

THE EFFECT OF CATION EXCHANGE OF TRIS(ETHYLENEDIAMINE)COBALT(III) FOR SODIUM ON NITROGEN SORPTION BY MONTMORILLONITE

M. I. KNUDSON, Jr.

Baroid Division, NL Industries, Inc., P.O., Box 1675, Houston, Texas 77001, U.S.A.

and

J. L. McATEE, Jr.

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

(Received 17 August 1972)

Abstract—The cation exchange process between tris(ethylenediamine)cobalt(III) and Na^+ on montmorillonite was studied by atomic absorption spectrophotometry, X-ray diffraction, differential thermal analysis, and nitrogen sorption at 78°K. The exchange of $\text{Co}(\text{en})_3^{3+}$ for Na^+ was found to be extremely favorable, with a tendency toward segregation of the two kinds of cations in the mixed clays studied. Small amounts of $\text{Co}(\text{en})_3^{3+}$ were found to lower the nitrogen sorption capacity of Na^+ montmorillonite while clays with high $\text{Co}(\text{en})_3^{3+}$ content had greatly enhanced sorption. An explanation is offered in terms of a dual role of the $\text{Co}(\text{en})_3^{3+}$ in determining the kind and amount of nitrogen sorption in the exchanged montmorillonite.

INTRODUCTION

THERE have been many studies of nitrogen sorption by homoionic montmorillonite clay minerals. Some recent examples are Aylmore (1970); Barrer (1967); Slabaugh (1971) and Thomas (1968). However, relatively little has been reported on nitrogen sorption by clays containing varying ratios of two different kinds of exchangeable cations. Barrer *et al.* (1963) showed that a study of the change in nitrogen sorption as a function of degree of exchange between two kinds of cations on a montmorillonite can give some information on the exchange process. This technique is most useful when the two cations involved give homoionic clays of greatly different sorption characteristics. Barrer's study did not cover a wide range of cation ratios and his data implied a linear change in nitrogen sorption with change in mixed cation ratios.

In the present study it was found that by preparing a $\text{Co}(\text{en})_3^{3+}$ montmorillonite from a Na^+ montmorillonite, the nitrogen sorption capacity of the clay was increased by over 500 percent. Also, the sorption isotherm in the partial pressure range studied ($P/P_0 = 0.05-0.25$) changed from B.E.T. for the Na^+ clay to Langmuir for the $\text{Co}(\text{en})_3^{3+}$ clay. Since the sorption capacities and isotherm characteristics of these two clays were so different, nitrogen sorption was used to study various mixed

$\text{Co}(\text{en})_3^{3+}$ - Na^+ montmorillonites in the hope of learning something about the cation exchange process. Atomic absorption spectrophotometry, X-ray diffraction, and differential thermal analysis were also used in this study. The results were somewhat unexpected.

EXPERIMENTAL

A one percent dispersion of sodium exchanged, centrifuged, and spray dried Wyoming bentonite (Baroid Division, NL Industries, Inc.) was prepared by mixing 40 g of the clay with 4 l. of water in a high speed Waring blender. Ten 100 ml portions of this dispersion were pipetted into separate 250 ml plastic bottles and 2, 4, 6, 8, 10, 12, 14, 20 and 30 ml portions of a 0.098 N $\text{Co}(\text{en})_3 \text{Cl}_3$ solution were added by buret to the respective clay samples. One sample was used for a control; i.e. no $\text{Co}(\text{en})_3 \text{Cl}_3$ was added to it. The total volume of each sample was brought to 130 ml by quantitatively adding the necessary amount of distilled water. This procedure was repeated three more times to give a total of forty samples. Each sample was shaken by hand and allowed to stand with occasional shaking.

After 16 hr, one set of ten samples was centrifuged and the centrifugate collected and sealed in marked bottles. The clays were then washed 4 times each by repeated dispersion in water and centrifugation. Twelve drops of each clay disper-

sion were taken prior to the last centrifugation and placed onto corrosion resistant Gold Seal Microslides. The samples were allowed to air dry on the slides, which were then placed in a desiccator over saturated $\text{Ca}(\text{NO}_3)_2$ (51% r.h.), until needed for X-ray diffraction. Portions of the final wash prior to centrifugation were also sprayed by a DeVilbiss nebulizer onto carbon coated, copper electron microscope grids.

After the final washing, the clay samples were dried overnight in an air circulation oven at 50°C , then lightly ground with a mortar and pestle to 40–140 mesh, and stored in a 51 per cent r.h. atmosphere.

The exchange solutions were analyzed for sodium with a Perkin-Elmer model 403 Atomic Absorption Spectrophotometer. A standard sodium chloride solution, purchased from Hartman-Leddon Company, was used for preparing the calibration solutions. The Perkin-Elmer Intensitron 7M hollow cathode lamp number 303–6065 was the source of the sodium resonance wavelength of 5890 \AA .

