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INTERLAMELLAR AND MULTILAYER NITROGEN SORPTION BY HOMOIONIC MONTMORILLONITES

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Abstract—Nitrogen sorption by various homoionic montmorillonites was studied at 78°K. The adsorption isotherms in the relative pressure range $P/P_0 = 0{\cdot}05$–$0{\cdot}25$ were found to be either Type I or Type II in the BET classification. The nitrogen sorption process was considered to be predominantly interlamellar when described by a Type I isotherm. With a Type II isotherm, the adsorption was assumed to be predominantly on those surfaces not in the interlamellar regions.

It was concluded that only cations within a certain size range promote significant interlamellar nitrogen penetration in montmorillonites. The role of the smaller cations in nitrogen sorption by montmorillonites seems to be their influence on the external aggregate structures. Very large cations tend to clog up the interlamellar pores as well as some of the external voids.

INTRODUCTION

Nitrogen sorption by homoionic montmorillonites has been studied for many years, and it has been shown that the exchangeable cations associated with a given montmorillonite influence the nitrogen sorption capacity of the clay. Earlier investigators suggested that the exchangeable cations determined the size of the individual clay aggregates (i.e. the number of platelets per aggregate) and thus gave the observed variation in surface area with exchangeable cations for a given clay (Books, 1955; Mooney *et al.*, 1952). More recently, however, there has arisen some controversy over the exact role of exchangeable cations in nitrogen sorption by montmorillonites (Aylmore *et al.*, 1970; Thomas *et al.*, 1970). Central to the controversy has been the question of whether or not interlamellar nitrogen penetration is a significant factor in nitrogen sorption by homoionic montmorillonites. It has been suggested by Aylmore *et al.* (1970b) and Aylmore and Quirk (1967) that significant interlamellar nitrogen penetration does not occur in montmorillonites, but that the variation in nitrogen sorption with change in exchangeable cation is due to changes in the external aggregate structure caused at the time of flocculation with the exchangeable cation. Pore size distribution studies by these authors (Aylmore and Quirk, 1967) indicated that the orderliness of stacking of the clay particles was strongly dependent on the exchangeable cations present. The more random stacking gave higher 'external' surface areas and thus greater nitrogen sorption capacities.

In direct conflict with Aylmore's conclusions, Thomas and Bohor (1968) in the case of alkali and alkaline earth cations and Barrer and Millington (1967) in the case of small alkylammonium cations proposed that the external structure or external surface area of a given montmorillonite was essentially independent of the exchangeable cations present. For their respective situations they concluded that the observed variation in nitrogen sorption capacities was due to a variation in the degree of interlamellar nitrogen penetration. Knudson and McAtee (1973) have also observed that interlamellar nitrogen penetration readily occurs for a tris(ethylenediamine) cobalt(III)—montmorillonite.

The purpose of this work was to study nitrogen sorption by various homoionic montmorillonites in an attempt to find a simple way of distinguishing interlamellar from external nitrogen sorption. The ability to make such a distinction could lead to a better understanding of the role of exchangeable cations in the interaction of montmorillonites with other nonpolar gases, vapors and perhaps liquids. In this paper, the interlamellar space is considered to be those well organized regions of the dry clay matrix that give rise to the (00*l*) X-ray diffraction bands. Rolled or buckled plates, weathered edges, or structural faults are not considered part of the interlamellar space.

It has been shown by Knudson and McAtee (1973) that the nitrogen sorption isotherm for tris(ethylenediamine) cobalt(III), $Co(en)_3^{3+}$, montmorillonite was

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Type I in the classification of Brunauer, Emmett, and Teller (see, for example Gregg and Sing, 1967), while Na^+ montmorillonite was Type II. The difference in isotherm types was attributed to predominance of interlamellar sorption for the $Co(en)_3^{3+}$–clay and to predominance of external or multilayer sorption for the Na^+–clay. In the present work, several cation exchanged forms of a given montmorillonite were studied by nitrogen sorption in the relative pressure range $P/P_0 = 0{\cdot}05$–$0{\cdot}25$ and the resulting isotherms used to help determine the role of the various exchangeable cations in the nitrogen sorption process.

