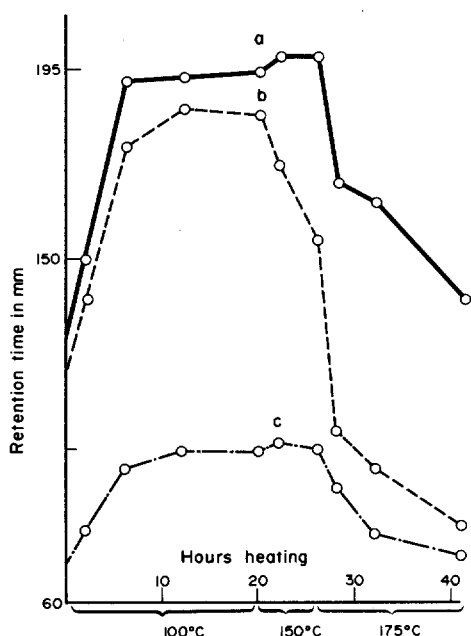


Fig. 8. Retention time vs hours of heating for (a) C_2H_6 at 30°C and 120 ml/min He flow, (b) N_2O at 50°C and 120 ml/min He flow, and (c) C_2H_6 at 50°C and 120 ml/min He flow obtained on a 110 cm column of 100 per cent $Cr(en)_3^{3+}$ -montmorillonite.

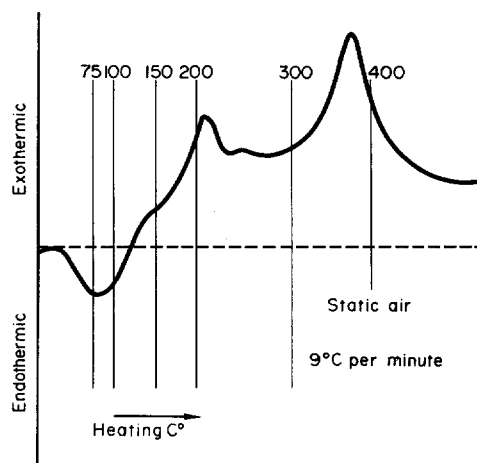


Fig. 9. DTA of 85 per cent $Cr(en)_3^{3+}$ -montmorillonite.

exchanged sample was similar except that the water loss peaks were less intense. The endotherm for water loss reaches its maximum at about 75°C. This additional water loss would increase available surface area which would increase retention time of N_2O and also increase the dimensions of the sieving paths and thus the retention of C_2H_6 .

No indication was found on the DTA patterns which showed that two types of water, surface and hydration, were coming off at different temperatures. Even by running DTA at very slow heating rates, two separate water loss endotherms were not obtained. It was found, however, that a pre-dehydration treatment on the clay sample made it possible to obtain two water loss peaks. (A more detailed discussion of this DTA technique with further examples has appeared elsewhere (McAtee, 1974)).

Again referring to Fig. 8, it is noted that the retention time for both C_2H_6 and N_2O show little change after the initial increase while heating at 100°C. After heating the clay for a period of two hours at 150°C, a noticeable decrease in retention time occurs for the nitrous oxide which continues to decrease after additional heating at 150°C. During this same period, however, the retention time of the ethane has shown little change.

On the DTA curve of Fig. 9 there is a deflection at 135°C which is slightly exothermic. Thermal deamination of $Cr(en)_3^{3+}$ has been studied in many matrices and has been found to go from the tris to bis form between 90 and 210°C depending upon the catalytic properties of the solid with which it is in contact. It is probable that the deflection at 135°C indicates the change from tris to bis (ethylenediamine). The decomposition would be endothermic but if the ethylenediamine molecule is immediately adsorbed on the clay surface (exothermic), the net change shown by DTA would be quite small. It is postulated that this adsorbed ethylenediamine would decrease the surface area thus resulting in a shorter retention time for N_2O .

The adsorbed ethylenediamine would undergo desorption upon temperature elevation. Large scale deamination, adsorption and desorption would occur as the temperature is increased. This appears to happen when the temperature is raised to 175°C. At that temperature both C₂H₆ and N₂O retention time begin to show a decrease. The large amount of released ethylenediamine would greatly reduce the surface area and also the micropore dimensions available for C₂H₆ retention.

Figure 9 shows a large exotherm beginning near 150°C and rising to a maximum near 210°C. This probably corresponds to the loss of the first ethylenediamine and its subsequent oxidation. To test for the presence of ethylenediamine coming from the column, the outlet gases from the Vapor Fractometer were bubbled through a solution of phenolphthalein. The presence of ethylenediamine could then be noted by the change from a colorless to a pink solution. For the 100 per cent Cr(en)₃³⁺-montmorillonite, this color change was not noticed until a column temperature of 175°C was reached. During the preceding six hr of heating at 150°C no color change was noted.