The oriented films of clay on the microslides were analyzed by X-ray diffraction. The General Electric XRD-III diffractometer was equipped with a copper X-ray tube, nickel filter, an 8-SPG proportional counter, and 1° divergence and detector slits. A special plastic humidity chamber was made to fit over the sample holder on the diffractometer. Mylar ports were provided for incident and diffracted X-rays. The humidity was controlled by placing a Petri dish of saturated $\text{Ca}(\text{NO}_3)_2$ in the sample holder chamber. Each sample was allowed to stand in the chamber for 20 hr prior to analysis.

The differential thermal analysis apparatus, built in these laboratories, used a model Sh-11BR2 Stone ring-type sample holder and a model HX-2A Tem-Pres temperature controller. The heating rate was controlled by a potentiometer driven by a variable speed motor. The thermocouple was $Pt-Pt+10\%$ r.h. and the differential output was fed to a Leeds and Northrup galvanometer and recorded by a model PRI Beckman Photopen Recorder. The cell temperature thermocouple was monitored by a Leeds and Northrup Type G Speedomax Recorder. The -200 mesh samples, including calcined Al_2O_3 as a reference, were packed into nickel dishes using only enough pressure to form a coherent pellet. The temperature calibration was checked by three metal melting points; 157°C (indium), 232°C (tin), and 327°C (lead).

All nitrogen sorption data were obtained from a Perkin-Elmer model 212 C Sorptometer. The details of design and theory of this instrument have been described elsewhere (Nelson *et al.*, 1958).

Basically, isotherms were obtained by measuring nitrogen sorption at 78°K (liquid N_2 as the coolant) from a continuously flowing stream of various mixtures of nitrogen and helium. A thermal conductivity cell was used as the nitrogen detector. For reasons discussed by Thomas *et al.* (1968), desorption rather than sorption was used to determine the capacities at various nitrogen concentrations. The sample cell was partially immersed in water at 50°C during each desorption. All samples were preheated in flowing helium at 50°C for 16 hr prior to the sorption analysis. Higher degassing temperatures could not be used because the $\text{Co}(\text{en})_3^{+3}$ clay began to decompose after prolonged heating above 50°C . The degassing was carried out with the sample cell in place on the Sorptometer to prevent atmospheric contamination between the degassing and sorption steps. Samples weighing approximately one tenth gram were used, dependent on the sorption capacity of the clay being studied. The helium flow rate was constant at 35 ml/min .

Three days after the initial titration of the forty clay dispersions, a second set of ten samples was centrifuged and prepared for analysis in the same manner as the first set. A third set was centrifuged after five days and the fourth and final set after eight days. All samples were analyzed by the procedures described for the first set.

RESULTS AND DISCUSSION

Cation exchange

The results of the atomic absorption study are shown in Fig. 1. The abscissa represents the milliequivalents of $\text{Co}(\text{en})_3\text{Cl}_3$ added per 0.90 g (dry weight) of sodium montmorillonite in 100 ml of water. The milliequivalents of sodium released by the exchange process are plotted on the ordinate. As can be seen from Fig. 1, each meq of $\text{Co}(\text{en})_3^{+3}$ added to the clay dispersion caused a release of almost one meq of sodium from the clay. This

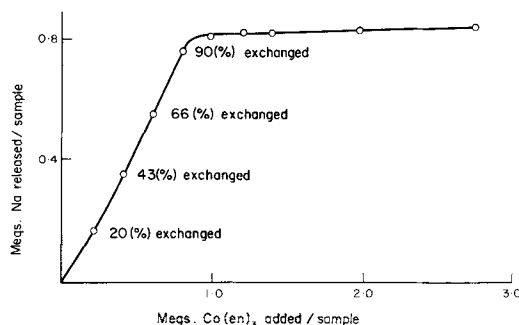


Fig. 1. Meqs. Na^+ released vs meqs. $\text{Co}(\text{en})_3^{+3}$ added per 0.90 g sodium montmorillonite as one percent dispersion.

result indicated that the most important exchange species was Co(en)_3^{+3} as opposed to $\text{Co(en)}_3\text{Cl}^{+2}$ or $\text{Co(en)}_3\text{Cl}_2^+$. The large preference of the clay for the Co(en)_3^{+3} ion over the Na^+ ion was illustrated by the almost total removal of Co(en)_3^{+3} from solution until the clay became saturated or fully exchanged by Co(en)_3^{+3} . The linearity of the curve in Fig. 1 at Co(en)_3^{+3} concentrations below the saturation point also indicated only that all the clay exchange sites had a large preference for the Co(en)_3^{+3} cation, but does not imply equally large preferences.