EXPERIMENTAL

The clay used in this study was a Wyoming bentonite which has been centrifuged, sodium exchanged and spray dried by Baroid Division of NL Industries. The various homoionic clays were prepared by shaking 2 g samples of the stock clay with 250 ml portions of 1 N solutions of the chloride salts of Na^+, Cs^+, Ba^{2+}, $Co(en)_3^{3+}$ and $(CH_3)_2NH_2^+$. The flocculated samples were allowed to stand overnight and were then washed by four successive centrifugations and redispersions in distilled water. The final centrifugates were dried at 50°C in an air circulation oven. The dried samples were lightly ground with a mortar and pestle to provide particles between 40 and 80 mesh in size.

The nitrogen adsorption was carried out in a Perkin–Elmer model 212 Sorptometer. The details of the procedure used have been described previously (Knudson and McAtee, 1973). Samples of the Na^+, Cs^+ and $(CH_3)_2NH_2^+$ clays were sent to Baroid Division, NL Industries for nitrogen adsorption isotherms for comparison with the Sorptometer results. The Baroid laboratory used a Micromeritics model 2100 surface area analysis instrument which is a static, vacuum system as opposed to the dynamic, gas flow Sorptometer. All the data presented in this paper were taken from the Sorptometer.

RESULTS AND DISCUSSION

Five nitrogen sorption data points in the relative pressure range $P/P_0 = 0{\cdot}05$–$0{\cdot}25$ were obtained for each homoionic montmorillonite. The clays could be divided into two groups according to these sorption results. In the given pressure range, the BET equation for Type II adsorption was found to describe closely nitrogen sorption for some of the montmorillonites, while the BET equation for Type I adsorption more satisfactorily described the sorption data for the remainder. Separation of the homoionic clays into two groups on the basis of isotherm type suggests some well defined difference in surface structures. The nature of this difference may be sought in the theoretical basis for the Types I and II adsorption equations.

The BET equation for Type II adsorption assumes adsorption in multilayers. It has been shown that this model is a good approximation when applied at low relative pressures (roughly $P/P_0 = 0{\cdot}05$–$0{\cdot}30$) and when adsorption is occurring on predominantly open surfaces where multilayer formation can occur freely. The external surfaces of montmorillonites (those surfaces not in the interlamellar regions) should allow multilayer adsorption with nitrogen.

The BET equation for the Type I isotherm differs from Type II in that only one layer of sorbate is assumed to be present. Historically, two systems have been found that give rise to Type I isotherms. One is chemisorption in which there are a finite number of sites with which a finite number of sorbate molecules may react. This situation is assumed not to be the case between nitrogen and montmorillonite. The second case is sorption on solids containing pores with dimensions which approach the dimensions of the sorbate molecules (Gregg and Sing, 1967). In such pores, multilayer formation is physically impossible. It is suggested that the interlamellar space of montmorillonites should fit this latter category.

In a practical sense, a perfect Type I isotherm probably would not be found for physical adsorption. While sorption is taking place in the micropores of a solid exhibiting Type I adsorption, multilayer sorption must necessarily be occurring on the external surfaces. Even though the majority of the total surface area may be in the micropores, adsorption on the external surfaces may well dominate at high relative pressures where multilayer formation is greatest (Barrer and Reay, 1958). Thus, the high relative pressure range of such isotherms would not be of much help in distinguishing between Types I and II behavior. Likewise, at very low relative pressures multilayer formation either does not occur or is insignificant. In this region the Types I and II equations are virtually identical. The relative pressure range used in this study ($0{\cdot}05 \leq P/P_0 \leq 0{\cdot}25$) gave a clear distinction between Types II and I adsorption. This distinction became quite obvious when the adsorption data were plotted in the linear forms of the Types II and I equations. With both plots on the same graph, a direct comparison of the fit of the data to the two equations could be made. Such comparative graphs were prepared for each clay in this study, and were used to assign the clays to Types I or II group. In

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detecting interlamellar nitrogen sorption by homoionic montmorillonites, the method of comparative plots was found to be in excellent agreement with conclusions based upon complete adsorption–desorption isotherms. The following sections on Na^+, Cs^+ and $(CH_3)_2NH_2^+$–montmorillonite illustrate this point.

Figure 1 shows the comparative plots of the nitrogen sorption data obtained for the sodium montmorillonite used in this work. The Type II equation gave the linear plot and was therefore assumed to define the adsorption process. The predominant process for nitrogen sorption on sodium–montmorillonite was thus concluded to be external sorption (i.e. not on the interlamellar surfaces). This conclusion has been generally agreed upon in the literature and is supported by complete N_2 isotherm studies (Brooks, 1955; Aylmore and Quirk, 1967; Barrer and MacLeod, 1954). The low surface area for the sodium clay also supports the lack of significant interlamellar sorption. The ideal surface area of montmorillonite, both external and interlamellar, is roughly 750 m^2/g (van Olphen, 1966) while in this work only 34 m^2/g could be measured by nitrogen sorption.

