SURFACE AREA OF HOMOIONIC ILLITE AND MONTMORILLONITE CLAY MINERALS AS MEASURED BY THE SORPTION OF NITROGEN AND CARBON DIOXIDE

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Abstract – The surface areas obtained by application of the B.E.T. theory to adsorption isotherms of nitrogen and carbon dioxide gases at 77°K and 195°K respectively on homoionic samples of illite and montmorillonite clays have been examined. The isotherms were obtained using a standard volumetric adsorption system and the results are compared with those obtained by Thomas and Bohor (1968) using a dynamic sorption system.

Small amounts of residual water have been shown to have a marked influence on the accessibility of the internal surfaces of the montmorillonite clays to nitrogen and carbon dioxide adsorption. In this respect the standard outgassing procedure under high vacuum seems more efficient than that used in dynamic systems. The present data indicate that provided the sample has been satisfactorily outgassed there is little penetration of nitrogen or carbon dioxide gases into the quasi-crystalline regions of montmorillonite clays. With the exception of the caesium saturated montmorillonites the surfaces of the clays are more accessible to the smaller nitrogen molecules than to carbon dioxide assuming the values used for molecular area are correct.

In a recent paper Thomas and Bohor (1968) have examined the accessibility of the surfaces of homoionic montmorillonite clays to nitrogen and carbon dioxide adsorbates at 77°K and 195°K respectively using a dynamic measuring system (Nelson and Eggertsen, 1958). From variations in the surface area obtained by application of the B.E.T. (1938) theory to these measurements these authors considered that there was a certain degree of penetration of both nitrogen and carbon dioxide between the unit platelets or lamellae forming the crystals of montmorillonite. Their experimental data indicated that the extent of penetration was time dependent and also a function of the interlayer forces as governed by the size and charge of the replaceable cations.

Aylmore and Quirk (1967) have recently pointed out that in the dry state montmorillonite clay forms a complexly interwoven matrix in which one lamella may conceivably pass through several apparently crystalline regions. It is considered that the term "quasi-crystalline" (Aylmore and Quirk, 1969) may be the most appropriate description here since in these regions the lamellae are stacked in parallel array but not necessarily in perfect crystalline order. In these circumstances

the definition of apparent crystal size must be somewhat arbitrary. It was considered that the area determined by nitrogen adsorption at low temperatures was essentially a measure of the surface area external to these quasi-crystalline regions. The differences in specific surface area observed between montmorillonite saturated with different exchangeable cations was attributed partly to differences in the degree of association of the lamellae in aqueous suspensions (Edwards, Posner and Quirk, 1965) and the subsequent statistical arrangement of the units on drying, and partly to variations in accessibility of areas of overlap of quasi-crystalline regions with size of the exchangeable cations.

Since the data reported by Thomas and Bohor (1968) was obtained using a dynamic sorption system (Nelson and Eggertsen, 1958) the results of similar sorption measurements obtained using a standard volumetric adsorption system are reported here.

MATERIALS

The clay samples used were obtained from the following natural deposits.

Fithian illite – from Ward's Natural Science

Establishment Inc., Illite No. 35 of the American Petroleum Institute Research Project No. 49 (1951).

Willalooka illite – B horizon from a solonized solonetz: Hundred of Laffer, South Australia.

Wyoming bentonite – montmorillonite from the John C. Lane Tract, Upton, Wyoming. Standard clay mineral No. 25b of the American Petroleum Institute Research Project No. 49.

Redhill montmorillonite – from Redhill, Surrey, England: supplied by Fullers Earth Company.

In general, samples of the clays were sodium saturated by repeated washing and centrifuging with molar sodium chloride during which the pH of the suspension was adjusted to 3·0 using hydrochloric acid. The samples were washed and dialysed against distilled water using Visking cellulose casing, and the $< 2\mu$ fractions obtained by accurate sedimentation. In addition, several size fractions of the sodium saturated Wyoming bentonite clay were obtained by centrifugation as described by Laffer, Posner and Quirk (1969). Samples saturated with other cations were prepared from these materials by washing with the appropriate molar chloride solution and finally dialysing against distilled water as before.

The air-dried clays were gently ground to a powder, equilibrated with 0·75 relative water vapour pressure and compressed into 200 mg cores at 1200 atmosphere pressure by means of an hydraulic jack (Aylmore and Quirk, 1962).

