

SURFACE PROPERTIES OF SMECTITES EXCHANGED WITH MONO- AND BIPROTONATED 1,4-DIAZOBICYCLO(2,2,2)-OCTANE

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Abstract—Smectites exchanged to various degrees with mono- or biprotonated 1,4-diazobicyclo(2,2,2)-octane (Dabco) have a porous structure in which the organic molecule acts as a “pillar.” Less Dabco²⁺ than Dabco¹⁺ was necessary both to initiate and to complete expansion, whereas for both Dabco¹⁺ and Dabco²⁺ the threshold for expansion increased with the charge density of the clay. Interstratification of 9.7-Å and 14.5-Å (Dabco¹⁺) or 14.1-Å (Dabco²⁺) layers was observed before full expansion occurred.

Nitrogen sorption isotherms on partially exchanged Dabco¹⁺- and Dabco²⁺-clays are of the BET II and Langmuir type respectively, whereas n-butane adsorbed according to BET type II for both cationic forms. The specific surface area was governed by the number of Dabco²⁺ pillars, irrespective of the inorganic cation, and increased with Dabco²⁺ content even beyond the composition where full expansion was reached and notwithstanding the increasing number of silicate layers in the c direction of the crystal units. This relationship is explained by an enhanced random interleaving of clay platelets in the stacking units containing Dabco²⁺.

Key Words—Dabco, Interlayering, Pillar, Smectite, Surface area.

INTRODUCTION

Permanent intracrystalline porosity can be obtained in layer silicates by exchange with organic cations such as (CH₃)₄N⁺, (C₂H₅)₄N⁺ (Barrer and McLeod, 1955; Barrer and Brummer, 1963; McBride and Mortland, 1975) or 1-4-diazobicyclo(2,2,2)-octane (Dabco) (Mortland and Berkheiser, 1976; Shabtai *et al.*, 1977), or cationic complexes such as trisethylenediaminecobalt(III) (Barrer and Jones, 1971; Knudson and McAtee, 1973). The available interlamellar space can be modulated (1) by varying the size and the charge of the “pillars” that control the lateral cation-cation distance as well as the free interlayer distance; (2) by varying the charge density of the clay mineral; and (3) by partial exchange of the inorganic cations.

Partially exchanged clay minerals tend to segregate into random interstratified layers and to have specific surface areas intermediate between the two fully exchanged end members. For Cu²⁺-(CH₃)₄N⁺ on Wyoming bentonite, McBride and Mortland (1975) observed a segregation into Cu²⁺-rich and (CH₃)₄N⁺-rich interlayers. However, incomplete segregation was evidenced by specific surface areas which exceeded the “theoretical value” corresponding to random interstratification of Cu²⁺- and (CH₃)₄N⁺-exchanged layers.

Mortland and Berkheiser (1976) studied three Dabco-clays. When Dabco²⁺ was the saturating cation on the exchange complexes, Dabco²⁺-smectite provoked a

hydrolysis of acetonitrile whereas Dabco²⁺-vermiculite did not. The proton lability of a Cu-smectite treated with molecular Dabco was studied with D₂O and C₆D₆. Shabtai *et al.* (1977) showed that Dabco²⁺-montmorillonite has a high catalytic activity for esterification of carboxylic acids. This clay has pronounced molecular sieve properties as expressed in a sharp drop in esterification rate with increase in the critical dimension of the alcoholic reactant.

The present paper deals with the structural characteristics of mixed Dabco¹⁺- and Dabco²⁺-inorganic cation (mostly Na⁺) systems on a series of smectites with different charge density to gain more information on the nature of the segregation and its relation to specific surface area. From these results suitable samples were selected for the study of the sorption behavior of normal olefins (see Stul *et al.*, 1982).

EXPERIMENTAL

Sample preparation

The <0.5-μm size fraction of montmorillonites from Otay (OT) (API No. 24),³ Moosburg (MO) (G.F.R.), Wyoming bentonite (WB) (Volclay, American Colloid Company, U.S.A.), and of hectorite (HE) (API No. 34)³ was obtained by centrifuging their respective Na-exchanged forms. The clays were then washed consecutively with acidified (pH = 4) and neutral 1 M NaCl solutions. Na cation-exchange capacities at pH 6 are given in Table 1. Na-smectites loaded to various degrees with

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Dabco¹⁺ and Dabco²⁺ were prepared from salt-free clay suspensions, using Dabco solutions at pH 6 and pH 2 ($K_1 = 10^{8.19}$; $K_2 = 10^{4.18}$, Sillèn and Martell, 1964) as follows:

- (1) Partially exchanged Dabco¹⁺-clays were obtained by overnight exchange with appropriate amounts of 5×10^{-4} M Dabco¹⁺ at pH 6. The clays were then washed twice with distilled water and freeze-dried.
- (2) Partially exchanged Dabco²⁺-clays were obtained using 2.5×10^{-4} M solutions at pH 2. Exchange times of 15 min were used to minimize acid breakdown. The exchange step was followed by three quick water washes (once at pH 2 and twice at pH 6) and freeze-drying.
- (3) Homoionic Dabco¹⁺-clays were obtained by repeated exchange with 0.01 M Dabco solutions (pH 6), followed by four water washes and freeze-drying.
- (4) Homoionic Dabco²⁺-clays were prepared by a single exchange step using 0.01 N Dabco²⁺ solution (pH 2) in an amount equal to three times the clay exchange capacity. This treatment is identical to the one for the partially exchanged Dabco²⁺ samples.