The comparative nitrogen sorption plots for the barium montmorillonite are shown in Fig. 2. The divalent barium cation is 0·8 Å larger in diameter than the sodium cation, yet Fig. 2 indicates that the interlamellar space has still not been opened up enough by the larger Ba^{2+} ions to allow detectable interlamellar penetration. The linearity of the Type II plot and the low surface area (29 m^2/g) provide evidence of no significant interlamellar sorption.

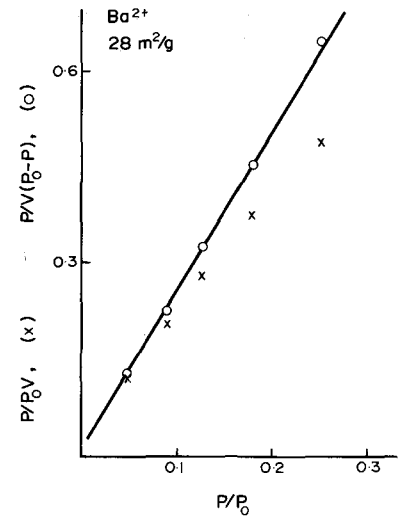


Fig. 2. Plots of nitrogen adsorption data for Ba^{2+}–montmorillonite.

There has been some question concerning interlamellar nitrogen penetration in cesium exchanged montmorillonite (Barrer and Reay, 1958; Thomas and Bohor, 1968). Comparative plots of our data for nitrogen sorption on cesium–montmorillonite are shown in Fig. 3. As for the sodium and barium clays, the Type II equation gives the linear plot. However, the surface area calculated from the nitrogen sorption data for the cesium–clay is 92 m^2/g, compared with 36 and 28 m^2/g for the sodium–and barium–clays respectively. In the previous samples, presence or absence of

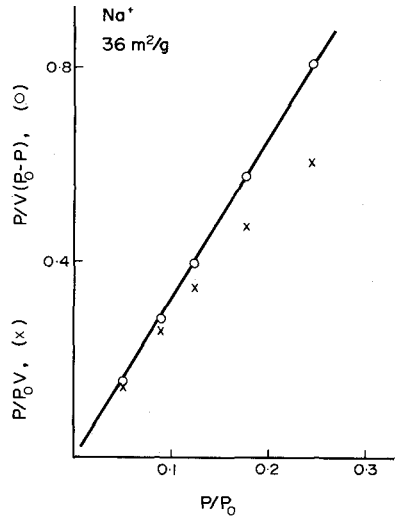


Fig. 1. Plots of nitrogen adsorption data for Na^+–montmorillonite.

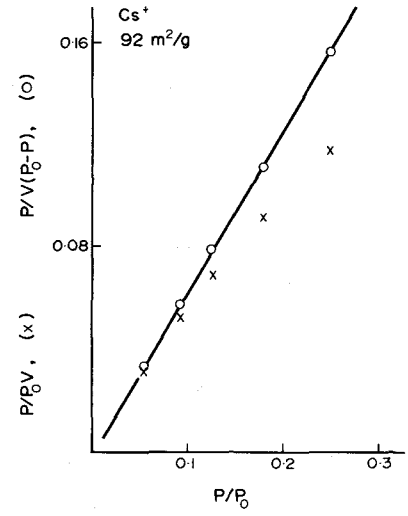


Fig. 3. Plots of nitrogen adsorption data for Cs^+–montmorillonite.

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interlamellar sorption was based on the type of isotherm and the surface area measured by nitrogen sorption. For cesium–montmorillonite, the Type II isotherm suggests no significant interlamellar penetration, a conclusion contradicted by the large increase in nitrogen sorption, attributed by Thomas and Bohor (1968, 1969) to such interlamellar sorption. There are at least two reasonable explanations for this contradiction. One is the possibility that the method of comparative plots as previously described in this paper is not sensitive enough to detect interlamellar sorption of the magnitude taking place in cesium–montmorillonite. Another possibility is that the ordering of the structural units of the clay aggregate is much more random in the cesium–clay than in the sodium and barium forms. This greater randomness would lead to a greater 'external' surface area and thus a greater external nitrogen sorption. The latter explanation has been suggested by Aylmore and Quirk (1967) and by Barrer and Reay (1958) on the basis of complete N_2 sorption isotherms.