PROCEDURE

The volumetric apparatus used (Aylmore 1960) was based on the original apparatus of Emmett and Brunauer (1934) and incorporated many of the refinements suggested by Harkins and Jura (1944) and Joyner (1949), including a mercury cut-off between the sample tube and mercury manometer to minimize free space volume. Saturation vapour pressures were measured by means of a vapour pressure thermometer.

In general, the clays were outgassed overnight at 300°C and 10^{-6} mm mercury pressure. Provided the pressure in the system remained below 10^{-3} mm mercury pressure after 30 min isolation from the pumps the sample was regarded as thoroughly outgassed. Previous determinations have shown that further outgassing for an extended period produces no significant change in the specific surface area obtained.

Nitrogen adsorption isotherms were determined by the usual doser technique after immersing the sample bulb in a liquid nitrogen bath. The sample was then allowed to return to room temperature and re-evacuated for 30 min to remove adsorbed nitrogen. Carbon dioxide adsorption isotherms at

195°K were obtained by immersing the sample bulb in a gently stirred solid carbon dioxide-ethanol slush. The saturated vapour pressure of carbon dioxide was taken as 760 mm. In some cases the entire procedure was repeated to check that the sorptive properties of the clay were unaltered by the previous sorption determination.

RESULTS AND DISCUSSION

The surface areas obtained by application of the B.E.T. theory to the nitrogen and carbon dioxide absorption isotherms on homoionic illite and montmorillonite clays are given in Table 1. The B.E.T. plots so obtained all had positive intercepts with C-values ranging from 20 to several hundred. In general the C-values for the nitrogen plots were higher than those for carbon dioxide. Surface areas were calculated using molecular areas of 16·2 Å² for nitrogen adsorption at 78°K and 22·1 Å² for carbon dioxide adsorption at 195°K. These values are the most consistently accepted in the literature and make the results directly comparable with those of Thomas and Bohor (1968).

Because of the time dependence of adsorption observed by Thomas and Bohor, the approach of equilibrium for a number of points on each isotherm were followed carefully for periods up to 48 hr. For the illite clays where there is little likelihood of penetration of adsorbate within the crystal structure, equilibrium pressures were always obtained within a period of some 20 min or less. Subsequent variations in relative vapour pressure within the volumetric system were considerably less than the limits of experimental error.

In the case of the montmorillonite clays the time

Table 1. B.E.T. surface areas from nitrogen and carbon dioxide adsorption on $< 2\mu$ fractions of homoionic illite and montmorillonite clays

Clay	Surface area, m²/g	
	Nitrogen adsorption	Carbon dioxide adsorption
Sodium Fithian illite	105	72·4
Sodium Willalooka illite	195	162
Caesium Willalooka illite	184	159
Sodium Wyoming bentonite	39·8	40·6
Caesium Wyoming bentonite	99·1	189
Sodium Redhill montmorillonite	147	132
Caesium Redhill montmorillonite	158	215

required for equilibration varied with the exchangeable cation present on the clay surface. For the sodium saturated samples a definite equilibrium, within the limits of experimental error, was established in less than 20 min for both nitrogen and carbon dioxide adsorption. On the other hand longer equilibration times up to some 4 hr were required for the initial dose for the caesium saturated samples for both nitrogen and carbon dioxide adsorption, indicating that some regions were less readily accessible than others. This was evidenced by a very small but measurable uptake after the initial rapid sorption. Equilibrium on subsequent points was again well established within 20 min.

The differences in B.E.T. specific surface area estimated on the basis of amounts adsorbed after periods of 30 min and 16 hr respectively were in all cases very small. The maximum difference observed was for example for carbon dioxide adsorption on 0.14μ–0.27μ e.s.d. caesium saturated Wyoming bentonite*, the sample equilibrated for 30 min giving a surface area of 198 m^2/g and that equilibrated for 16 hr giving 206 m^2/g. Other differences were generally less than 0.5 per cent of the 30 min value.

Previous investigations by others (Barrer and McLeod, 1955; Brooks, 1955) and in these laboratories, have shown that the sorption of non-polar gases and hence the B.E.T. area obtained for a montmorillonite clay is particularly dependent on the efficiency of the outgassing procedure used. Brooks (1955) noted that the specific surface area of Ca-Wyoming bentonite increased to a value of about 120 m^2/g with decreasing hydration due to the accessibility to nitrogen of surfaces propped apart by water molecules, before decreasing to a value of 41.3 m^2/g on effectively complete desorption. Similar effects have been noted in these laboratories in detailed studies of the surface areas of both illite and montmorillonite clays with small amounts of presorbed water. Invariably the specific surface area increased to a maximum with the gradual removal of adsorbed water from the clay surfaces, followed by a decrease due to the collapse of regions between surfaces propped apart by the last remaining water molecules.