Different adsorbents in which Na⁺ was replaced by Tl⁺, Ag⁺, Cu²⁺, Zn²⁺, Ca²⁺, or Ni²⁺ prior to the adsorption of Dabco¹⁺ or Dabco²⁺ were prepared in a similar fashion. All freeze-dried samples were ground to pass a 0.1 mm sieve. The chemical composition of the various Dabco-exchanged smectites was calculated from micro-Kjeldahl analyses and the weight loss upon calcination at 800°C and expressed per gram of cation-free silicate framework (g.s.f.) such as (Si,Al)₄(Al_{2-x}R_x)O₁₀(OH)₂ and Si₄(Mg_{3-x}R_x)O₁₀(OH)₂. In some products the amount of Na (or Cu) was analyzed by conventional atomic absorption techniques (Varian Techtron AA6).

X-ray powder diffraction analysis

Basal X-ray powder diffraction (XRD) spacings were measured on samples outgassed in vacuum (1.36×10^{-6} kgf/m²) during 24 hr at 120°C, while contained in glass capillaries. The capillaries were sealed and transferred to the Debye-Scherrer camera for irradiation.

The apparent *c* and *a*,*b* dimensions of the clay particles were determined from line broadening of the (001) and (33,06) reflections of air-dry random powder samples and were calculated from the Scherrer equation $t = 0.9\lambda/B \cos \theta_B$ (Cullity, 1966), where λ (in Å) is the wavelength of the radiation used. The parameter *t* (Å) gives the apparent particle dimension in a direction perpendicular to the crystallographic planes causing the reflection at θ_B (rad) with a line broadening of *B* (rad). A modified version (Mortier, 1980) was used to fit the experimental CuK α_1 diffraction band profile. The variation in the experimental line broadening was calibrated with a muscovite reference and a silicon standard. All XRD measurements were recorded on an automated Seifert-Scintag diffractometer (PAD II).

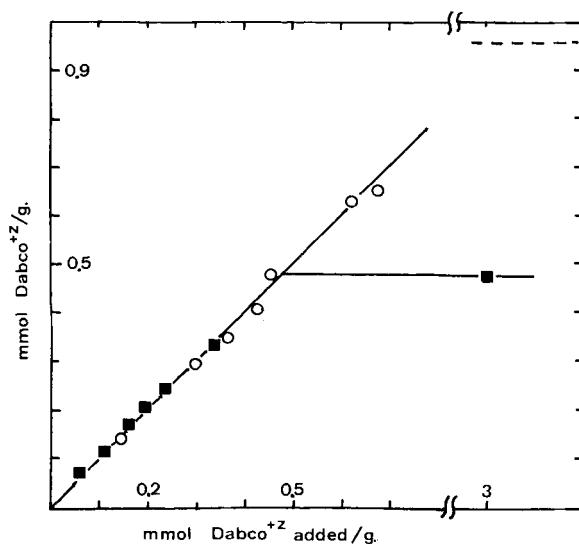


Figure 1. The amount of Dabco adsorbed on the Moosburg smectite (mmole/gsf) vs. the amount added (equally expressed as mmole/gsf) for solutions of Dabco¹⁺ at pH 6 (○) and Dabco²⁺ at pH 2 (■). The maximum adsorption level for Dabco¹⁺ obtained by repeated exchange is indicated by the horizontal dotted line.

Volumetric adsorption

Nitrogen (99.8%, L'Air Liquide) and n-butane (99.9%, Matheson) adsorption isotherms were measured at 77° and 273.16°K, respectively, using a volumetric, static adsorption apparatus. The samples (0.2 g) were dehydrated by evacuation during 24 hr at 393°K and 1.36×10^{-6} kgf/m² vacuum prior to adsorption.

RESULTS

Sample composition

Typical data, representative of all four clay minerals studied are presented for sample MO in Figure 1. Dabco was quantitatively adsorbed as Dabco¹⁺ at pH 6 and as Dabco²⁺ at pH 2. The maximum level of adsorption (mmoles) at pH 2 is half the amount adsorbed at pH 6, proving the presence of Dabco²⁺ and Dabco¹⁺, respectively. In a few products the amount of Na (or Cu) was determined (Table 1) and confirms the conclusion that the sum of Dabco¹⁺ and Na⁺ (or Cu²⁺) corresponds to the cation-exchange capacity. The data in Table 1 also indicate that in partially exchanged Dabco²⁺-smectites, almost all of the Na was exchanged for H⁺ as a result of the low pH values used in the preparation. Thus, H-Dabco²⁺ is used here to designate partially exchanged Dabco²⁺-smectites.