Thomas and Bohor (1968 and 1969) propose that interlamellar N_2 sorption occurs in Cs–montmorillonite. Their conclusions are based on comparison of nitrogen and carbon dioxide sorption. The relative magnitudes of N_2 and CO_2 sorption by several homoionic clay minerals are used to support their conclusions. However, the data gave linear Type II plots, even for the extensive CO_2 sorption by Cs–montmorillonite. Further, their results for Li^+–montmorillonite were admittedly inconsistent with their model. Also, the literature contains some serious controversy over the significance of such CO_2 adsorption data (Thomas *et al.*, 1970; Aylmore *et al.*, 1970). Therefore, their data do not unequivocally establish interlamellar nitrogen sorption by Cs–montmorillonite.

Comparative plots of the nitrogen sorption data for a dimethylammonium–montmorillonite are given in Fig. 4. Interlamellar sorption is implied by the linear Type I plot and the large nitrogen sorption capacity. Barrer has conducted numerous studies of sorption by alkylammonium–montmorillonites and has included dimethylammonium–montmorillonite. Barrer and McLeod (1955) proposed that interlamellar sorption of nitrogen readily occurred for this clay. They did not report Type I isotherms, but, later, Barrer and Millington (1967) mentioned distorted plots resulting from the linear Type II equation. Their 'linear' plot curved upward at lower relative pressures than expected. In order to restudy this situation, the authors sent samples of the $(CH_3)_2NH_2^+$ clay to Baroid Div., NL Ind., Inc. for conventional nitrogen sorption analysis. The relative pressure range was $0{\cdot}005 \leq P/P_0 \leq 0{\cdot}35$. The Type I plot gave a definite region of linearity in the middle of this pressure range, while no region of linearity was observed for the Type II plot. Thus, in agreement with Barrer, interlamellar nitrogen penetration does occur in dimethylammonium–montmorillonite.

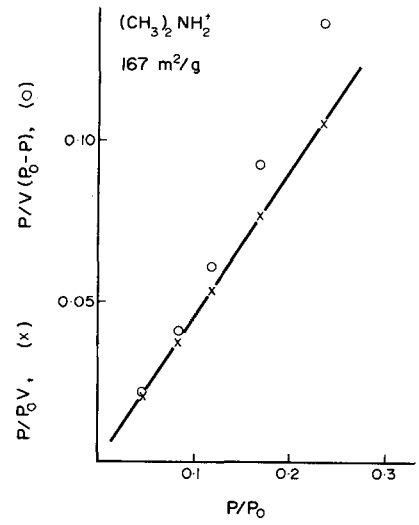


Fig. 4. Plots of nitrogen adsorption data for $(CH_3)_2NH_2^+$–montmorillonite.

Figure 5 illustrates the comparative plots for $Co(en)_3^{3+}$–montmorillonite. The Type I plot is linear, while the Type II plot distinctly turns upward. The nitrogen monolayer volume is similar to that of the $(CH_3)_2NH_2^+$–clay. It is concluded, therefore, that interlamellar nitrogen penetration also occurs in $Co(en)_3^{3+}$–montmorillonite. The monolayer volume

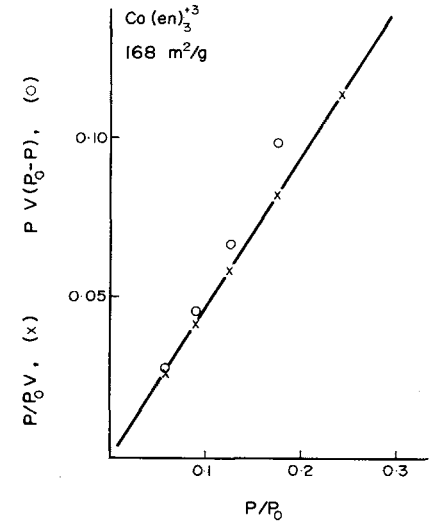


Fig. 5. Plots of nitrogen adsorption data for $Co(en)_3^{3+}$–montmorillonite.

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is still low compared to the total interlamellar area that theoretically should be available. Barrer and McLeod (1955) have discussed this problem in detail, but could account only in part for the difference between the observed and theoretical surface areas.