Upon saturation of the clay with Co(en)_3^{+3} , 93 meq of sodium per 100 g of dried clay were released into solution. The results shown in Fig. 1 were obtained after allowing the titrated dispersion to stand with occasional shaking for 16 hr. The sets of samples that were allowed to stand for three, five, and eight days gave the same results.

X-ray diffraction

X-ray diffraction data were collected for each of the partially exchanged Co(en)_3^{+3} clays. The results are given in Fig. 2. Each sample, prepared as described earlier, was allowed to equilibrate at 51% r.h. for 20 hr prior to analysis. The diffraction patterns for clays with mixed Na^+ and Co(en)_3^{+3} ions are indicative of segregation of cations into two different kinds of interlayers (Brown, 1961). It appears, that instead of complete randomness of interlayers of Co(en)_3^{+3} cations and Na^+ cations, there is a tendency of the two different kinds of interlayers to reside in segregated aggregates. Segregation of cations is known to occur in other mixed cation montmorillonites (Barrer, 1963;

Glaser, 1954). At 51% r.h. the d_{001} of the Na^+ clay was found to be 12.3 Å and that of the saturated Co(en)_3^{+3} clay, 14.2 Å.

Differential thermal analysis

Each sample, after equilibration at 51% r.h., was also investigated by D.T.A. The results are shown in Fig. 3. At this high initial water content, the clay dehydration peaks were so large that the Co(en)_3^{+3} decomposition peaks were not easily studied. Therefore the 20, 66 and the 100 percent Co(en)_3^{+3} exchanged clay samples were re-examined. The samples were stored over concentrated sulfuric acid for 20 hours prior to analysis and the purge gas (N_2) was first bubbled through concentrated sulfuric acid and over anhydrous silica gel. The results are shown in Fig. 4. Little difference was seen between the 66 and 100 per cent exchanged samples, but the D.T.A. curve for the 20 percent sample was significantly different. This observation may relate to the change in the environment of a Co(en)_3^{+3} cation as the occupancy of clay exchange sites by Co(en)_3^{+3} increases. Such a difference was neither confirmed nor rejected by the atomic absorption or X-ray diffraction results. Of course, the differences in the D.T.A. curves could be due to higher local concentrations of decomposition gases for the higher percent Co(en)_3^{+3} samples.

Nitrogen sorption

As shown by Barrer *et al.* (1963), gas sorption can be, under the proper conditions, a useful method for studying partial cation exchange in montmorillonites. Therefore, the partially exchanged Co(en)_3^{+3} clays were studied by the sorption technique described above. The sorption

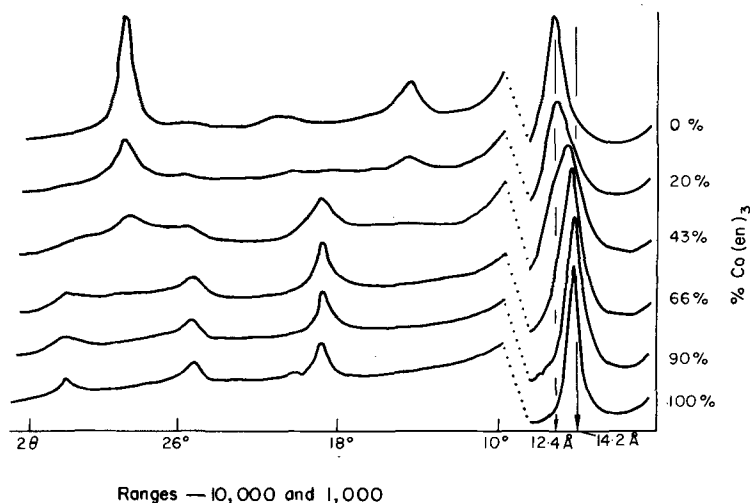


Fig. 2. X-ray diffractions of mixed Co(en)_3^{+3} - Na^+ montmorillonites.

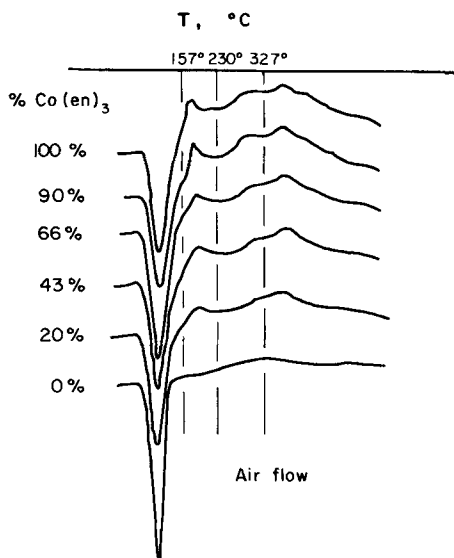


Fig. 3. D.T.A. curves for mixed $\text{Co}(\text{en})_3^{+3}\text{-Na}^+$ montmorillonites (pretreated at 51% r.h.).