Trioctahedral clay minerals are particularly sensitive to acid breakdown (Robert and Veneau, 1979). An indication of the possible structural breakdown in the H-Dabco²⁺ samples was obtained by treating Na-HE and Na-MO for 15 min with solutions of pH 2 in the

Table 1. Cationic composition of different Na⁺-clay minerals partially exchanged with Dabco¹⁺ and Dabco²⁺.¹

	Dabco μmole/g	Na μeq/g	Na + Dabco μeq/g	Na CEC μeq/g
Dabco ¹⁺ -OT	221	1037	1258	1235
Dabco ¹⁺ -MO	403	749	1152	919
	330	690	1020	919
Dabco ¹⁺ -WB	277	664	941	867
	393	524	917	867
Dabco ¹⁺ -HE	330	246	576	732
Dabco ²⁺ -MO	327	28	682	
Dabco ²⁺ -WB	153	57	363	
	213	37	463	
Dabco ²⁺ -HE	127	43	297	
	258	42	558	

¹ All data are expressed on a gram cation-free silicate framework basis.

presence and absence of Dabco. In the absence of Dabco very intense reflections were noted at 2.84, 2.0, 1.64, 1.42, and 1.16 Å for Na-HE only, indicative of structural changes. These reflections, however, were not detected even when small amounts of Dabco²⁺ (10% of CEC) were adsorbed. Structure damage is therefore believed to be minimal.

Interlayer distances

Figure 2 shows the d(001) spacings of Na-Dabco¹⁺ and H-Dabco²⁺ adsorbents of varying composition as a function of the amount of Dabco expressed on a molar basis. Fully exchanged Dabco¹⁺- and Dabco²⁺-clays give spacings of 14.5 Å and 14.1 Å, respectively.

The transition from the dry, collapsed (d(001) = 9.7 Å) Na-smectites to the fully exchanged Dabco clays depends on the charge density of the clay mineral and on the degree of protonation of the amine. Between the collapsed and fully expanded Dabco clays a range of

Table 2. Unit layers and apparent particle dimensions in the c- and a,b-directions of Dabco-smectites derived from the X-ray line broadening.

	mmole Dabco/ gsf	c (Å)	Unit layers	a,b (Å)
MO-Na	0	53 ± 0.5	4.4	104 ± 3
-Na/Dabco ¹⁺	0.623	77 ± 0.1	5.3	104 ± 2
-Na/Dabco ¹⁺	0.959	99 ± 1.0	6.8	154 ± 7
-Na/Dabco ²⁺	0.253	65 ± 0.7	4.8	101 ± 2
-Dabco ²⁺	0.481	94 ± 1.0	6.6	98 ± 2
-Ca	0	63 ± 0.5	4.4	118 ± 3
-Ca/Dabco ¹⁺	0.383	52 ± 1.0	3.8	185 ± 8
OT-Na	0	48 ± 0.5	4.0	126 ± 3
-Dabco ¹⁺	1.260	92 ± 0.5	6.5	182 ± 13
-Cu(α)	0	67 ± 1.4	6.7	110 ± 0.3
-Cu/Dabco ¹⁺ (β)	0.412	62 ± 0.5	4.4	130 ± 4

Samples (α) and (β) were outgassed under vacuum at 150°C and 125°C, respectively.

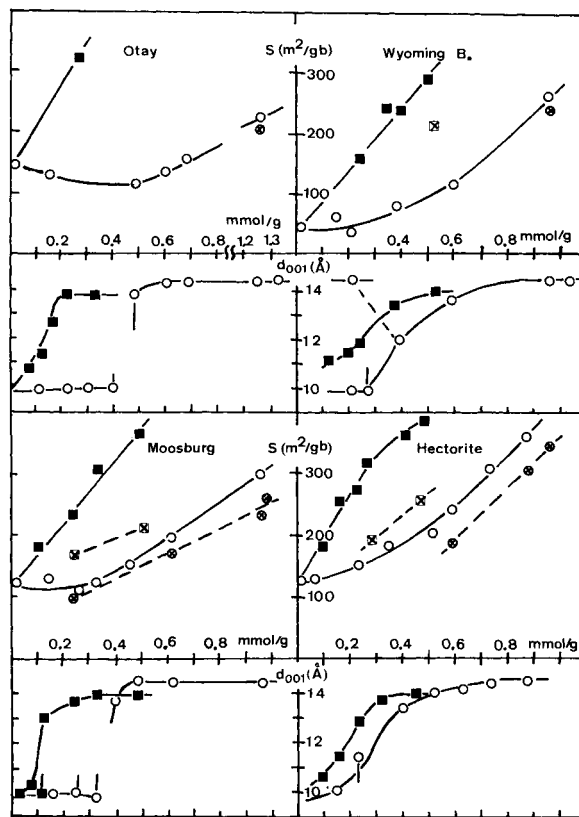


Figure 2. Variation of the specific surface area (m²/gsf) from nitrogen (■, ○) and n-butane (⊠, ⊞) adsorption (■ = BET-type I; ○, ⊠, ⊞ = BET-type II) and the d(001) spacings (Å) with the Dabco¹⁺ (○, ⊞) and Dabco²⁺ (■, ⊠) content (mmole/gsf) of different smectites.

