Interlayer Porosity in Montmorillonite Intercalated with Keggin-like Cation Studied by Molecular Mechanics Simulation

Pavla Capková[1,2,*], Rene A.J. Driessen[1], Henk Schenk[1], and Zdenek Weiss[3]

[1]Laboratory of crystallography, AIMS, University of Amsterdam, Nieuwe Achtergracht 166, NL-1018 WV Amsterdam, The Netherlands (paulac@crys.chem.uva.nl; hs@crys.chem.uva.nl; rdr@crys.chem.uva.nl)

[2]Faculty of Mathematics and Physics, Charles University Prague, Ke Karlovu 3, CZ-12116 Prague, Czech Republic (capkova@karlov.mff.cuni.cz)

[3]Central Analytical Laboratory, Technical University Ostrava, CZ-70833 Ostrava, Czech Republic (Zdenek.Weiss@vsb.cz)

Abstract

Molecular mechanics simulation using Cerius[2] modeling environment have been used to investigate the structure of montmorillonite, intercalated with Keggin-like cation[7+]. Present work is focused to the strategy of modelling in case of intercalated layered structures and to investigation of structure parameters characterizing the interlayer porosity, that means: the interlayer distance, the position, orientation and distribution of Keggin cations in the interlayer space and the stacking of layers. Molecular simulations revealed the structure of the interlayer and led to the following conclusions: In the most stable configuration the 3-fold axis of Keggin cation is perpendicular to the silicate layer. This orientation of Keggin cations leads to the basal spacing 19.51 (10^{-10} m). Energy minimization during the translation of Keggin cation along the silicate layer gives only small fluctuations of basal spacing and no correlation has been found between the shift of cation along the layers and the value of basal spacing. No systematic relationship has been found between the shift of cation and crystal energy and no systematic relationship exists between the mutual shift of two successive layers and the values of basal spacing and crystal energy. Consequently, no two-dimensional ordering of Keggin cations in the interlayer and no regular stacking of layers can be expected. X-ray diffraction diagrams obtained for montmorillonites, intercalated with Keggin cation, confirm present conclusions.
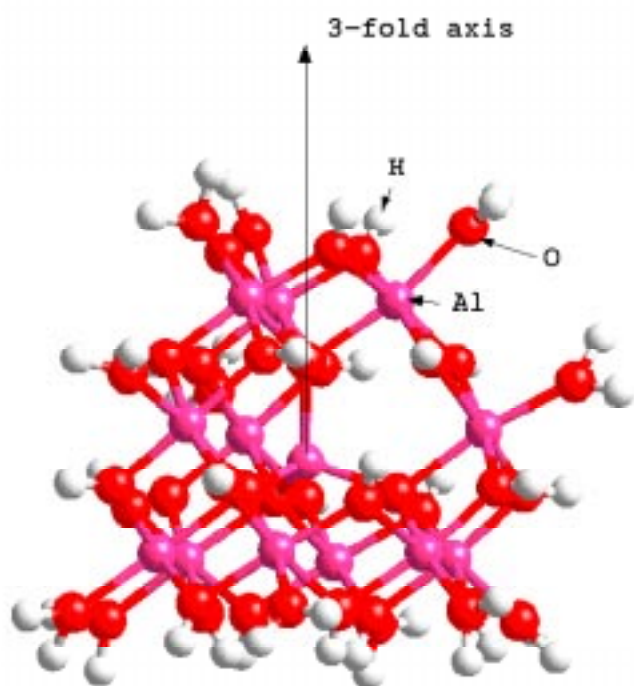
Keywords: Molecular mechanics, Intercalated clays, Keggin cation.

* To whom correspondence should be addressed

Introduction

The main objective in pillaring clays is to achieve as large a basal spacing as possible. Large basal spacings and consequently large interlayer porosity are the first requirements of sorbents and catalysts. To design intercalated clays as selective catalysts or selective sorbents, the size and shape of the interlayer cavities should be controlled by using different types of intercalating species and by their proper arrangement in the interlayer space. In present work we investigate the structure of montmorillonite, intercalated with Keggin-like cation[7+] (further denoted as Al_{13}^{7+}). This study is focused to the structure parameters characterizing the interlayer porosity, i.e. the interlayer distance, the position, orientation and distribution of Keggin cations in the interlayer space and the stacking of layers, as these parameters represent the crucial factors in numerous practical applications, suggested for intercalated clays.

