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RELATION BETWEEN SWELLING, SURFACE AREA AND *b* DIMENSION OF Na-MONTMORILLONITES*

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Abstract—From swelling and surface area measurements, it was found that the swelling of a montmorillonite depends linearly on the fraction of its layers that fully expand in water and that this fraction, in turn, depends linearly on the *b* dimension of the unit cell. Therefore, swelling is a linear function of the *b* dimension. However, the specific surface area of a montmorillonite is a linear function of its *b* dimension only if no partially expanded layers exist. It was also found that the distance between fully expanded layers at a given applied pressure is the same for all montmorillonites.

Key Words—Expansion, Interlayer, Montmorillonite, Surface, Swelling.

INTRODUCTION

Previous studies in this laboratory have shown that the swelling of montmorillonite is linearly related to the *b* dimension of its unit cell (Davidtz and Low, 1970; Ravina and Low, 1972). The same is true of the specific expansibility of the interlayer water (Ruiz and Low, 1976) and of the liquid limit of a montmorillonite paste (Margheim, 1977). These relations can be explained by assuming that epitaxy exists between water and montmorillonite (Ravina and Low, 1972) and that, as a result, the *b* dimension of the montmorillonite affects the structure of the water and all properties that depend on it. However, there is the possibility that the *b* dimension governs the proportion of expanded layers in the montmorillonite crystal and, thereby, all properties that depend on surface area. It was to examine this possibility that the present study was undertaken.

MATERIALS AND METHODS

The origins of the montmorillonites used in this study and some of their properties are listed in Table 1. The Panther Creek montmorillonite was obtained from The American Colloid Co. All of the others were obtained from Ward's Natural Science Establishment. The Cameron montmorillonite, which is known to contain some illite-like layers (Schultz, 1969), was prepared by Lerot and Low (1976). With the exception of the Panther Creek montmorillonite, the others were suspended in a 0.1% solution of Calgon (technical sodium metaphosphate), washed once with a 2 N solution of NaCl and then fractionated in a centrifuge by the method of Jackson (1969). Thereafter, the <2-μm fraction was converted completely to the sodium form by washing it twice with a 2 N solution of NaCl and then with deionized water until it was salt free. Washing was accomplished by centrifugation and decantation. Water was removed from the resulting montmorillonite by freeze-drying.

The preparation procedure for the Panther Creek montmorillonite differed from that described above in that all separations were accomplished by gravitational rather than centrifugal sedimentation. Also, excess NaCl was removed by dialysis.

The specific surface area of the <2-μm, sodium-saturated montmorillonites was measured by four methods.

Method I

This method was the same as that described by Carter et al. (1965), except that we equilibrated the 2-ethoxyethanol with the montmorillonite for 40 days instead of 4 hr. Periodic weighings showed that, to achieve true equilibrium, this period of time was necessary. The montmorillonite retaining the most 2-ethoxyethanol was assumed to have the theoretical specific surface area, i.e., 8×10^6 cm^2/g. The specific surface areas of the other montmorillonites were obtained by using this montmorillonite as standard and assuming that specific surface areas were in the same ratio as the amounts of 2-ethoxyethanol retained.

Method II

The montmorillonite was dispersed in deionized water, enough glycerol was added to more than saturate it and the resulting suspension was allowed to evaporate to an oriented film on a glass slide. The slide was mounted in a Siemens X-ray diffractometer and the first seven orders of the *c*-axis spacing of the montmorillonite were determined using Cu$K\alpha$ radiation. Since none of the montmorillonites exhibited a rational sequence of spacings (with the possible exception of those identified as Upton, Belle Fourche and Panther Creek), random interstratification of 10 Å and 17.9 Å layers was indicated. Therefore, the peak migration curves of Brown and MacEwan (1951) were used to determine the fraction of expanded layers. The specific surface area was assumed to be equal to this fraction multiplied by the theoretical specific surface area (8×10^6 cm^2/g).