intermediate spacings was observed which is characteristic of a random interstratification of Na-rich and Dabco²⁺-rich interlayers. In both the Na-Dabco¹⁺- and H-Dabco²⁺-clays the amount of Dabco necessary to make the transition from 9.7 to 14.1 Å (Dabco²⁺) or 14.5 Å (Dabco¹⁺) increased with decreasing charge density of the clay. At low charge density (sample HE), the range of intermediate spacings extended over 0.6 mmole, whereas at high charge density (sample OT) about 0.1 mmole was sufficient to obtain complete expansion.

In all four smectites fewer moles of Dabco²⁺ as compared to Dabco¹⁺ were necessary to initiate and to complete expansion. The amount of Dabco necessary to start interlayer expansion was smaller (<0.1 mmole) for all Na-Dabco²⁺-clays and decreased with decreasing charge density from 0.4 mmole (sample OT) to 0.1 mmole (sample HE) for Na-Dabco¹⁺-clays. A considerable fraction of the Dabco¹⁺ cations which were adsorbed before expansion started (see samples OT and MO) should be located at external surfaces because the d(001) remained constant at 9.7 Å. Full expansion was reached before complete exchange of the organic cation was attained. For these compositions, the Na⁺ and Dabco¹⁺

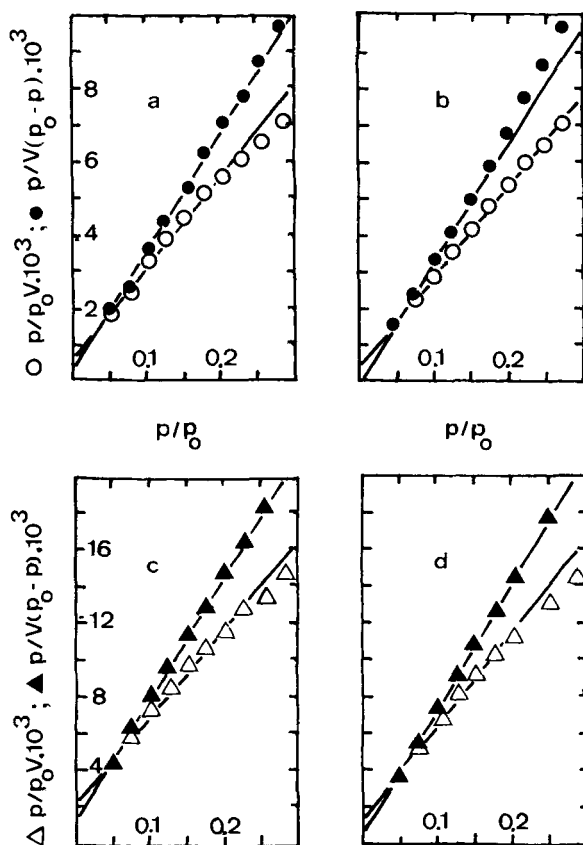


Figure 3. Typical plots of nitrogen (\circ , \bullet) and n-butane (Δ , \blacktriangle) adsorption data for partially exchanged Dabco²⁺ (mmole)-Moosburg samples. (a) 0.330 Dabco¹⁺-Na-MO; (b) 0.172 Dabco²⁺-H-MO; (c) 0.623 Dabco¹⁺-Na-MO; (d) 0.253 Dabco²⁺-H-MO.

or H⁺ and Dabco²⁺ cations were probably homogeneously distributed in the interlamellar phase.

X-ray diffraction line broadening

Apparent particle dimensions in the c and a,b directions were calculated from measurements of the XRD line broadening of Dabco-smectites (Table 2). The number of unit layers calculated from the apparent c dimensions of the particles and the apparent basal distances are also given. In calculating the width functions the composite (33,06) reflection, was used without decomposition. The complex nature of this diffraction peak makes further discussion of the apparent a,b dimensions speculative.

Table 2 shows that the introduction of Dabco¹⁺ in Na-smectites increased the apparent particle dimensions both in the c and a,b directions. In the presence of Ca or Cu, however, a slight decrease in c dimension and larger a,b dimensions were found. Dabco²⁺ adsorption on the Na-MO sample seemed to affect only the c-direction.

Table 3. Observed and calculated specific surface areas (m²/gsf) for different interlamellar orientations of Dabco²⁺.