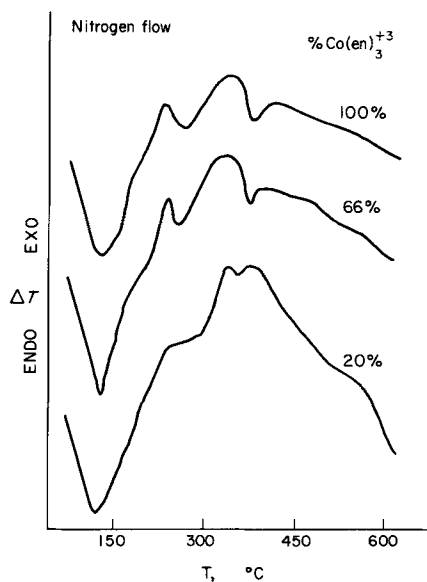


Fig. 4. D.T.A. curves for selected $\text{Co}(\text{en})_3^{+3}\text{-Na}^+$ montmorillonites (pretreated over $\text{con-H}_2\text{SO}_4$, analyzed in nitrogen flow).

isotherms obtained in the range $P/P_0 = 0.5-0.25$ fell into either B.E.T., Type II isotherm or the B.E.T. Type I (Langmuir) isotherm. Although originally derived for monolayer sorption on open surfaces, the Langmuir isotherm has been shown to

be characteristic of microporous materials (Gregg *et al.*, 1967). Thus, even though a plot of the isotherm data for a microporous solid may give a straight line in the linear form of the classical Langmuir equation, the constants involved will certainly have different meanings than when classical Langmuir sorption is occurring. Figures 5-7 show typical plots for the mixed $\text{Co}(\text{en})_3^{+3}\text{-Na}^+$ montmorillonites. The surface areas were calculated from the equation which gave the more linear plot (B.E.T., Type II, for the Na^+ and 20% $\text{Co}(\text{en})_3^{+3}$ clays and the Langmuir equation for the others). For clays containing the higher levels of $\text{Co}(\text{en})_3^{+3}$ where interlamellar penetration by nitrogen is assumed, the term surface area is probably incorrect or at best ill defined. Due to the uncertainty about the packing of the nitrogen molecules in the clay interlayers, the partially exchanged clays may be better compared by their nitrogen monolayer capacities. Fig. 8 is a plot of the level of $\text{Co}(\text{en})_3^{+3}$ exchange versus the monolayer volume (STP) of sorbed nitrogen. The initial decrease in sorption with increase in $\text{Co}(\text{en})_3^{+3}$ content was totally unexpected. Several isotherms were obtained for the 0, 20 and 100 per cent exchanged $\text{Co}(\text{en})_3^{+3}$ clays to insure reproducibility. The precision was found to be good. The linear Langmuir plots for the higher $\text{Co}(\text{en})_3^{+3}$ levels were assumed to indicate extensive interlayer penetration by nitrogen. After this unexpected initial