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Table 1. Origins and properties of the Na-saturated, <2-μm fraction of the montmorillonites used in this study.

Origin	API No.	Measured CEC (meq/100g)		Theoretical CEC (meq/100g)	b-dimension (A)
Upton, WY	25	84*	84†	102	8.9805
Belle Fourche, SD	27	85	73	95	8.9815
Panther Creek, MS	—	—	77	87	8.9879
Polkville, MS	21	90	90	141	8.9885
Otay, CA	24	112	111	160	8.9940
Cameron, AZ	31	68	64	167	9.0180

* Values in this column are from Margheim, J. (1973).
† Values in this column are from this study.

Method III

If the surface charge density is essentially the same for all layers within a montmorillonite crystal, the ratio of the observed cation exchange capacity to the theoretical cation exchange capacity, calculated from the elemental composition, must equal the fraction of expanded layers. This fraction, multiplied by the theoretical specific surface area (8×10^6 cm^2/g), gives the actual or accessible specific surface area.

The cation exchange capacities of the montmorillonites that we used had already been measured by Margheim (1973). However we measured them again by determining the amounts of methylene blue that they adsorbed. Our procedure was the same as that of Brindley and Thompson (1970). The theoretical cation exchange capacities of all but the Panther Creek montmorillonite were calculated from the elemental compositions reported by Schultz (1969). The theoretical cation exchange capacity of the Panther Creek montmorillonite was calculated from the elemental composition reported by Foster (1953) for Aberdeen montmorillonite because the two montmorillonites come from the same formation. Both measured and theoretical cation exchange capacities are given in Table 1. In keeping with the concepts mentioned earlier, we divided the measured cation exchange capacities by the corresponding theoretical cation exchange capacities and multiplied the results by the theoretical specific surface area (8×10^6 cm^2/g) to obtain the respective specific surface areas.

Method IV

The work of Lerot and Low (1976) provided the basis for this method. They showed theoretically that the absorption of infrared radiation by suspended montmorillonite particles should obey Beer's law. Then they assumed that the interparticle water obeyed the same law and formed the ratio

$$(A_m/A_w) = (\epsilon_m/\epsilon_w)\,(m_m/m_w) \qquad (1)$$

where A is the absorbance, ϵ is the absorptivity, m is the mass and the subscripts m and w designate the montmorillonite and water, respectively. Consistent with this equation, a straight line was obtained when measured values of A_m/A_w were plotted against m_m/m_w for values of m_m/m_w below $\approx$0.1 g/g. The values of A_m and A_w were measured at 1050 cm^{-1} and 1650 cm^{-1}, respectively. The former corresponds to Si—O absorption, whereas, the latter corresponds to H–O–H (bending) absorption.

Lerot and Low (1976) also showed theoretically that

$$\epsilon_m = \{1 - \exp(-\beta_m\delta_m)\}/2.3\rho_m\delta_m \qquad (2)$$

where β_m, δ_m, and ρ_m are the true linear absorptivity, thickness and density of the crystal layers, respectively. The magnitude of $\beta_m\delta_m$ is unknown. We were unable to find in the literature a value of β_m for Si—O absorption at the specified wavelength. They assumed that $\beta_m\delta_m \ll 1.0$. However, it is convenient for us to assume that $\beta_m\delta_m \gg 1.0$. Then Eq. 2 reduces to

$$\epsilon_m = 1/2.3\rho_m\delta_m \qquad (3)$$

and since $1/\rho_m\delta_m = S_m/2$, where S_m is the specific surface area of the montmorillonite,

$$\epsilon_m = 0.217S_m. \qquad (4)$$

Combining Eq. 1 and 4 we have

$$(A_m/A_w) = (0.217S_m/\epsilon_w)(m_m/m_w). \qquad (5)$$

It is known that ϵ_w is quite insensitive to structural perturbations in water (Falk and Ford, 1966) and can, as a first approximation, be regarded as constant. Therefore,

$$S_m = \alpha(A_m m_w/A_w m_m) \qquad (6)$$

where α is a proportionality constant.