In view of the results obtained by Thomas and Bohor (1968) and the different outgassing procedure used in the dynamic system the effect of incomplete outgassing on the relative sorption of nitrogen and carbon dioxide was investigated. The changes in nitrogen and carbon dioxide B.E.T. specific surface areas with percentage residual

water based on the weight of sample outgassed at 300°C and 10^{-6} mm mercury pressure are shown in Fig. 1. After outgassing at room temperature for 30 min the area obtained using carbon dioxide is considerably greater than that using nitrogen. During the initial stages of further dehydration at 50°C and then at 110°C the nitrogen area increased rapidly, presumably due to the increased accessibility of surfaces previously blocked by water molecules. The carbon dioxide area increases slightly at first for the same water loss between room temperature and 50°C suggesting that the presence of the water molecules causes sufficient separation of some surfaces to enable the penetration of the more strongly adsorbed carbon dioxide. However, further dehydration above 110°C causes a decrease in specific surface area as these regions collapse and become inaccessible to the larger carbon dioxide molecules. The magnitude of the area involved suggests that in this case it may be only the surfaces between quasi-crystalline regions (i.e. within discontinuities in ordering) which are involved and that much of the internal area of the clay matrix is in fact not accessible to nitrogen or carbon dioxide adsorption.
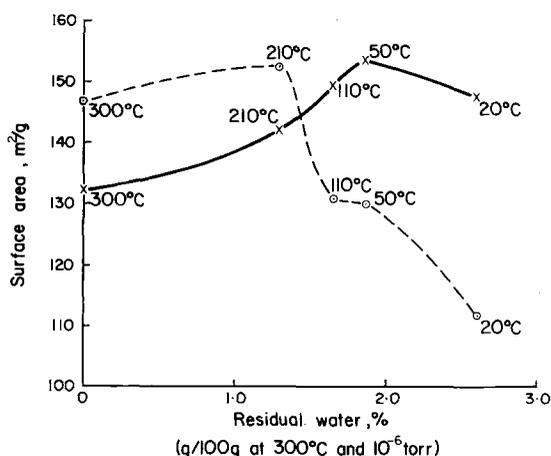

Fig. 1. Changes in nitrogen and carbon dioxide specific surface areas of sodium Redhill montmorillonite with percentage residual water based on the weight of sample outgassed at 300°C and 10^{-6} torr. O Nitrogen; × Carbon dioxide.

The outgassing procedure used in dynamic sorption systems involves the passing of a stream of helium gas over the heated sample usually at pressure of 5–10 p.s.i. Under these conditions the mean free path for water vapour movement and hence the rate of desorption of water from the clay surfaces, would be considerably less than in systems evacuated at 10^{-6} mm mercury pressure

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*The CO_2 surface area for < 2μ Cs Wyoming bentonite is 189 m^2/g.

at any given temperature. Thus it seems likely that the samples of montmorillonite examined by Thomas and Bohor contained considerably more residual water than those in the present study. This is also indicated by the observation that the data of Thomas and Bohor for temperature effects follow the same general trends as shown in Fig. 1 except that the temperatures at which the final stages of dehydration and collapse of regions propped apart by residual water molecules occur, are higher for the dynamic outgassing procedure. That is, the nitrogen surface areas for most clays show a slight increase as the temperature of outgassing increases from 110°C to 175°C followed by a decrease at the highest temperatures (300°C–500°C). The carbon dioxide areas decrease considerably and continuously as the outgassing temperature is raised.

Comparison of the specific surface areas given in Table 1 shows that with the exception of the caesium saturated montmorillonites the internal areas of the completely outgassed clay cores are less accessible to the larger carbon dioxide molecule than to nitrogen, i.e. assuming the given values for molecular area. Even for the non-expanding illite clays there are obviously regions of overlap of the clay crystals which are accessible to nitrogen but not to carbon dioxide. Only for the caesium montmorillonites which apparently have a much less well ordered packing arrangement, is the greater affinity of the carbon dioxide molecule for the surface more effective in penetrating between the quasi-crystalline regions.