A comparative heating study was carried out on 100 per cent Co(en)₃³⁺-montmorillonite and it showed a rather drastic difference in behavior from the chromium complex. Figure 10 shows that the initial heating at 100°C again results in the rapid increase in retention time for N₂O. The retention time for ethane, however, immediately drops rapidly and then levels off after six hours of heating at 100°C. When heating is carried out at 125°C, both N₂O and C₂H₆ show decreases in retention time.

A check by the phenolphthalein method on the temperature at which ethylenediamine was lost from the cobalt complex column indicated that it occurred between 125 and 150°C. DTA data (Fig. 11) indicates

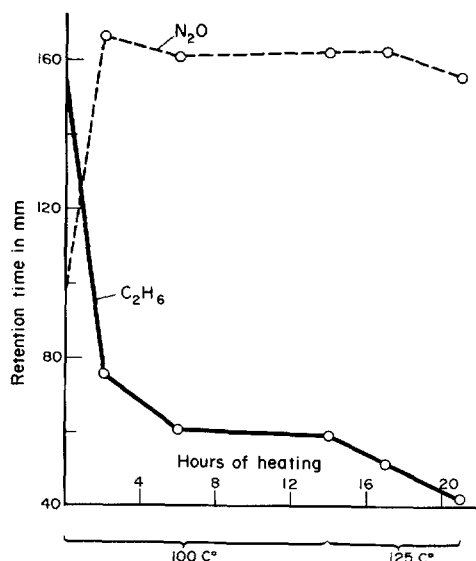


Fig. 10. Retention time vs hours of heating. 110 cm column of 100 per cent Co(en)₃³⁺-montmorillonite at 50°C and 120 ml/min He flow.

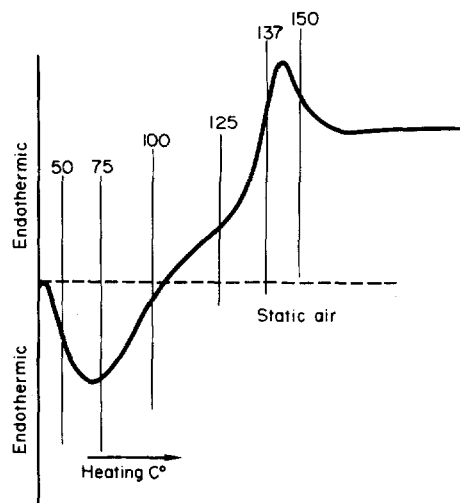


Fig. 11. DTA of 100 per cent Co(en)₃³⁺-montmorillonite. Heating at 2°/min.

that the exotherm corresponding to the loss and oxidation of the first ethylenediamine occurs at approximately 140°C in contrast to the 200°C for Cr(en)₃³⁺-montmorillonite. This loss at 140°C corresponds quite well to the decrease in retention time of N₂O after heating at 125°C but does not help explain the decrease in C₂H₆ retention time.

Measurement of the *d*₀₀₁-spacing for the heated Co(en)₃³⁺-montmorillonite indicated a fairly large decrease in the basal spacing. It was this fact and the rapid decrease in retention time of C₂H₆ that indicated that a study of *d*₀₀₁-spacing versus heating was necessary.

HEATING-OSCILLATING X-RAY POWDER DIFFRACTION ANALYSIS

To carry out the study of the relationship between *d*₀₀₁-spacing and temperature, heating-oscillating X-ray analysis, McAtee and Hawthorne (1964), was carried out.

Oriented samples were prepared on 1 × 1 in. aluminum plates. These plates were then placed in the special heating X-ray diffractometer chamber. Heating was controlled at approximately 2°/min. The diffractometer was oscillated over a 2θ range of 1.5°2θ.

Figure 12 shows a plot of *d*₀₀₁-spacing for 100 per cent Cr(en)₃³⁺-montmorillonite and 100 per cent Co(en)₃³⁺-montmorillonite. Both have a very gradual decrease in *d*₀₀₁-spacing as the temperature increases from 30 to 70°C. This decrease is probably due to dehydration of the clay.