We used a Perkin-Elmer infrared spectrophotometer (Model 180) to measure A_m and A_w for montmorillonite-water mixtures in which $m_w/m_m > 10$ g/g. From the results, corresponding values of $A_m m_w/A_w m_m$ were calculated. The montmorillonite with the highest value of $A_m m_w/A_w m_m$ was assigned the theoretical specific surface area (8×10^6 cm^2/g). This assignment permitted the calculation of α and, subsequently, the calculation of the specific surface area of the other montmorillonites by means of Eq. 6.

The dry-state *b* dimensions of all but the Panther Creek montmorillonite were determined by Margheim (1977). We used his method to determine the *b* dimension of this montmorillonite. All determinations were made on samples which were kept dry by silica gel. The results are collected in Table 1.

The swelling of the different montmorillonits in water was determined at a water tension of 42.6 cm by means of a tensiometer in which a blotter served as membrane. The swelling of these montmorillonites in methanol, 2-ethoxyethanol and 98% formamide was determined at a tension of 6 cm of solvent by the same means except that the solvent replaced the water and a fritted glass filter replaced the blotter. In all cases, about 1 week

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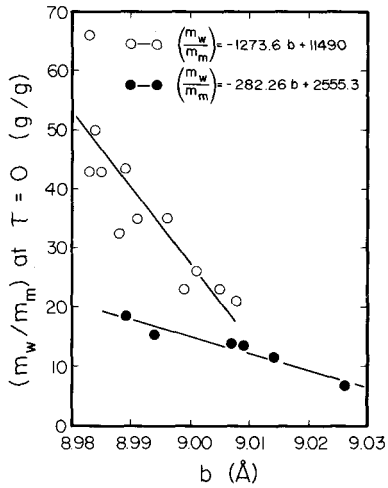


Fig. 1. The relation between m_w/m_m, the mass ratio of water to montmorillonite, and b, the *b*-dimension of montmorillonite, when τ, the water tension, is zero (●, data of Ravina and Low [1972]; ○, calculated from data of Foster [1953].

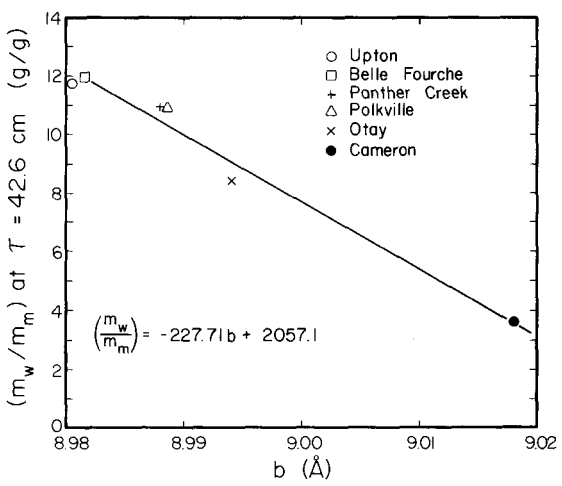


Fig. 2. The relation between m_w/m_m, the mass ratio of water to montmorillonite, and b, the *b*-dimension of montmorillonite, when τ, the water tension, is 42.6 cm of water.

equilibration time was allowed. Only the results with 2-ethoxyethanol were duplicated.

RESULTS AND DISCUSSION

Equilibrium values of m_w/m_m for montmorillonites that had swelled under a water tension, τ, of zero are plotted against the *b* dimension of their respective unit cells in Figure 1. The closed circles represent values of m_w/m_m measured by Davidtz and Low (1970) combined with *b* dimensions measured by Ravina and Low (1972). The open circles represent values of m_w/m_m derived from the swelling volumes reported by Foster (1953) combined with *b* dimensions calculated by using her data on elemental composition in the empirical equation of Radoslovich (1962), viz.,