Figure 6 compares Type I and Type II plots for nitrogen sorption on a mixed $Co(en)_3^{3+}$–sodium–montmorillonite in which approximately 40 per cent of the exchange sites are occupied by $Co(en)_3^{3+}$. As in the case of the fully exchanged $Co(en)_3^{3+}$ clay, Type I plot is linear, but the monolayer nitrogen volume is much less, even less than the value observed for cesium–montmorillonite. This decreased monolayer volume has been attributed to segregation of $Co(en)_3^{3+}$ and Na^+ in montmorillonite (Knudson and McAtee, 1973). The importance of these observations for the partially exchanged $Co(en)_3^{3+}$–clay is that while the nitrogen monolayer volume is about one third that of the fully exchanged $Co(en)_3^{3+}$–clay, the amount of interlamellar sorption is still sufficient to cause a linear Type I and nonlinear Type II plot of the data. Thus, if the 60 m^2/g increase in surface area due to replacement of sodium by cesium on montmorillonite were due to interlamellar sorption, the level of such interlamellar sorption should result in a linear Type I plot and be detected by the method of comparative plots.

If linearity of Type I or Type II plots in the range $0{\cdot}05 \leq P/P_0 \leq 0{\cdot}30$ is a suitable technique for detecting significant interlamellar sorption of nitrogen in montmorillonites, then most of the variation in surface area of a montmorillonite containing various exchangeable cations the size of Cs^+ and smaller must be due to a cause other than varying degrees of interlamellar sorption. Edwards *et al.* (1965) have discussed in detail how different exchangeable cations would be expected to give different degrees of orderliness of clay plate stacking in the clay aggregate structure. They related these differences to different nitrogen sorption capacities. The importance of the arrangement of the clay plates in the dry clay aggregate in determining nitrogen sorption capacity has been demonstrated by Greene-Kelly (1964). In our laboratory a film, prepared by evaporation of an aqueous dispersion of Na–montmorillonite, had an extremely low surface area (4 m^2/g). If the same dispersion were centrifuged and the wet solids oven dried, a higher surface area resulted (34 m^2/g). In the former case, a very high orientation of the clay plates is probable, while much less orientation should have existed for the latter case. Similar results are reported by Greene-Kelly (1964).

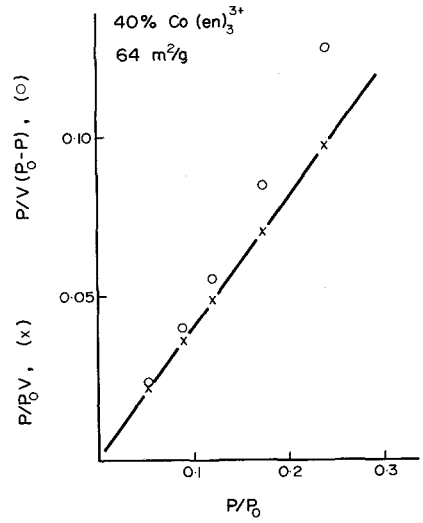


Fig. 6. Plots of nitrogen adsorption data for 40 per cent $Co(en)_3^{3+}$—60 per cent Na^+–montmorillonite.

Large plate separations are a necessary but not sufficient condition for interlamellar nitrogen penetration. The recent work of Slabaugh (1971) is a good example of large plate separations (16 Å) with no accompanying interlamellar penetration. Apparently the very large alkylammonium cations used by Slabaugh completely filled the interlamellar space created by the exchange. The surprisingly low surface areas obtained by Slabaugh (~ 1 m^2/g) indicate that even some of the aggregate pores described by Edwards *et al.* (1965), are also filled or plugged by the long alkyl chains of the cations. Barrer and Reay (1957) have similarly illustrated the clogging effect of large exchangeable cations in the clay interlayer. There thus appears to be an upper and a lower limit to the size of exchangeable cations that can induce free interlamellar nitrogen sorption in montmorillonites.

One apparent way around the clogging effect of large exchangeable cations would be to form a mixed clay containing a few large cations and many small cations in each interlayer. Ideally the few large cations would cause the same plate separation as at saturation, but the free space obtained by the remaining smaller inorganic cations should be available for nitrogen sorption. Attempts by Barrer and Brummer (1963) and Knudson and McAtee (1973) to accomplish this effect have failed. In both cases segregation of the large and small cations occurred.