Between 70° and 100°C there is, however, a very large difference in the two curves. The Cr(en)₃³⁺-montmorillonite shows only a slight decrease in *d*₀₀₁-spacing whereas the Co(en)₃³⁺-montmorillonite shows a 0.8 Å decrease. If C₂H₆ is following a sieving path, such a decrease in *d*₀₀₁-spacing should cause a very large decrease in its retention time. This was the case

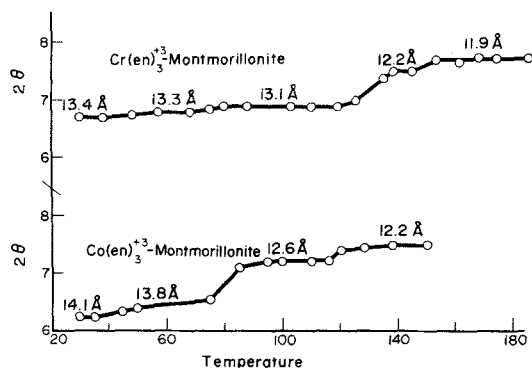


Fig. 12. Heating-oscillating X-ray data for 100 per cent $\text{Cr}(\text{en})_3^+$ and 100 per cent $\text{Co}(\text{en})_3^+$ -montmorillonite.

for the C_2H_6 (Fig. 10). The cause of this collapse cannot be explained until further studies are carried out.

A second appreciable decrease in the d_{001} -spacing for the $\text{Co}(\text{en})_3^+$ -montmorillonite occurs between 115 and 125°C. This again is reflected in the retention time of the C_2H_6 as heating of the column at 125°C was carried out.

As mentioned previously, the presence of ethylenediamine in the outlet gas of the Vapor Fractometer did not occur until near 125°C. At this temperature the N_2O retention time also began to decrease.

The correlation between d_{001} -spacing changes and retention time changes of C_2H_6 for the 100 per cent $\text{Cr}(\text{en})_3^+$ -montmorillonite are also quite good. The first major change in the d_{001} -spacing occurs between 130 and 150°C and the retention time for C_2H_6 showed only minor change until a temperature of over 150°C was obtained. This, however, would not seem to be unreasonable, as in the case of the heating-oscillating X-ray diffraction one is using a very thin film, while in the gas chromatographic work one has a large bulk of material. Most likely a longer heating time or a slightly higher temperature may be needed to bring about an appreciable change in such a large bulk of material as that present in the G.C. column.

Acknowledgements—The authors wish to acknowledge the Baroid Division, NL Industries and the Robert A. Welch Foundation for financial support of this research.

REFERENCES

- Delventhal, J., Keck, H. and Kucken, W. (1972) Coordination-polymeric metal complexes as stationary phases in gas chromatography: *Angew. Chem. Int. Edit.* **11**, 830.
- Grim, R. E. (1968) *Clay Mineralogy*, p. 193, McGraw-Hill, New York.
- Hughes, M. A., White, D. and Roberts, A. L. (1959) Separation of meta-and-para-isomers of the xylenes, cresols, and toluidines by gas solid chromatography: *Nature, Lond.* **184**, 1796-1797.
- Kiselev, A. V., Lebedeva, N. P., Frolov, I. I. and Yashin, Ya. I. (1972) Liquid-solid chromatography on Bentone-34: *Chromatographia* **5**, 341-345.
- Knudson, M. I., Jr. and McAtee, J. L., Jr. (1974) Interlamellar and multilayer nitrogen sorption by homoionic montmorillonites: *Clays and Clay Minerals* **22**, 59-65.
- Knudson, M. I., Jr. and McAtee, J. L., Jr. (1973) The effect of cation exchange of tris(ethylenediamine)cobalt(III) for sodium on nitrogen sorption by montmorillonite: *Clays and Clay Minerals* **21**, 19-26.
- Manara, G. and Taramasso, M. (1972) Sieving effects of hormites in gas-adsorption chromatography: *J. Chromatog.* **65**, 349-353.
- Manara, G. and Taramasso, M. (1973) Selective adsorption properties of the surfaces of attapulgite and sepiolite: *J. Chromatog.* **77**, 109-118.
- McAtee, J. L., Jr. and Hawthorne, J. M. (1964) Heating-oscillating X-ray diffraction studies of some organo-montmorillonite: *Am. Miner.* **49**, 247-257.
- McAtee, J. L., Jr. and Thielmann, V. J. (1974) A pretreatment method to determine differences in adsorbed water by DTA: *Thermochim. Acta* September, 1974.
- van Olphen, H. (1966) *An Introduction to Clay Colloid Chemistry*, p. 244, Interscience, New York.
- Taramasso, M. and Fuchs, P. (1970) The organic complexes of the clay minerals and their use in gas chromatography: *J. Chromatog.* **49**, 70-75.
- Taramasso, M. and Veniale, F. (1969) Gas chromatographic performance of long-chain alkylammonium complexes with "beidellite type" clay minerals: *Chromatographia* **2**, 239-242.
- Thomas, J., Jr. and Bohor, B. F. (1968) Surface area of montmorillonite from the dynamic sorption of nitrogen and carbon dioxide: *Clays and Clay Minerals* **16**, 83-92.
- White, D. (1957) Use of organic-montmorillonite compounds in gas chromatography: *Nature, Lond.* **179**, 1075-1076.