$$b = (8.944 + 0.096\ Mg_{VI}^{2+} + 0.096\ Fe_{VI}^{3+} + 0.037\ Al_{VI}^{3+} \quad (7)$$

in which b is the observed *b* dimension, Mg_{VI}^{2+} and Fe_{VI}^{3+} represent the atoms of divalent magnesium and trivalent iron, respectively, in octahedral positions and Al_{IV}^{3+} represents the atoms of trivalent aluminum in tetrahedral positions per unit cell. Despite the difference in the two sets of data (which is believed to be attributable to a difference in experimental procedure) it is evident that, in each case, the equilibrium value of m_w/m_m is linearly related to b. This relation is substantiated by the results of the present study which are presented in Figure 2. It will be substantiated further in a forthcoming paper by J. F. Margheim and the junior author.

In Figure 3, values of S_m measured by each of the four methods are plotted against the corresponding values of b. The respective best-fitting lines were determined by linear regression. Note that, regardless of the method used to obtain the data, the result is the same, namely, a linear decrease in S_m with increasing b.

Of the four methods, Method I is considered to be the most reliable. Method II is only qualitative because all of the layers in a montmorillonite crystal may not be randomly interstratified with *c*-axis spacings of 10 Å and 17.9 Å, as assumed. Method III is subject to error because all of the montmorillonite layers may not have the same charge density, as assumed; or the elemental compositions from which the theoretical cation exchange capacities are derived may not be accurate be-

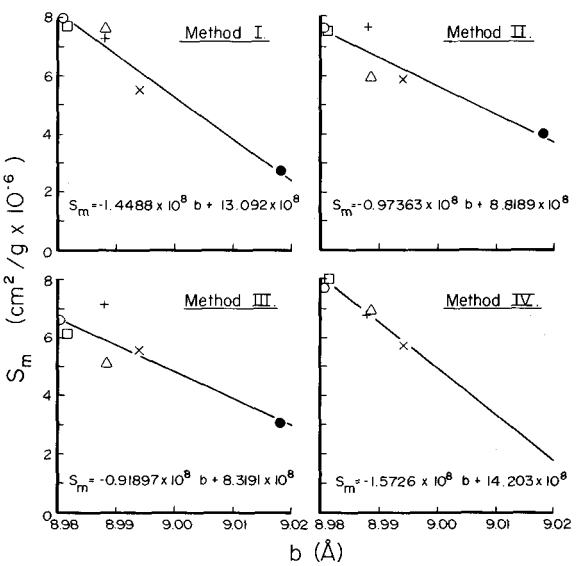


Fig. 3. The relation between S_m, the specific surface area, and b, the *b*-dimension of montmorillonite, as determined by the four methods of this study (see Figure 2 for definition of symbols).

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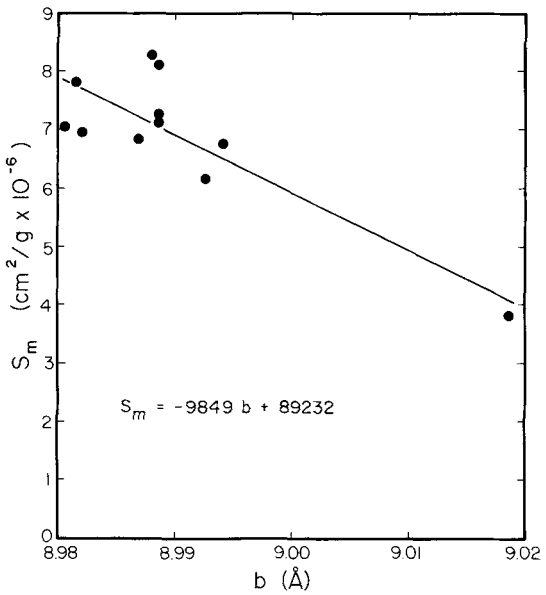


Fig. 4. The relation between S_m, the specific surface area, and b, the *b*-dimension of montmorillonite (data on S_m from Philen et al. [1971]; data on b from different sources).