		S _{obs}	S _{cal} ¹		S _{obs} - S _{Na}
			⊥	∥	
Dabco ¹⁺	OT	226	287	232	79
Dabco ¹⁺	MO	300	296	235	175
Dabco ¹⁺	WB	264	275	198	220
Dabco ¹⁺	HE	360	331	286	235
Dabco ²⁺	MO	364	336	330	
Dabco ²⁺	WB	282	336	310	
Dabco ²⁺	HE	391	384	362	

S_{Na} data from Stul and Van Leemput (1982a).

¹ Calculated from model described in Appendix I.

Specific surface areas

Figure 3 shows typical examples of N₂- and butane-adsorption isotherms obtained on Na-Dabco¹⁺- and Na-Dabco²⁺-clays. The experimental curves were fit to the BET I (Langmuir) and BET II equations by taking p/p₀ increments of 0.025 in the region 0.05 < p/p₀ < 0.20. N₂ and butane cross sections were taken as 16.2 and 44 Å², respectively.

Na-Dabco¹⁺- and H-Dabco²⁺-smectites showed a type II and Langmuir behavior, respectively, upon N₂ adsorption. Additional data with Dabco¹⁺-Ag⁺, -Tl⁺, -Ca²⁺, -Cu²⁺, -Co²⁺, or -Zn²⁺ combinations also fit the type II isotherm equation. The interlayer distance of the Dabco²⁺-clays (14.1 Å) is comparable to that of tetramethylammonium Wyoming bentonite (13.8 Å) (McBride and Mortland, 1975), and both systems consistently showed a Langmuir behavior upon N₂ adsorption. The Langmuir behavior is consistent with a free space comparable to the N₂ dimensions. The pore dimensions of Dabco¹⁺-clays (14.5 Å - 9.6 Å = 4.9 Å) exceed the diameter of N₂ (3.5 Å) rendering the possibility of filling up the interlayer volume in a way different from the perfect monolayer (pseudo bilayer) and resulting in a behavior that is better described by the type II model. Butane adsorbed according to a type II pattern in both Na-Dabco¹⁺- and Na-Dabco²⁺-clays. The underlying physical reasons are yet unclear.

The specific surface areas corresponding to the best fit curves are shown in Figure 2 as a function of the degree of Dabco¹⁺- or Dabco²⁺-exchange in Na-smectites. In all four clay minerals studied the specific surface areas of Dabco²⁺ exceeded the values for Dabco¹⁺ as could be predicted from the lower Dabco²⁺ content.

The incorporation of organic cations, acting as pillars, into collapsed Na-clays should result in a higher available surface area which increases with decreasing charge density of the mineral or decreasing number of interlamellar props. This prediction is verified (see Table 3) by the fact that the S_{obs} values of the pure Dabco²⁺-clays exceeded the S₀ values of their Na counter-

Table 4. BET-II specific surface areas from N_2 adsorption and $d(001)$ spacings of partially exchanged $Dabco^{1+}$ smectites.

	mmole $Dabco^{1+}$ / gsf	$d(001)$ (Å)	Surface area (m^2 /gsf)
OT-Na-Dabco ¹⁺	0.575	14.3	140
OT-Ag-Dabco ¹⁺	0.569	14.3	143
OT-Tl-Dabco ¹⁺	0.583	14.1	142
OT-Cu-Dabco ¹⁺	0.324	14.2	180
MO-Ag-Dabco ¹⁺	0.577	14.5	203
MO-Tl-Dabco ¹⁺	0.401	14.0	157
MO-Ca-Dabco ¹⁺	0.383	14.5	210
MO-Zn-Dabco ¹⁺	0.382	14.0	211
MO-Cu-Dabco ¹⁺	0.158	10.1	127
MO-Cu-Dabco ¹⁺	0.318	14.2	188
MO-Cu-Dabco ¹⁺	0.387	14.3	211

parts and by the increasing difference between them with decreasing charge density.

Specific surface areas calculated from butane and N_2 adsorption isotherms varied similarly with $Dabco^{2+}$ content, the former always lower in magnitude (see Figure 2). The molecular dimensions ($4.0 \times 4.9 \times 7.7$ Å) of butane are responsible for the less effective packing in the interlamellar space, thereby explaining the lower S_0 value. In Table 4 specific surface areas and $d(001)$ spacings are listed for $Dabco^{1+}$ -Ag, -Tl, -Ca, -Cu, -Co, and -Zn systems. Equal $Dabco^{1+}$ loadings led to identical surface areas as can be observed for Ag, Tl, and Na-Dabco¹⁺-Otay mixtures at about 0.57 mmole $Dabco^{1+}$ and Ca-, Zn-, Cu-Dabco¹⁺-Moosburg samples containing 0.38 mmole $Dabco^{1+}$. These data indicate that the S_0 value was essentially determined by the organic cation.