Montmorillonite (MMT) is 2:1 smectite clay. Each layer of a 2:1 clay mineral consists of two sheets of distorted SiO_4 tetrahedra connected by a sheet of $(Al/M)O_6$ octahedra, (M having one positive charge less than Al). For MMT not containing water, the contents of one unite cell are given by the formula $(Al_{4-x}M_x)Si_8O_{20}(OH)_4Mi_{x/n}^{n+}$. The loss of positive charge by the replacement of Al by M can be compensated by intercalation with Mi^{n+} ions. In the case of MMT, polyoxocations containing Al are often used for this purpose.

Under favourable conditions the main molecular prop is the Keggin cation, the structure of which is given in Fig.1 (according to Johansson).

Why we use molecular simulations to investigate the structure of intercalated montmorillonite? X-ray diffraction structure analysis of intercalated clays is extremely difficult in case of smectites. The diffraction diagrams are usually affected with sample effects, like small particle size and preferred orientation of crystallites. The interpretation of diffraction pattern is also obstructed with irregular stacking of layers and with inhomogeneity in basal spacing due to the inhomogeneity in cation distribution in the interlayer. In such a case the molecular modelling represent very powerful tool in structure analysis, providing the deeper and more detailed insight into structure, than we could get from x-ray diffraction or IR spectroscopy.

Strategy of modelling

To create the modelling strategy in general case of intercalated layered structures one has to consider the nature of host - guest and guest - guest interactions and consequently the possible changes of host resp. guest structures after intercalation. That means: all the informations available from experiment have to be used to build and parameterize the initial model, to assign the rigid units to this model, to set up the energy expression and to choose a proper force field. The results of modelling should be in any case in agreement with the experimental data.

Figure 1. *Structure of Keggin cation; according to Johansson [1].*
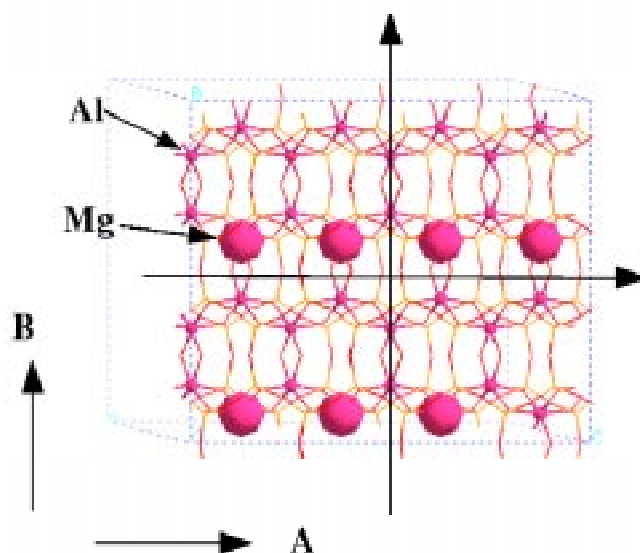
Figure 2. *Arrangement of Aluminium and Magnesium cations in the octahedral sheet of silicate layer, (Mg - large balls, Al - small balls).*

Table 1. Results of energy minimization for three models with two Al_{13}^{7+}-cations in the double supercell 16-MMT. The values of VDW, COUL, HB, total crystal energy E_c, basal spacing d_{001} and the distance of central aluminium atoms of Keggin cations Al(c)-Al(c) are presented for three selected models. Models -IA (see fig.6a) and -IB (see fig.6b) with the close contact of Keggin cations are compared with the MODEL-I, where the distance between cations is 20.83 (10^{-10} m).