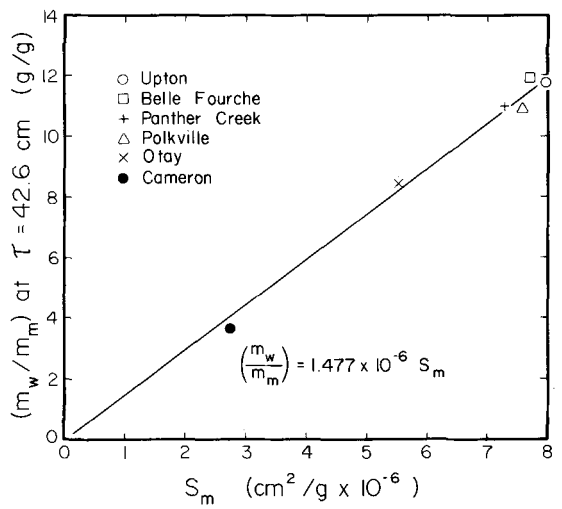


Fig. 5. The relation between m_w/m_m, the mass ratio of water to montmorillonite, and S_m, the specific surface area of montmorillonite, when τ, the water tension, equals 42.6 cm of water (S_m determined by Method I).

cause of impurities in the samples analyzed; or these compositions may not be strictly applicable if they are taken from the literature and not determined on the actual samples under investigation. Method IV has not been used previously and requires further testing before its reliability can be assessed. Therefore, hereafter, we will assume that the curve based on Method I is most representative. Its regression equation is

$$S_m = -1.4488 \times 10^8 b + 13.092 \times 10^8 \quad (8)$$

or, alternatively,

$$b = -0.6902 \times 10^{-8} S_m + 9.0364 \quad (9)$$

in which S_m is in cm²/g and b is in Å.

It should be mentioned here that efforts were made to determine values of S_m by other methods, especially by methods that are applicable at relatively high values of m_w/m_m. However, none of these methods proved to be satisfactory. Negative adsorption as described by Schofield (1949) was an unreliable criterion of surface area because anion adsorption obscured it. Methylene blue adsorption (Hang and Brindley, 1970) was also an unreliable criterion because it correlated only with cation exchange capacity. The shift in the infrared absorption peak of structural hydroxyls on layer expansion, which Prost (1975) related to surface area, was not sufficiently distinct to be measurable for our montmorillonites. Also, measurements of light scattering (Banin and Lahav, 1968) were uninterpretable because the major axis of the different montmorillonites had different lengths. For light scattering to be related to the number of layers per tactoid, the major axis must be constant.

A plot of S_m versus b for several Na-saturated montmorillonites is shown in Figure 4. All the values of S_m were determined by Philen et al. (1971) by Method I except that they used shorter equilibration times than we did. Corresponding values of b were taken from the literature (Earley et al., 1953; Margheim, 1977) and from this study. The scatter in the data may be attributable to the fact that both variables were not determined on the same samples. Also, there may have been errors in the measurement of S_m because of the relatively short equilibration time that was used. Nevertheless, the linear relation between S_m and b seems to hold.

In order to facilitate the interpretation of our results, let us suppose that the superimposed layers in montmorillonite are distributed between three different states corresponding to *c*-axis spacings of about 10 Å, 20 Å and >40 Å and that these states are separated by energy barriers. The three states will be referred to as unexpanded, partially expanded, and fully expanded, respectively. Their existence in Na-saturated montmorillonite has been demonstrated by Norrish (1954), Foster et al. (1955), and Rhoades et al. (1969). We will designate the fraction of unexpanded layers by f_u, the fraction of partially expanded layers by f_p, and the fraction of fully expanded layers by f_e. Then

$$f_u + f_p + f_e = 1. \quad (10)$$

Since nearly all of the water in a montmorillonite–water system is in interlayer regions, we can write as a close approximation