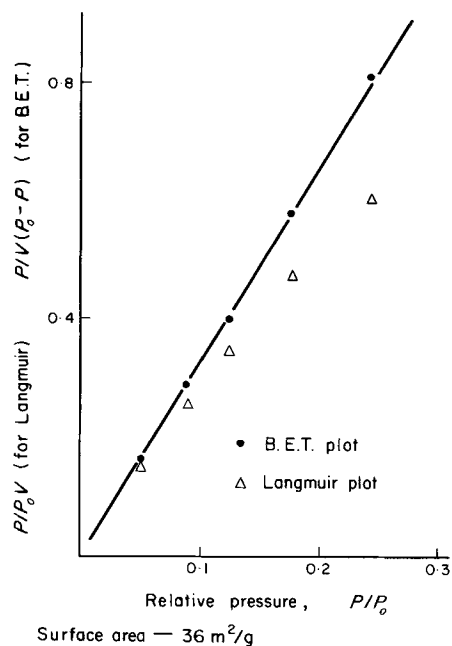
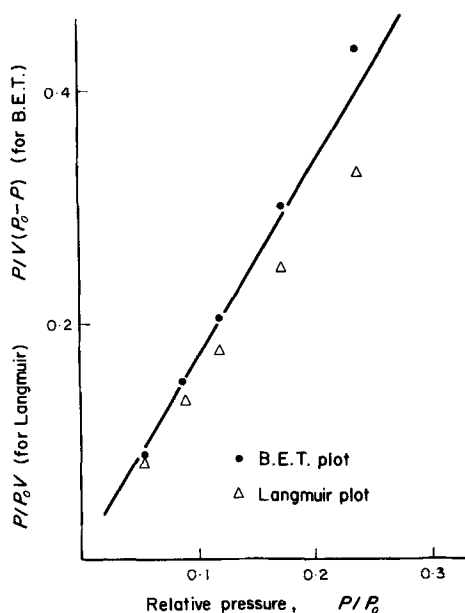
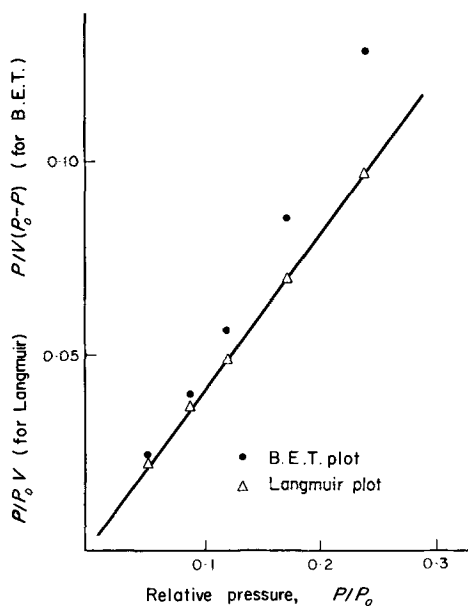


Fig. 5. Nitrogen sorption data for Na^+ montmorillonite.



Surface area — $14 \text{ m}^2/\text{g}$

Fig. 6. Nitrogen sorption data for 20 per cent $\text{Co}(\text{en})_3^{+3}$, Na^+ montmorillonite.



Surface area — $64 \text{ m}^2/\text{g}$

Fig. 7. Nitrogen sorption data for 43% $\text{Co}(\text{en})_3^{+3}$, Na^+ montmorillonite (similar to plots for 66, 90 and 100 per cent exchanged clays).

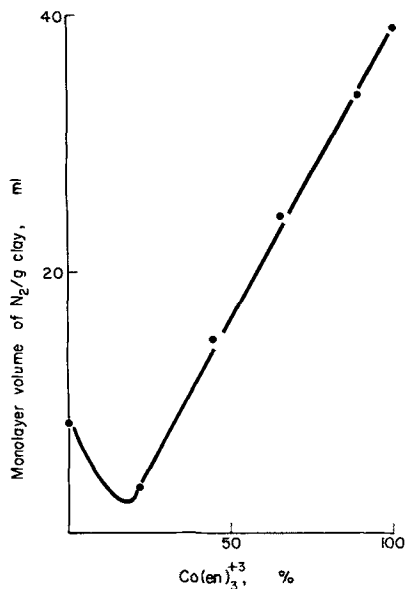


Fig. 8. Nitrogen monolayer volume (STP) as a function of per cent $\text{Co}(\text{en})_3^{+3}$ exchange, for mixed $\text{Co}(\text{en})_3^{+3}$, Na^+ montmorillonites.

decrease, nitrogen sorption increases almost linearly with $\text{Co}(\text{en})_3^{+3}$ content. This increase would be expected if, as implied by the X-ray diffraction data, there is a strong tendency toward segregation of $\text{Co}(\text{en})_3^{+3}$ and Na^+ cations into separate interlayers in the mixed clays. As more $\text{Co}(\text{en})_3^{+3}$ is added to the clay, more interlayers would be opened for nitrogen penetration and the sorption capacity of the clay should increase accordingly. This mechanism, however, does not explain the initial decrease in Fig. 8. In fact, if the above mechanism held over the entire range of $\text{Co}(\text{en})_3^{+3}$ content, a relatively straight line would be observed with an intercept at the monolayer volume for pure sodium montmorillonite.

Therefore, the cation exchange process between $\text{Co}(\text{en})_3^{+3}$ and Na^+ on montmorillonite is not as simple as expected. There seems to have been at least two different processes involved in determining the nitrogen sorption values of Fig. 8. One process was, most likely, the segregation of cations and subsequent nitrogen penetration into $\text{Co}(\text{en})_3^{+3}$ interlayers as described above. However, rough extrapolation of the right hand branch of Fig. 8 indicates that this process began at about 15 per cent exchange of $\text{Co}(\text{en})_3^{+3}$. Therefore, a second process must dominate at low $\text{Co}(\text{en})_3^{+3}$ content and, as opposed to the first process, it must lead to a decrease in nitrogen sorption with increasing $\text{Co}(\text{en})_3^{+3}$. If two separate and independent pro-

cesses were controlling sorption by these partially exchanged clays and if each process could be measured independently, the two contributions might be similar to those shown in Fig. 9. The lack of data at very low Co(en)_3^{+3} contents makes curve A somewhat speculative.