MODEL	IA	IB	I
VDW (kJ/mol)	-1181.2	-1201.2	-1158.7
COUL (kJ/mol)	-18914.6	-16995.8	-16998.3
HB (kJ/mol)	-91.6	-103.8	-137.1
E_c (kJ/mol)	-20187.4	-18300.8	-18294.1
d_{001} (10^{-10} m)	19.73	19.48	19.42
Al(c)-Al(c) (10^{-10} m)	10.26	10.92	20.83

Molecular mechanics simulations were carried out in Cerius² modeling environment using Crystal Packer module. Crystal Packer is based on DreidingII force field developed by Mayo *et al* (1990) . Energy calculations in Crystal Packer take into account the nonbond terms only, i.e. van der Waals interactions (VDW), Coulombic interactions (COUL), hydrogen bonding (HB), internal rotations and hydrostatic pressure. The asymmetric unit of the crystal is divided into fragment-based rigid units. Nonbond (VDW, COUL, H-B) energies are calculated between the rigid units. During energy minimization, the rigid units can be translated and rotated and the unit cell parameters varied. In our case the rigid units were: silicate layers and Keggin cations.

The use of Crystal Packer in case of intercalated smectites is based on the two main assumptions:

(1) The bonding between intercalant and silicate layer is non-covalent. Because in MMT's, intercalated by hydroxy-Al species, the bonding between intercalant and silicate layer is supposed to be non-covalent (see Figures *et al* 1990), we set up the energy term including VDW, COUL and H-B only, using Crystal Packer module.

(2) The silicate layers and Keggin cations can be considered as a rigid units. The assumption of the rigid silicate layers is based not only on the generally accepted opinion, that the layers behave as rigid units during intercalation, but this assumption is supported by the two different experimental results: x-ray diffraction and infrared spectroscopy.

Diffraction pattern of Al-intercalated monmorillonites have been compared with the diffraction pattern of the original host structure, i.e. Na-montmorillonite. In both cases the diffraction pattern exhibits the same character , that means the turbostratic stacking of layers with typical hk-bands. The positions of hk-bands, characterising the lattice parameters

a, b in silicate layers are exactly the same within the error 0.005 (10^{-10}) m for intercalated and non-intercalated structure, that means a possible expansion , resp contraction of silicate layers after intercalation should not exceed 0.005(10^{-10}) m. (Diffraction profiles were analysed using profile fitting with asymmetric Pearson function.)

Keggin cation in 8MMT supercell
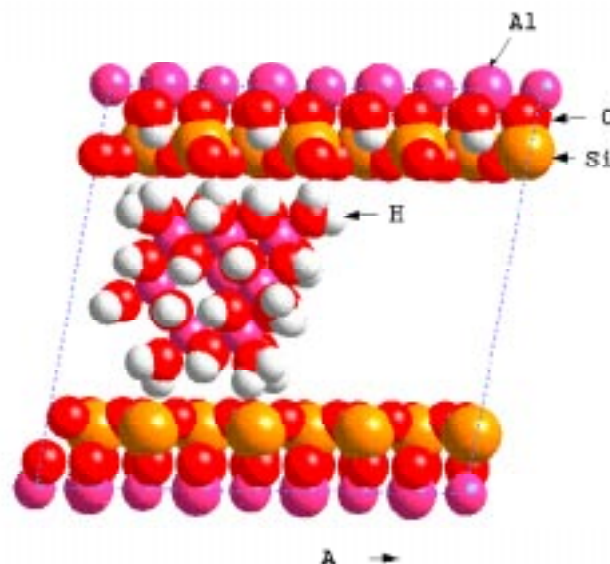

Keggin cation in 8MMT supercell
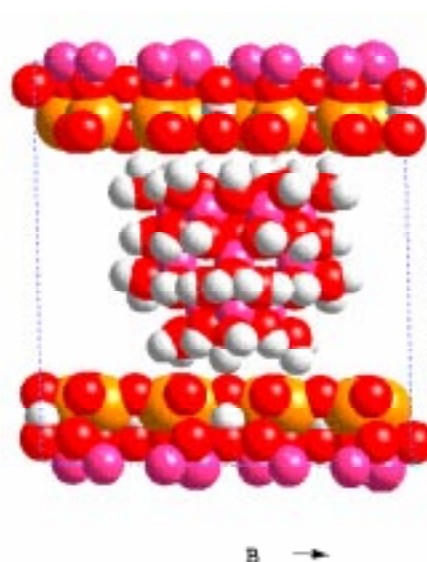
Figure 3. *Packing of Al_{13}^{7+}-intercalated monmorillonite. The 3-fold axis of the Keggin-like cation is perpendicular to the silicate layers. (above) view along A axis direction, (below) view along B axis direction.*