$$(m_w/m_m) = (1/2)\rho_w S_t(f_p\lambda_p + f_e\lambda_e) \quad (11)$$

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where S_t represents the theoretical specific surface area and λ_p and λ_e are the distances between the partially expanded and fully expanded layers, respectively. Further, the specific surface area accessible to water is given by

$$S_m = (f_p + f_e)S_t = (1 - f_u)S_t. \quad (12)$$

Under the condition that $f_p = 0$, combination of Eq. 11 and 12 yields

$$(m_w/m_m) = (1/2)\rho_w\lambda_e S_m. \quad (13)$$

Thus m_w/m_m will be proportional to S_m if, as an additional condition, λ_e has the same value in all systems at the given pressure (or tension). That these two conditions existed in our systems is indicated by Figure 5. The data for this figure were obtained from Figures 2 and 3 (Method I). The regression equation for the best fitting curve (solid line) in Figure 5 is

$$(m_w/m_m) = 1.477 \times 10^{-6}S_m. \quad (14)$$

Comparison of Eq. 13 and 14 shows that $(1/2)\rho_w\lambda_e = 1.477 \times 10^{-6}$ and, if $\rho_w \simeq 1.0$, $\lambda_e = 2.95 \times 10^{-6}$ cm = 295 Å.

It should be noted here that, had Eq. 11 been extended to include terms for additional partially expanded layers with different interlayer distances, the conclusion would necessarily have been the same, i.e., that the value of f_p for these layers equals zero. Otherwise Figure 5 could not be obtained.

The observation that λ_e has the same value at a given tension in every montmorillonite–water system is of considerable significance. If it is valid, we must also conclude that minor differences in the geometry of montmorillonite surfaces have no significant effect on their interaction with water. *This conclusion should not be construed to mean that the water does not fit epitaxially on these surfaces* as described by Ravina and Low (1972) and Margheim (1977). It does mean, however, that *specific* aberrations in surface geometry are not reflected in the structure of the water to any great distance. According to the theory of epitaxy or pseudomorphism (van der Merwe, 1964; Jesser, 1969) the overgrowth structure is strained to exactly match the substrate structure up to a critical thickness which depends on the initial misfit between the two structures, the strength of the bonds between them and their elastic properties. Differences in the geometry of the montmorillonite surfaces are small and, probably, the elastic modulus of the interlayer water is too low for the second-order perturbations arising from these differences to extend very far.

If we let $f_p = 0$ and $S_t = 8 \times 10^6$ cm²/g in Eq. 12 and combine the result with Eq. 8, we obtain

$$f_e = -18.11b + 163.65. \quad (15)$$

This equation applies to our systems. However, a similar equation has applied to all of the systems investigated thus far. This is indicated by the data in Figure 1. The systems represented therein had swelled to their maximum at $\tau = 0$. Under such conditions, $\lambda_e >> \lambda_p$ and Eq. 11 reduces to

$$(m_w/m_m) \simeq 1/2\rho_w S_t f_e \lambda_e. \quad (16)$$

We know that ρ_w and S_t were essentially the same in every system. On the basis of the evidence just presented, it can be assumed that was also true of λ_e. Therefore, f_e must have been a linear function of b.

In the systems being considered, the montmorillonite layers were distributed between two states, namely, the unexpanded, dehydrated state, and the fully expanded, hydrated state. Therefore, by virtue of the Maxwell-Boltzmann distribution law, we can write

$$f_e/f_u = f_e/(1 - f_e) = \exp(-\Delta e/kT) \quad (17)$$

where Δe is the energy difference per layer between the two states, k is the Boltzmann constant and T is the absolute temperature. We were able to calculate f_e for different values of b by means of Eq. 15. These values were inserted into Eq. 17 with T = 298°K to obtain the corresponding values of Δe. Thus, Figure 6 was obtained.