Curve B of Fig. 9 has already been attributed to a linear relationship between the amount of Co(en)_3^{+3} in the clay interlayers and the volume of nitrogen sorbed. Curve A, however, is more difficult to explain. Curves A and B could represent changes in the extent of each of two kinds of surface, the external surface on which multilayer sorption occurs and the interlamellar surface in which micropore sorption occurs. It is proposed that the latter process occurs only in those clay interlayers which contain Co(en)_3^{+3} . If this proposal is correct then curve A must be the variation in external surface area with Co(en)_3^{+3} content.

Since the first point in Fig. 8 occurs before the intercept of curve B (in Fig. 9) only external sorption of nitrogen should have occurred. The linear B.E.T. plot in Fig. 6, for the Co(en)_3^{+3} free clay is consistent with this argument. The second point in Fig. 8 occurs at a place where both curve A and curve B contribute significantly to the total sorption. The intermediate sorption isotherm in Fig. 6 (neither linear B.E.T., Type II, nor linear Langmuir) could have arisen from nitrogen sorption that was neither predominantly multilayer nor pre-

dominately microporous. The other points on Fig. 8 appear where a large amount of micropore, but relatively little multilayer, sorption was occurring. This conclusion is supported by the linear Langmuir plots observed for samples of 43 per cent exchange and greater.

There are possibly two kinds of exchange sites that Co(en)_3^{+3} cations can occupy and still not cause interlamellar separation and consequent nitrogen penetration. The more obvious kind is edge exchange sites. It has been proposed that such edge sites make up roughly 20 per cent of the total exchange capacity of montmorillonites (Grim, 1968), although this is subject to question. However, this value is especially interesting since the proposed curve B of Fig. 9 requires no Co(en)_3^{+3} exchange with the interlamellar sites until the Co(en)_3^{+3} occupancy of the exchange sites reaches about 15 per cent. That is, exchange tends to occur at edge sites before interlayer sites. This proposed preference of Co(en)_3^{+3} for the edge exchange sites is certainly not unique. Sawhney (1972) pointed out that similar claims have been made for Cs^+ and K^+ exchange on illite and vermiculite. Therefore, Co(en)_3^{+3} cations at edge exchange sites may well lead to the behavior shown by Curve A, Fig. 9. The multivalent Co(en)_3^{+3} cations could conceivably bind clay edges together to give wider clay aggregates and a correspondingly smaller external surface area. The decrease in surface area could be due to stacking of these edge-to-edge bound particles to give denser aggregates. The overall result of this process would be to greatly diminish the internal pore structure caused by clay sheet overlap as described by Aylmore *et al.* (1967). Preliminary electron microscope investigations in this laboratory indicated that the Co(en)_3^{+3} clays had much greater particle-particle association than did the sodium clay. Larger, more complex aggregates were characteristic of the Co(en)_3^{+3} clay; the sodium clay had finely dispersed, well oriented particles. Also, incomplete work in this laboratory on mixed Cs^+ - Na^+ montmorillonites has shown that small amounts of Cs^+ do not lower the nitrogen sorption capacity of the sodium clay as do corresponding amounts of Co(en)_3^{+3} (the fully exchanged Cs^+ clay had a surface area some three times greater than the Na^+ clay). The monovalent Cs^+ cation would not be expected to hold clay particle edges together in the same manner as proposed for the Co(en)_3^{+3} cations.

Another possible contribution to curve A in Fig. 9 is as follows. Suppose each aggregate of the Na^+ montmorillonite on the average was five plates thick. Without regard to the edge surface two clay aggregates would sorb four monolayers of nitrogen at low partial pressures; i.e. one monolayer for the

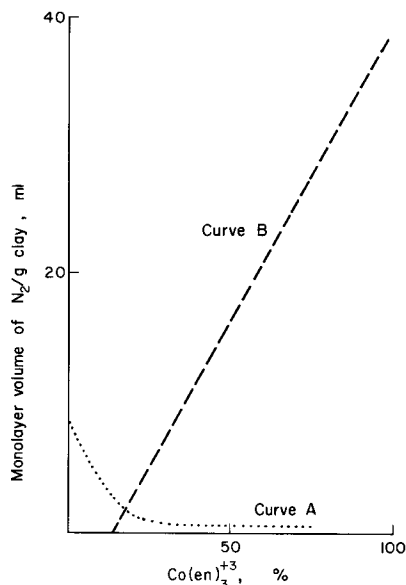


Fig. 9. Proposed variation of external nitrogen sorption (Curve A) and interlamellar nitrogen sorption (Curve B) as a function of Co(en)_3^{+3} percentage exchange with Na^+ montmorillonite.