Infrared spectroscopic measurements for both samples - intercalated and non-intercalated were carried out using a NICOLET IMPACT 400 (FTIR) spectrophotometer with DTGS detector in the wavelength 400 - 4000 cm^{-1}. The absorption spectra were obtained using KBr pellets and by ATR technique on ZnSe crystal. The comparison of bands corresponding to the silicate layers in IR spectrum showed the same positions and profiles of these bands for intercalated and non-intercalated montmorillonites. That means the possible distortions of Si-O or Al-O bonds must be less then the treshold level of IR detection in the region 1300 to 600 cm^{-1}. The same conclusions are reported by Jones : infrared spectra for a series of ion-exchanged clays indicate that the basic structure of the clay sheet is not altered by the ion-exchange.

The initial model of montmorillonite was built using structural data for montmorillonite, given by Tsipursky & Drits (1984) . The unit cell parameters according to Méring & Oberlin (1967) have been used to define the orthogonal planar unit cell: a=5.208 $(10^{-10}$ m) and b=9.020 (10^{-10}) m. (The 2:1 layers in the initial model were removed to the interlayer distance d=21.0 $(10^{-10}$ m) allowing to place the Al_{13}^{7+} cation into the interlayer space.

Supposing the layer formula: $(Al_{3.125}Mg_{0.875}(Si_8O_{20}(OH)_4)$, the layer charge per one unit cell is -0.875. This negative layer charge was compensated by intercalation of one Al_{13}^{7+} cation into the supercell containing 8 montmorillonite unit cells (8-MMT supercell). This concentration of aluminium
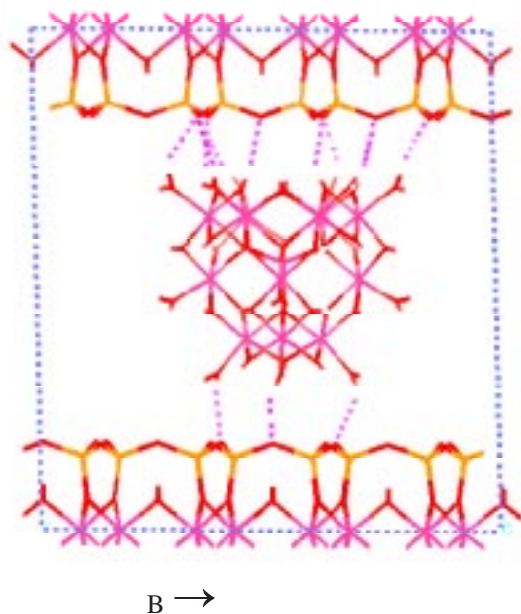
atoms in the interlayer of Al_{13}^{7+}-intercalated montmorillonites is in agreement with the data reported in literature (see Hsu). According to the layer composition in the present model, the 8-MMT supercell contains 7 Mg atoms and their arrangement is shown in the figure 2. The structure of Keggin cation was built according to Johansson (1960) , (see fig.1).

The strategy of minimization using Crystal Packer can be summarized as follows:

• The model is a crystal consisting of rigid MMT layers with rigid Al_{13}^{7+} cations, placed between layers. The 8-MMT supercell, containing one Al_{13}^{7+} ion is defined by:

A = 4**a** = 20.83 $(10^{-10}$ m), fixed

B = 2**b** = 18.04 $(10^{-10}$ m), fixed

γ = 90°, fixed

C, **α** and **β**- which define the translation of successive layers with respect to each other are varied during the minimization. The Al_{13}^{7+} cation is allowed to translate and rotate in the supercell.