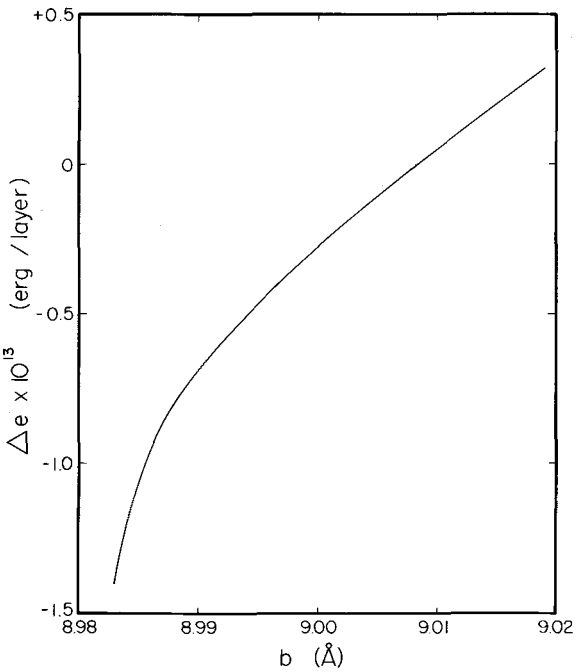


Fig. 6. The relation between Δe, the energy difference between the expanded and unexpanded states, and b, the *b*-dimension of montmorillonite.

When adjacent layers separate, the only energy expended is that required to increase the area of the layer–water interface by an amount equal to *a*, the planar sur-

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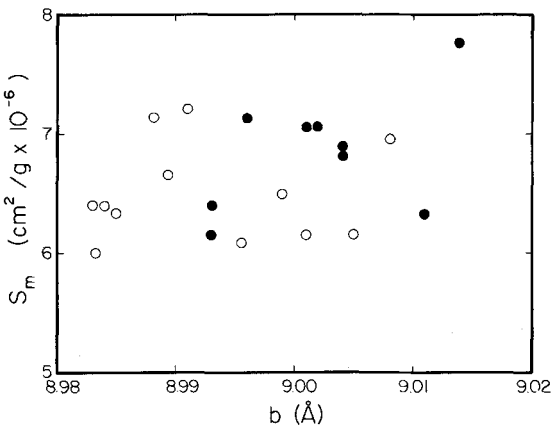


Fig. 7. The relation between S_m, the specific surface area, and b, the *b*-dimension of montmorillonite (○, calculated from data of Foster [1953]; ●, calculated from data of Earley et al. [1953].

face area of a single layer or twice the area of the initial layer–layer interface. Hence,

$$\Delta e = \gamma a \qquad (18)$$

where γ is the interfacial tension between the montmorillonite and water. Current theory (van der Merwe, 1964) indicates that the interfacial tension between elastic crystals is governed by the misfit between their respective structures. As the misfit increases, the strength of the bonds between neighboring atoms on opposite sides of the interface decreases and the interfacial tension rises accordingly. If it is assumed that water has elastic properties when it is immediately adjacent to a layer surface, the magnitude of γ (and, hence, of Δe) should depend on how well the structures of the montmorillonite and water coincide. This, in turn, should depend on the *b* dimension of the montmorillonite (Ravina and Low, 1972). Therefore, the relation between Δe and b in Figure 6 is understandable.

The evidence that we have presented heretofore indicates that f_e is a linear function of b. Hence, in keeping with Eq. 12, S_m will be a linear function of b if $f_p = 0$. That this is not always true is illustrated by Figure 7. The data points represented therein by open circles are based on the work of Foster (1953), whereas, those represented by closed circles are based on the work of Earley et al. (1953). All values of S_m were determined by Method III. The corresponding values of b were calculated by Eq. 7 in the former case but were measured in the latter.

Note from Figure 7 that the value of S_m remained within experimental error of 6.55×10^6 cm^2g. The value of S_t is 8×10^6 cm^2/g. When these two values are substituted into Eq. 12, we see that f_u must have remained within experimental error of 0.18. In our systems, f_p remained within experimental error of zero. Thus, it appears that, while f_e is a linear function of b, f_u and f_p are influenced by experimental conditions and can be either constant or variable within the limits imposed by Eq. 10.