The specific surface area was closely related to the interlamellar swelling both in Na-Dabco¹⁺ and H-Dabco²⁺ systems as shown (Figure 2) by the coincidence of the composition for which S_0 started to increase and for which $d(001)$ indicated the opening of the clay layers and by the fact that S_0 increased regularly with organic cation content. For Na-Dabco¹⁺-OT (and eventually Na-Dabco¹⁺-MO) a slight decrease in S_0 was observed from the Na-clay to a minimum value, which corresponded to the "threshold" $Dabco^{1+}$ contents which initiated interlamellar swelling, as seen from $d(001)$ values (Figure 2). These observations can be explained by the decrease in the external part of the S_0 due to the surface occupied by organic cations (McBride and Mortland, 1975) or cationic complexes (Knudson and McAtee, 1973). Alternatively, the increased c-dimensions of $Dabco^{1+}$ clays may be invoked to explain the decreasing external surface area. As the charge density decreased, the S_0 minimum disappeared or shifted to lower $Dabco^{1+}$ contents (see Figure 2) because the opening of the clay layers and the concomitant increase in internal S_0 neutralized or exceeded the changes in the external S_0 .

A regular increase in S_0 with organic cation content, as long as interlayer expansion proceeds, was experimentally verified in samples; however, it was surprising to observe a smooth change of S_0 with Dabco content in those samples (especially OT and MO) for which $d(001)$ indicated the opening of all interlayers in a small composition range. Beyond the composition for which maximum expansion was obtained, the S_0 should have decreased because the introduction of additional $Dabco^{2+}$ cations reduced the available free volume. Experimentally S_0 values (see Figure 2) were observed which continued to increase beyond the limit where, according to $d(001)$ data (Figure 2), maximum swelling was reached.

DISCUSSION

The steady increase in S_0 observed beyond the start of opening of the interlayers can be interpreted as a segregation into Na^+ (H^+)- and $Dabco^{1+}$ ($Dabco^{2+}$)-rich interlayers, the resulting S_0 being a linear combination of the S_0 values of the end members. XRD data, however, point to a region of interstratification which is highly dependent on charge density and which occurs only in a limited range of $Dabco^{2+}$ compositions. Other factors must therefore be invoked to explain the apparent incompatibility between the XRD and the S_0 data.

Because the number of unit layers present in the clay aggregates increased with $Dabco^{2+}$ content (see Table 2), the data may be explained by a random interleaving of the clay plates in the crystal units that creates increasing amounts of uncovered surface or supermicropores with increasing $Dabco^{2+}$ content. (In case of an orderly, vertical, and composition-independent stacking, a decrease in S_0 with increasing $Dabco^{2+}$ content should take place.) Such an explanation accounts for the observations made for the alkali cation-exchanged clays in that the size of the exchangeable cation influenced the organization in the clay aggregates, i.e., S_0 increased from Na- to Cs-exchanged clays (Stul and Van Leemput, 1982b). For mixed inorganic-organic cation-exchanged clays, the organic cation is the bulky constituent and consequently determines the aggregate structure. The results shown in Table 4 indeed suggest that the organic cation content determined the value of S_0 whatever the nature of the inorganic cation.

More information on the behavior of fully exchanged $Dabco^{2+}$ -clay minerals is gained from a simple geometrical model given in Appendix I. Experimental and calculated surface areas are compared in Table 3. The molecular dimensions of $Dabco^{1+}$ ($6.3 \times 4 \times 6.4$ Å) and $Dabco^{2+}$ ($7 \times 4 \times 6.4$ Å) do not allow a final conclusion as to their interlamellar orientation. The corrections for the area occupied by the organic cations in Table 3 were therefore calculated using cross-sectional areas of 28 Å^2 ($Dabco^{1+}$ and $Dabco^{2+}$) for the perpendicular and 40 Å^2 ($Dabco^{1+}$) or 44 Å^2 ($Dabco^{2+}$) for the parallel orientation.

Except for Dabco¹⁺-OT and Dabco²⁺-WB, good correspondence is obtained, if a perpendicular orientation of both Dabco^{z+} cations is assumed. The smaller value obtained experimentally for Dabco¹⁺-OT can be explained by the fact that the free intercalation distance at this charge density is smaller than the N₂ diameter (see also Figure 5 in Appendix I). Note that the calculated S₀ values carry the burden of the incorporation of experimental S₀^{Na} data as the total external surface, S_e (Stul and Van Leemput, 1982a). Indeed, Na-clays which themselves have a characteristic structural organization are taken as a reference. This procedure is justified because the number of clay platelets among the Na¹⁺ and Dabco^{z+} series remains constant at 4.4 and 6.5 units per aggregate, respectively. In view of the difference in units per aggregate, the relevance of the correspondence between S_{obs} and S_{calc} is only qualitative. Furthermore, changes in the horizontal organization of the clay platelets needs further study and should be incorporated in the model.