The conclusions of Edwards *et al.* (1956) on the role of cation size and charge on the external aggregate structure of dry montmorillonites should apply to all exchangeable cations. However, the contribution of the external surface to the total nitrogen monolayer would be small and difficult to detect when a large amount of interlamellar surface is involved. The external aggregate structure of the trivalent $Co(en)_3^{3+}$–

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montmorillonite is probably quite different from that of the monovalent $(CH_3)_2NH_2^+$ montmorillonite. Quantitative determination of the relative contributions of external and internal sorption for each clay requires other methods than the technique discussed here. Possible methods are described by Barrer and Reay (1958) and Pierce (1959).

CONCLUSIONS

Comparison of Types I and II plots of nitrogen adsorption data in the relative pressure range of 0·05–0·30 can give a qualitative measure of whether or not interlamellar sorption is a significant part of the total sorption process on homoionic montmorillonites. Small amounts of interlamellar sorption and quantitative contributions of interlamellar sorption can not be readily determined by this method.

Significant interlamellar nitrogen sorption by homoionic montmorillonites occurs only for a narrow size range of exchangeable cations. These cations must cause large enough plate separations to allow nitrogen penetration, but they must not be so large as to fill completely (clog) the interlamellar voids.

There are probably two relatively independent mechanisms by which exchangeable cations influence nitrogen sorption by homoionic montmorillonites. One mechanism determines the external aggregate structure (i.e. randomness of sheet stacking), while the other controls the interlamellar pore size and thus the interlamellar nitrogen sorption.

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Résumé—On a étudié la sorption d'azote à 78°K par différentes montmorillonites homoioniques. Les isothermes d'adsorption dans le domaine des pressions relatives étudiées (P/P_0 = 0,05–0,25) sont soit du Type I, soit du Type II selon la classification BET. Ce phénomène de sorption d'azote est considéré comme principalement interlamellaire lorsqu'il est décrit par un isotherme du Type I; avec un isotherme du Type II, on suppose que l'adsorption a lieu principalement sur les surfaces non situées dans les régions interlamellaires.

On conclut que seuls des cations d'une certaine taille permettent une pénétration interlamellaire notable de l'azote dans les montmorillonites. Le rôle des cations plus petits dans la sorption de l'azote par les montmorillonites semble consister en l'influence qu'ils ont sur la structure externe des agrégats. Les très gros cations tendent à obstruer aussi bien les pores interlamellaires que les vides externes.

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Kurzreferat—Die Stickstoffsorption durch verschiedene homoionische Montmorillonite wurde bei 78°K untersucht. Die Adsorptionsisothermen im relativen Druckbereich P/P_0 = 0,05–0,25 entfielen entweder auf Typ I oder Typ II in der BET-Klassifikation. Der Vorgang der Stickstoffsorption wurde als vorwiegend interlamellar angenommen, wenn er sich durch eine Isotherme vom Typ I beschreiben ließ und vorwiegend an solchen Oberflächen ablaufend, die nicht im interlamellaren Bereich liegen, wenn eine Isotherme vom Typ II vorlag.

Es wurde geschlossen, daß nur Kationen in einem bestimmten Größenbereich ein signifikantes Eindringen von Stickstoff in den Zwischenschichtbereich von Montmorilloniten ermöglichen. Die Rolle kleiner Kationen bei der Stickstoffsorption von Montmorillonit scheint in ihrem Einfluß auf die äußeren Aggregatstrukturen zu liegen. Sehr große Kationen neigen dazu, sowohl unterlamellare Poren als auch einige äußere Hohlräume zu verstopfen.

Резюме — Изучается сорбция азота различными гомоионными монтмориллонитами при 78°К. Нашли, что изотермы адсорбции в сравнительном диапазоне давления (P/P_0 = от 0,05 до 0,25) были по классификации BET или типа I или II. В присутствии изотерма типа I процесс сорбции считается преимущественно межслойным. А изотерм типа II адсорбируется большей частью на поверхностях, а не между слоями.

В заключение решили, что только катионы в пределах определенного размера стимулируют межслойную пенетрацию в монтмориллонитах. Роль более малых катионов на сорбцию азота монтмориллонитами, кажется, является их влияние на наружную структуру агрегата. Очень крупные катионы имеют тенденцию засаривать поры промежуточных слоев и также некоторые наружные пустые пространства.

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