Table 2 presents data on the swelling of the different montmorillonites in three organic solvents and water. If these data are used to construct plots of the weight of solvent absorbed versus the *b* dimension, it is found that, with the possible exception of the formamide, a linear relation is characteristic of the water only. This observation is consistent with the concept that epitaxy exists between the montmorillonite and water structures.

In summary, we have shown that the swelling of montmorillonite, at least at low water tensions, depends linearly on the fraction of layers that fully expand and that this fraction, in turn, depends linearly on the *b* dimension of the unit cell. Therefore, swelling is a linear function of *b* dimension. On the other hand, the specific surface area accessible to water depends on both the fraction of partially expanded layers (i.e., those with a *c*-axis spacing of ~20 Å) and the fraction of fully expanded layers and is a linear function of the *b* dimension only if the fraction of partially expanded layers is zero. Further, we have shown that, at a given tension, the distance between fully expanded layers is the same for all montmorillonites.

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Table 2. Amount of solvent absorbed by different Na-saturated, <2-μm montmorillonites at the specified tension, τ, in cm of solvent.

	Water τ = 42.6 cm	Methanol τ = 6 cm		98% Formamide τ = 6 cm		2-Ethoxyethanol τ = 6 cm	
Clay Mineral	(g/g)	(g/g)	(ml/g)	(g/g)	(ml/g)	(g/g)	(ml/g)
Upton, WY	11.72	0.2333	0.2948	12.82	11.31	1.562	1.680
Belle Fourche, SD	11.93	2.128	2.689	13.11	11.57	2.952	3.175
Polkville, MS	10.90	1.438	1.817	9.184	8.103	4.189	4.506
Panther Creek, MS	10.88	0.2128	0.2689	9.002	7.942	0.6470	0.6959
Otay, CA	8.39	1.650	2.085	6.244	5.509	4.304	4.629
Cameron, AZ	3.62	0.1182	0.1494	2.218	1.957	0.9157	0.9849

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Резюме- С помощью измерения разбухания и поверхностной площади было обнаружено,что разбухание монтмориллонита линейно зависит от той части слоев, которые полностью расширяются в воде и что эта часть слоев в свою очередь линейно зависит от размера b элементарной ячейки. Таким образом,разбухание является линейной функцией размера b. Однако удельная площадь поверхности монтмориллонита является линейной функцией его размера b,если только отсутствуют частично расширяющиеся слои. Было обнаружено также,что расстояние между полностью расширенными слоями при данном приложенном давлении одинаково для всех монтмориллонитов.

Kurzreferat- Von Quell-und Oberflächenmessungen wurde herausgefunden,daß das Montmorillonitquellen von dem Anteil seiner Schicht abhängt,der sich in Wasser voll ausdehnt und,daß die Größe dieses Anteils in linearischer Weise von der b Dimension der Einzelzelle abhängt. Deshalb ist das Quellen eine lineare Funktion der b Dimension.Die spezifische Oberfläche eines Montmorilloniten jedoch, hängt von der b Dimension allein ab, wenn keine teilweise ausgedehnten Schichten existieren. Es wurde auch gefunden, daß der Abstand zwischen voll ausgedehnten Schichten bei jedem gegebenen Druck für alle Montmorilloniten derselbe ist.

Résumé-On a constaté à partir du gonflement et des mesures de la surface externe que le gonflement d'une montmorillonite dépendait de manière linéaire de la fraction de ses couches se dilatant totalement dans l'eau,et que cette fraction à son tour dépendait de manière linéaire de la dimension b de la maille.Le gonflement est par conséquent une fonction linéaire de la dimension b .La surface externe spécifique d'une montmorillonite n'est cependant une fonction linéaire de sa dimension b que s'il n'existe pas de couches partiellement dilatées.On a aussi trouvé que la distance entre les couches totalement dilatées à une pression donnée est la même pour toutes les montmorillonites.

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