APPENDIX

Model for calculating the free surface area of organosmectite

Assume a homogeneous distribution of the mineral charge over the silicate surface. Consequently the exchangeable cations occupy positions at a maximum mutual distance. The area available per unit charge, A_e, is determined by the mean charge density, ξ, of the mineral and by the unit-cell parameters (a, b). Polyvalency of the exchanged cations is allowed for by introducing A_z, equal to the product of A_e and the valence, Z, of the exchanged cations. The area occupied per cation, A_c, is a function of its orientation between the clay layers.

Free intercalation distance (λ). Both A_z and A_c are considered as hexagons with a common center. The free intercalation distance, λ, is obtained from twice the difference between the minimum lengths (apothema h_z and h_c from the center of A_z and A_c to the respective perimeters (see Figure 4). The calculation is as follows:

$$\begin{aligned} A_e &= (ab)/2\xi = 46.5/2\xi \\ A_z &= A_e \times Z \\ A_z &= 6 \times R_z h_z/2 = 3R_z^2 \cos 30^\circ = 3.464h_z^2 \\ A_c &= 3.464h_c^2 \\ \lambda &= 2(h_z - h_c) = 2[(A_z/3.464)^{1/2}] - [(A_c/3.464)^{1/2}] \\ &= 1.07(A_z^{1/2} - A_c^{1/2}) \end{aligned}$$

In Figure 5 the free intercalation distance λ is related to the mean charge density, ξ, of the fully exchanged smectites by considering a perpendicular and parallel intercalation of Dabco¹⁺ and Dabco²⁺ cations. λ is inversely proportional to the charge density and may become smaller than the dimension of N₂, in which case N₂ penetration becomes impossible. Because real clay

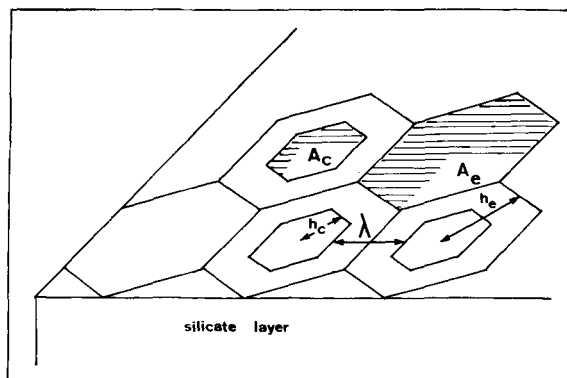


Figure 4. A model of the free intercalation distance λ.

minerals have a "non-ideal" charge density distribution (Stul and Mortier, 1974; Lagaly and Weiss, 1976), part of the surface corresponding to that fraction having a charge density exceeding 0.34e/(Si,Al)₄O₁₀ will be unavailable for N₂ sorption with a diameter of 3.5 Å.

Free surface areas. The free surface area of organosmectites is obtained by correcting the internal component, S_i, and the external component, S_e, of the theoretical surface, S_t = 750 m²/g, for the area covered by the organic cations. The expected area is considered as the sum of the free external area S_{e,f} and half the free internal area S_{i,f}, because the basal spacing of Dabco^{z+} smectites indicate that the interlamellar coverage is restricted to a monolayer. Thus,

$$\begin{aligned} S_{e,c} &= S_e \cdot A_c \xi / (ab) 10^{20} \cdot \frac{1}{Z} \\ S_{i,c} &= S_i \cdot A_c \cdot 2\xi / (ab) 10^{20} \cdot \frac{1}{Z} \end{aligned}$$

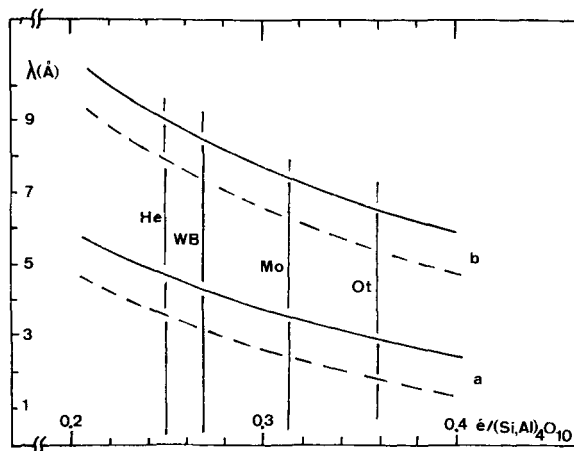


Figure 5. Variation of the intercalation distance λ (Å) with the mean charge density ξ (e/(Si,Al)₄O₁₀) of fully exchanged Dabco¹⁺- and Dabco²⁺-clay minerals. Results are shown for both the perpendicular (A_c = 28 Å; full line) and the parallel (A_c = 40 Å; dotted line) interlamellar orientation of Dabco¹⁺ (a) and Dabco²⁺ (b) cations.

$$S_{e,f} = S_e - S_{e,c} \text{ and}$$

$$S_{i,f} = S_i - S_{i,c},$$

$$S_{t,f} = S_{e,f} + \left(\frac{1}{2}\right)S_{i,f}$$

The specific surface areas predicted for Dabco¹⁺- and Dabco²⁺-exchanged smectites are given in Table 3. The present model is easily extended to calculate the interlamellar porosity by use of the basal distance. Also, extension to smectites which are only partially exchanged with organic cations is possible by reducing the actual charge density, ξ , by a factor F, equal to the equivalent fraction of the organic cations on the clay.