top and bottom faces of each aggregate. However, if $\text{Co}(\text{en})_3$ cations were exchanged onto these outer surfaces and if, by their trivalent charge, they bound two of these five layer aggregates together, only three monolayers of nitrogen would be sorbed for each two of the five layer aggregates (assuming only one monolayer of nitrogen in the resulting $\text{Co}(\text{en})_3^{+3}$ interlayer). As more and more Na^+ aggregates are bound along the *c*-axis with further $\text{Co}(\text{en})_3^{+3}$ exchange, the total number of monolayers would be continually decreased. The observed nitrogen surface area would decrease accordingly. In the limit of obtaining one long clay column in which every fifth interlayer is $\text{Co}(\text{en})_3^{+3}$ exchanged, the observed surface area could be reduced by almost one-half with respect to the hypothetical Na^+ clay of five layer aggregates. Since 20 per cent $\text{Co}(\text{en})_3^{+3}$ exchange on the Na^+ clay was shown to decrease the nitrogen sorption by some 60 per cent, and since, in the obviously unattainable limit of the above stacking mechanism, only a 50 per cent decrease can be envisioned, this particular stacking mechanism is not the only contributor to curve A. The former mechanism requires enhanced edge-edge association only with respect to the pure Na^+ clay while the latter mechanism requires only enhanced plate-plate association. Some combination of both mechanisms would probably better represent the true situation.

Curve A, therefore, appears to arise from the ability of $\text{Co}(\text{en})_3^{+3}$ cations to bind clay plates and clay edges together by electrostatic forces. The resulting aggregates would be thicker and wider than those of the parent Na^+ clay. The $\text{Co}(\text{en})_3^{+3}$ clay would therefore have less external surface area, which is what curve A represents. However the lack of data on the clays of less than 20 per cent $\text{Co}(\text{en})_3^{+3}$ makes these arguments highly speculative and further study of the low per cent $\text{Co}(\text{en})_3^{+3}$ clays is necessary.

CONCLUSION

$\text{Co}(\text{en})_3^{+3}$ is readily exchanged for Na^+ on montmorillonite. The exchange appears to be complete within 16 hr for all $\text{Co}(\text{en})_3\text{Cl}_3$ concentrations studied. Each $\text{Co}(\text{en})_3^{+3}$ cation replaces three Na^+ cations and the exchange appears to be enhanced on those surfaces where exchange had already begun. This latter effect results in a tendency toward segregation of the $\text{Co}(\text{en})_3^{+3}$ and Na^+ cations into different interlayers. However, there is some evidence that the exchange occurs on the clay edges first, then on the flat surfaces. Perhaps as a result of initial edge exchange, small amounts of $\text{Co}(\text{en})_3^{+3}$ cause a decrease in nitrogen sorption below that noted for Na^+ montmorillonite. This

decrease could be caused by edge to edge binding of the clay platelets by the multivalent $\text{Co}(\text{en})_3^{+3}$. The resulting larger, denser aggregates would have a correspondingly lower external surface area. The probable ability of $\text{Co}(\text{en})_3^{+3}$ to bind the flat surfaces of clay aggregates together might also have some part in the initial lowering of the external surface area of the Na^+ clay as a function of $\text{Co}(\text{en})_3^{+3}$ exchange. As the $\text{Co}(\text{en})_3^{+3}$ content increases, exchange in the clay interlayers occurs and the resulting expansion of the interlamellar spacing of the aggregate permits penetration by nitrogen. Thus, the nitrogen sorption capacity increases. Therefore, the $\text{Co}(\text{en})_3^{+3}$ cations decrease the external surface area of the clay and increase the internal surface area. This proposed dual role of the $\text{Co}(\text{en})_3^{+3}$ offers a qualitative explanation of the variation in nitrogen sorption in mixed $\text{Co}(\text{en})_3^{+3}$ - Na^+ montmorillonites as a function of $\text{Co}(\text{en})_3^{+3}$ exchange (Fig. 9). Further study must be made of the surface area lowering by small amounts of $\text{Co}(\text{en})_3^{+3}$ on Na^+ montmorillonite.

Acknowledgement—The authors wish to thank the Robert A. Welch Foundation for financial support during this period.