• Energy term consisting of VDW, COUL and HB interactions was set up using the following parameters: Non-bond cut-off distance for the VDW interactions was 7.0 $(10^{-10}$ m), that means VDW interactions between atoms further apart than this distance are ignored. Ewald sum constant was 0.5 $(10^{-10}$ m^{-1}). Minimum charge taken into Ewald sum was 0.00001e. All atom pairs with separation less than 10.0 $(10^{-10}$ m) are included in the real-space part of the Ewald sum. All reciprocal-lattice vectors with lengths less than 0.5 $(10^{-10}$ m^{-1}) are included in the reciprocal part of the Ewald summation.

• In minimizing a very low density cell, the intermolecular distances may be greater than the nonbond cutoff distance and no attractive inter-unit forces are calculated. However, by applying an external pressure at the start of minimization one can bring the rigid units into closer contact. The external pressure 99 kbar has been applied for the first minimization and than the external pressure was removed and new minimization started.

Keggin cation in 8MMT supercell

B $\rightarrow$

Figure 4. *Schematic illustration of the bonding geometry inside the Al_{13}^{7+} cation and Al_{13}^{7+} attachment to the silicate layer. Hydrogen bonds are marked by dotted lines.*
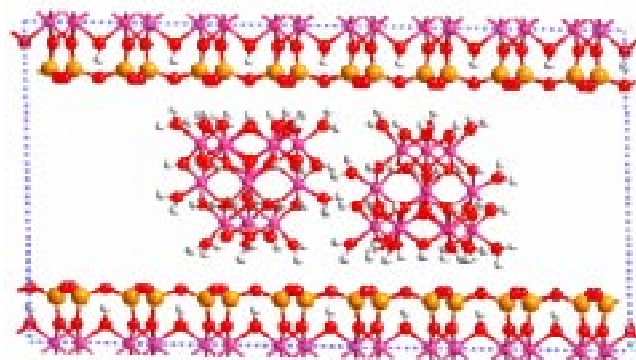
Figure 5. *Double supercell 16-MMT for models with the close contact of Keggin cations in the antiparallel arangment.*

Results

Position and orientation of Keggin cation in the interlamellar space: The most stable crystal packing obtained by the Crystal Packer energy minimization is shown in fig.3a,b , where two different views of 8-MMT supercell are presented: in **B** direction (3a) and in **A** direction (3b). As can be seen in figures 3a,b, the aluminium and oxygen planes perpendicular to the 3-fold axis in Keggin cation are parallel with the silicate layers. Several attempts were made, to minimize the initial model with the Al_{13}^{7+} cations, strongly tilted with respect to silicate layer. In all cases the energy minimization led to the arrangement presented in fig.3. It is evident, that this is the closest crystal packing, with respect to the shape of Al_{13}^{7+} cation. The oxygens in Al_{13}^{7+}-cation adjacent to the silicate layers are bonded via hydrogen bridges to the silicate layer oxygens (see fig.4). The 8-MMT supercell parameters for the minimized model in the fig.3 are: **A** = 20.83 (10^{-10} m), **B** = 18.04 (10^{-10} m) **C** = 19.79 (10^{-10} m), **α** = 88.25°, **β** = 99.84° and **γ** = 90°. Corresponding basal spacing d_{001} is 19.49 (10^{-10} m). The values of VDW, COUL, HB and crystal (potential) energy per supercell E_c for this model are: VDW= −574.9kJ/mol, COUL= −11300.1kJ/mol, HB= -79.1kJ/mol and E_c= −11954.1kJ/mol.

A large number of initial models have been derived from the first minimized model in fig. 3a,b, to investigate:

(a) The effect of Al_{13}^{7+}-cation position in the supercell with respect to the positions of Mg atoms, on the basal spacing end energy values. For this purpose Al_{13}^{7+}-cation was systematically translated along the silicate layers in A and B direction and the coordinates x,y of the central aluminium atom in these initial models followed the pathways indicated by straight lines in fig. 2.