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Резюме—Смектиты, обмененные в разной степени с моно- и двупротонными 1,4-диазодвухцикло-(2,2,2)-октаном (Дабко), имеют пористую структуру в которой органическая молекула играет роль "опоры". Меньшее количество Дабко²⁺, чем Дабко¹⁺ было необходимо, чтобы начать и закончить экспансию. Для обоих Дабко¹⁺ и Дабко²⁺ порог экспансии увеличивался пропорционально плотности заряда глины. Впластование слоев 9,7-Å и 14,5-Å (Дабко¹⁺) или 14,1-Å (Дабко²⁺) наблюдалось перед появлением полной экспансии.

Изотермы сорбции азота для частично обмененных Дабко¹⁺- и Дабко²⁺-глин являются типа БЭТ II и лангмуира соответственно, тогда как n-бутан адсорбировался согласно типу БЭТ II для обоих катионных форм. Удельная площадь поверхности регулировалась числом "опор" Дабко²⁺ независимо от неорганического катиона. Эта величина увеличивалась с содержанием Дабко²⁺ даже вне состава, при котором достигалась полная экспансия, и несмотря на увеличивающееся число силикатовых слоев по с-направлению в кристалле. Это взаимоотношение объясняется увеличенным неупорядоченным переслаиванием глиновых пластинок в единицах, содержащих Дабко²⁺. [Е.С.]

Resümee—Smektite, die bis zu verschiedenen Graden mit mono- oder biprotoniertem 1,4-Diazobicyclo(2,2,2)-Oktan (Dabco) ausgetauscht wurden, haben eine poröse Struktur, in denen organische Moleküle als "Pillar" wirken. Es war weniger Dabco²⁺ als Dabco¹⁺ notwendig, um eine Expansion zu beginnen und zu vervollständigen, während sowohl für Dabco¹⁺ als auch für Dabco²⁺ der Schwellenwert der Expansion mit der Ladungsdichte des Tons anstieg. Es wurde eine Wechsellagerung von 9,7 Å und 14,5 Å (Dabco¹⁺) oder 14,1 Å (Dabco²⁺) Lagen beobachtet, bevor eine vollständige Expansion eintrat. Die Stickstoff-Adsorptionsisotherme an teilweise ausgetauschten Dabco¹⁺- und Dabco²⁺-Tonen sind vom BET II-bzw. Langmuir-Typ, während n-Butan an beide kationische Arten nach dem BET II-Type adsorbiert wird. Die spezifische Oberfläche wurde von der Zahl der Dabco²⁺-Pillars, unabhängig vom anorganischen Kation, bestimmt, und nahm mit dem Dabco²⁺-Gehalt zu, und zwar über das Maß hinaus, bei dem maximale Expansion erreicht wurde, und ungeachtet der zunehmenden Zahl der Silikatschichten in Richtung der c-Achse der Einheitszelle. Diese Beziehung ist durch eine zunehmend unregelmäßig erfolgende Stapelung von Tonteilchen in den Stapelungseinheiten, die Dabco²⁺ enthalten, zu erklären. [U.W.]

Résumé—Les smectites échangées à un taux variable avec 1,4-diazobicyclo(2,2,2)-octane (Dabco) mono- ou biprotoné ont une structure poreuse dans laquelle Dabco agit comme un "pilier." On a besoin de moins de Dabco²⁺ que de Dabco¹⁺ aussi bien pour débiter que pour compléter l'expansion des feuillets d'argile, tandis que, aussi bien pour Dabco¹⁺ que pour Dabco²⁺ le nombre nécessaire pour l'expansion augmente avec la densité de charge de l'argile. L'interstratification des couches de 9,7 Å et 14,5 Å (Dabco¹⁺) ou 14,1 Å (Dabco²⁺) est observée avant que l'expansion complète ne soit réalisée.

Les isothermes de sorption de nitrogène sur les argiles partiellement échangées avec Dabco¹⁺ ou Dabco²⁺ sont respectivement d'un type BET II ou Langmuir, tandis que quand n-butane adsorbe, il en ressort un type BET II pour les deux formes cationiques. La surface spécifique est gouvernée par le nombre de piliers de Dabco²⁺, indépendamment du cation inorganique et augmente avec le contenu du Dabco²⁺ même pour la composition après que l'expansion complète soit obtenue, et malgré l'augmentation du nombre des feuillets de silicate dans la direction C des unités cristallines. Ceci est expliqué par une augmentation de la façon quelconque d'intercalation des feuillets d'argile dans les unités d'empilement qui contiennent le Dabco²⁺.