REFERENCES

- Alymore, L. A. G., Sills, I. D. and Quirk, J. P. (1970) Surface area of homoionic illite and montmorillonite clay minerals as measured by the sorption of nitrogen and carbon dioxide: *Clays and Clay Minerals* **18**, 91–96.
- Alymore, L. A. G. and Quirk, J. P. (1967) The micropore size distributions of clay mineral systems: *J. Soil. Sci.* **18**, 1–17.
- Barrer, R. M. and Millington, A. D. (1967) Sorption and intracrystalline porosity in organo-clays: *J. Colloid Sci.* **25**, 359–372.
- Barrer, R. M. and Brummer, K. (1963) Relations between partial ion exchange and interlamellar sorption in alkylammonium montmorillonites: *Trans. Faraday Soc.* **59**, 959–968.
- Glaeser, R. and Mering, J. (1954) Isotherms d'hydratation des montmorillonites bi-ioniques (Na, Ca): *Clay Minerals Bull.* **2**(12), 188–193.
- Gregg, S. S. and Sing, K. S. W. (1967) *Adsorption Surface Area and Porosity*, p. 195. Academic Press, New York.
- Grim, R. E. (1968) *Clay Mineralogy*, p. 193. McGraw-Hill, New York.
- MacEwan, D. M. C., Amil, A. R. and Brown, G. (1961) Interstratified clay minerals. In *The X-ray Identification and Crystal Structure of Clay Minerals* (Edited by Brown, G.). Mineralogical Society, London.
- Nelson, F. M. and Eggertson, F. T. (1958) Adsorption measurements by a continuous flow method: *Anal. Chem.* **30**, 1387–1390.
- Sawhney, B. L. (1972) Selective sorption and fixation of cations by clay minerals: a review: *Clays and Clay Minerals* **20**, 93–100.

- Slabaugh, W. H. (1971) Surface chemistry of thermally decomposed organo-montmorillonite complexes: *Clays and Clay Minerals* **19**, 201–204.
- Thomas, J. 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.

Résumé—Le phénomène d'échange cationique entre le tris (éthylène-diamine) cobalt (III) et le sodium sur la montmorillonite a été étudié par spectrophotométrie d'absorption atomique, diffraction X, analyse thermique différentielle et sorption d'azote à 78°K.

L'échange de Na^+ par $\text{Co}(\text{en})_3^{3+}$ s'est révélé très favorable, avec une tendance vers la ségrégation des deux sortes de cations dans les argiles mixtes étudiées. On a trouvé que de petites quantités de $\text{Co}(\text{en})_3^{3+}$ abaissent la capacité de sorption pour l'azote de la montmorillonite Na^+ , tandis que les argiles riches en $\text{Co}(\text{en})_3^{3+}$ ont une sorption fortement augmentée. On fournit une explication de ce fait sur la base du double rôle que joue le $\text{Co}(\text{en})_3^{3+}$ dans la détermination de la nature et de l'intensité de la sorption de l'azote dans la montmorillonite ayant subi l'échange d'ion.

Kurzreferat—Der Kationenaustausch zwischen Tri(äthylendiamin)kobalt(III) und Na^+ bei Montmorillonit wurde durch atomische Absorptionsspektrophotometrie, Röntgenbeugung, differentielle Wärmeanalyse und Stickstoffsorption bei 78°K untersucht. Der Austausch von $\text{Co}(\text{en})_3^{+3}$ für Na erwies sich als außerordentlich günstig, und es besteht eine Tendenz zur Absonderung der beiden Kationenarten in den untersuchten gemischten Tonsorten. Kleine Mengen $\text{Co}(\text{en})_3^{+3}$ senken, wie erwiesen wurde, die Stickstoffsorptionsfähigkeit von Na^+ Montmorillonit, während Tonarten mit hohem $\text{Co}(\text{en})_3^{+3}$ Gehalt eine stark erhöhte Sorption aufwiesen. Dies wurde dadurch erklärt, daß $\text{Co}(\text{en})_3^{+3}$ bei der Bestimmung der Art und des Ausmaßes der Stickstoffsorption in dem ausgetauschten Montmorillonit eine doppelte Rolle spielt.

Резюме—Изучался процесс обмена катионов трис-(этилендиамин) кобальта (III) и Na^+ монтмориллонита посредством ядерной абсорбционной спектроскопии, рентгеновской дифракции, дифференциального термического анализа и сорбции азота при 78°K. Нашли, что обмен $\text{Co}(\text{en})_3^{+3}$ для Na^+ был очень благоприятный, но с тенденцией сегрегации двух видов катионов в изучаемых смешанных глинах. Заметили, что небольшое количество $\text{Co}(\text{en})_3^{+3}$ понижает способность сорбции азота монтмориллонитом Na^+ , в то время как высокое содержание $\text{Co}(\text{en})_3^{+3}$ в глинах очень повышает их сорбцию. Объясняется это двойной ролью $\text{Co}(\text{en})_3^{+3}$ в установлении какое количество азота абсорбируется обменным монтмориллонитом.