Thomas and Bohor (1968) in comparing the marked tailing of the adsorption peak which they obtained with Cs-montmorillonite suggest that there is no reason to believe that this is due to a significant difference in the mean particle size or in pore characteristics (greater proportion of micropores) that evolves during sample preparation. However, specific surface areas obtained by measurements of chloride exclusion from homoionic Wyoming Bentonite in aqueous suspension (Edwards, Posner & Quirk, 1965) indicate that there is a marked variation in the degree of association of the lamellae with the size and charge of the exchangeable cation. The size of these units in aqueous solution could be expected to have some influence on the porous structure formed on drying. Since these chloride exclusion areas are invariably much larger than the nitrogen areas obtained on the dried clay we may infer that overlap of these units results in larger quasi-crystalline regions.

In addition, the pore size distributions obtained by Aylmore and Quirk (1967) on Cs and Na saturated montmorillonites indicate that there is a far greater proportion of micropores of less than 10 Å plate separation, presumably between quasi-crystalline regions, which is available to rapid nitrogen adsorption, in the Cs clays than in the Na clays. As pointed out by these authors the distinction between internal and external surfaces is essentially one of alignment of the lamellae and its effect on the accessibility of these surfaces to the adsorbate. The larger Cs cation results in greater accessibility of the areas of overlap between quasi-crystalline regions but it is apparent from Table 1, that even here much less than the total interlamellar surface area of more than 700 m^2/g is available to nitrogen adsorption, even doubling the values of 99 m^2/g and 158 m^2/g on the assumption that a single layer is adsorbed between two adjacent surfaces. Even for the more strongly absorbed carbon dioxide, it is evident that the surface area remains inaccessible.

In Table 2, the specific areas obtained from nitrogen and carbon dioxide adsorption on homoionic samples of the different size fractions of the Wyoming bentonite clay are given. One particularly interesting feature is the small area and slight variation in area obtained by nitrogen adsorption for the different sodium fractions despite electron microscopic confirmation that the lateral dimensions of the lamellae forming the smaller size fractions were of the order of one tenth those of the larger fraction. The authors have repeatedly observed this reproducibility in surface area for a given homoionic montmorillonite despite wide variations in the preparative technique. Thus, it is apparent that the exchangeable cation on the clay surface can be more important in determining the accessibility of the dry clay matrix to gas sorption than the lateral dimensions of the lamellae.

Table 2. B.E.T. surface areas from nitrogen and carbon dioxide adsorption on different size fractions of Wyoming bentonite obtained by centrifugation

Size fraction	Exchangeable cation	Surface area m^2/g	
		Nitrogen adsorption	Carbon dioxide adsorption
0·14 μ–0·27 μ e.s.d.	Na⁺	39·8	41·1
	Cs⁺	120	207
0·041 μ–0·065 μ e.s.d.	Na⁺	44·6	54·9
	Cs⁺	147	228

CONCLUSIONS

Provided the sample has been satisfactorily outgassed there is little penetration of nitrogen or carbon dioxide gases into the quasi-crystalline

regions of these montmorillonite clays. The gas sorption which does occur appears, with the possible exception of the Cs montmorillonites, to be essentially between rather than into quasi-crystalline regions. Although it is reasonable to expect that there will be some delayed diffusion of even non-polar adsorbates into less accessible surfaces of the clay matrix the present data indicate that this is very small for all but the caesium clays. Under these conditions the sorption of such gases can be used to estimate the external surface area of these regions.

The increase in area which occurs with initial outgassing is probably due to the removal of water from and hence the greater accessibility of the surfaces between quasi-crystalline regions in the same way as it is for nonexpanding crystals such as illites. Subsequently the presence of a few residual water molecules will allow some penetration between lamellae forming quasi-crystals (see Brooks, 1955).

When the removal of adsorbed water is essentially complete the surface area obtained will depend, for a given clay, and on the size and charge of the exchangeable cations and their effects on the porous matrix formed during preparation, and the size of the adsorbate molecules. Differences in area obtained with different sorbate molecules will occur as a result of variations in molecular exclusion from the smallest micropores between crystals and quasi-crystalline regions and in micropore filling (see Dubinin, 1967). For this reason the surface area of the clays is generally more accessible to nitrogen than to carbon dioxide.

In the case of larger exchangeable cations such as caesium the imperfections in packing of the lamellae are sufficiently large to permit a more extensive penetration of the gases into the clay matrix. However, even for carbon dioxide sorption the increase in volume sorbed after 16 hr is very small compared with that after 30 min and much of the clay matrix remains essentially inaccessible.

The penetration of gas molecules between the lamellae is enhanced by the presence of residual water molecules and it seems likely that the out-gassing used in dynamic systems is less efficient than standard procedures under high vacuum.

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Résumé—Les ares de surface obtenues par l'application de la théorie B.E.T. aux isothermes d'adsorption du nitrogène et du gaz carbonique, à 77°K et 195°K respectivement, sur des échantillons homoioniques d'argiles illite et montmorillonite, ont été étudiées. Les isothermes ont été obtenus en utilisant un système standard d'adsorption volumétrique et les résultats sont comparés à ceux obtenus par Thomas et Bohor (1968) qui emploient un système d'adsorption dynamique.

De petites quantités d'eau résiduelle ont fait apparaître une influence marquée sur l'accessibilité des surfaces internes des argiles montmorillonites à l'adsorption du nitrogène et du gaz carbonique. A cet égard, la méthode de dégazéification standard, sous un vide élevé, semble plus efficace que celle utilisée dans les systèmes dynamiques. Les données actuelles indiquent que, pourvu que l'échantillon ait été dégazéifié d'une manière satisfaisante. il se produit une faible pénétration de gas carbonique et de nitrogène dans les régions quasi-cristallines des argiles montmorillonites. A l'exception des mont-

morillonites saturés de Cs, les surfaces des argiles sont plus accessibles aux plus petites molécules
de nitrogène qu'au gaz carbonique en supposant que les valeurs utilisées pour le are moléculaire
soient correctes.

Kurzreferat— Die durch Anwendung der B.E.T. Theorie auf Adsorptionsisothermen von Stickstoff
und Kohlendioxyd Gasen bei 77°K bzw. 195°K an homoionische Proben von Illit und Montmorillonit
Tonen erhaltenen Oberflächen wurden untersucht. Die Isothermen wurden unter Anwendung eines
Standard volumetrischen Adsorptionssystems erhalten, und die Resultate werden mit jenen durch
Thomas und Bohor (1968), unter Verwendung eines dynamischen Sorptionssystems erhaltenen,
verglichen.

Es konnte festgestellt werden, dass kleine Mengen von Restwasser einen deutlichen Einfluss auf
die Zugänglichkeit innerer Oberflächen der Montmorillonit Tone für die Adsorption von Stickstoff
und Kohlendioxyd ausüben. In dieser Hinsicht scheint das Standard Ausgasungsverfahren im Hoch-
vakuum wirksamer zu sein als das in dynamischen Systemen verwendete. Die gegenwärtig verfüg-
baren Werte deuten darauf hin, dass, vorausgesetzt die Probe ist genügend ausgegast worden, nur
geringfügige Eindringung von Stickstoff oder Kohlendioxyd Gasen in die quasikristallinen Bereiche
der Montmorillonit Tone stattfindet. Mit der Ausnahme der an Caesium abgesättigten Montmorillon-
ite sind die Oberflächen der Tone für die kleineren Stickstoffmoleküle besser zugänglich als für
Kohlendioxyd, angenommen, dass die für die Molekülfläche verwendeten Werte korrekt sind.

Резюме—Изучены поверхностные области, выявленные при применении теории В.Е.Т. к
анализу изотерм адсорбции газов NO_2 и CO_2 при 77°К и 195°К, соответственно, для гомо-
ионных образцов иллитовых и монтмориллонитовых глин. Изотермы сняты с использованием
стандартной волюметрической адсорбционной системы и полученные результаты сравнимы
с результатами, полученными Томасом и Боором (1968) при использовании динамической
сорбционной системы.

Показано, что небольшие количества остаточной воды оказывают заметное влияние на
чувствительность внутренних поверхностей монтмориллонитовых глин к поглощению
NO_2 и CO_2. В связи с этим стандартная методика дегазации в условиях высокого вакуума
очевидно является более эффективной, чем методика, используемая в динамических системах.
Полученные данные показывают, что при условии удовлетворительной дегазации образца
имеет место лишь незначительное проникновение газов NO_2 и CO_2 в квази-кристаллические
области монтмориллонитовых глин. За исключением монтмориллонита, насыщенного
катионами цезия, поверхности глин более чувствительны к небольшим молекулам NO_2,
чем к молекулам CO_2, при предположении, что значения, используемые для молекулярных
поверхностей, являются правильными.