(b) The effect of layer stacking on basal spacing and energy values. Mutual positions of two successive silicate layers have been varied changing the angles α and β in the initial models.

The results of energy minimization for all these initial models in both cases (a),(b) mentioned above led to the following conclusions:

• The values of VDW, COUL, HB, E_c and d_{001}-parameter for all minimized models are in the range:

VDW	−564.8 – (−593.3) kJ/mol
COUL	−10619.8 – (−11455.4) kJ/mol
HB	−44.35 – (−94.14) kJ/mol
E_c	−11257.1 – (12094.7) kJ/mol
d_{001}	19.42 – 19.60 (10^{-10} m)

• No systematic relationship has been found between the Al_{13}^{7+}-cation position in the 8-MMT supercell and the values of VDW, COUL, HB, E_c and d_{001}. The same is valid for the relationship between the mutual shift of two successive silicate layers (i.e. between the angles α and β and VDW, COUL, HB, E_c and d_{001}.

• Instead of a deep global minimum of energy, the system exhibits an endless number of local minima with the values of energy and basal spacings within the ranges mentioned above. Following these results we can conclude, that no ordering of Keggin cations in the interlayer and no regular stacking of layers can occur in intercalated montmorillonites.

Porosity control in the interlayer space - clustering of cations: It is evident that the pore dimensions can be hardly controlled in the intercalated montmorillonites with the irregular distribution of Keggin cations. However, one question still remains: can interactions between Al_{13}^{7+} cations in their present concentration influence their distances and consequently the pore dimensions? To answer this question, we

Double supercell - cluster, minimized model

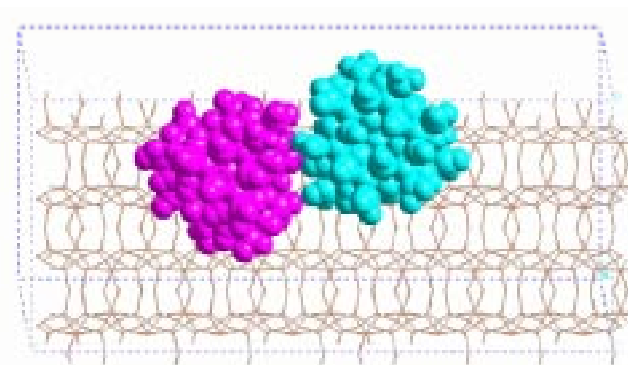Antiparallel arrangement of Keggin cations
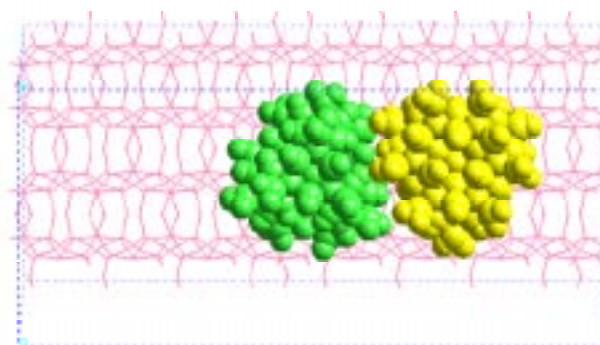
COUL = 18,915 kJ/mol	Al(c)–Al(c) = 10.26 (10^{-10} m)
E(c) = 20,187 kJ/mol	d = 19.73 (10^{-10} m)

Double supercell - cluster, minimized model

Antiparallel arrangement of Keggin cations

COUL = 16,996 kJ/mol	Al(c)–Al(c) = 10.92 (10^{-10} m)
E(c) = 18,301 kJ/mol	d = 19.48 (10^{-10} m)

Figure 6. *Double supercell 16-MMT with two Al_{13}^{7+} cations in the close contact and in the antiparallel arrangement for two selected minimized models: (left) MODEL-IA, (right) MODEL-IB.*

investigated mutual interactions between Al_{13}^{7+} cations in the interlayer of montmorillonites. For this purpose we created the double supercell containing 16 MMT unit cells with parameters $\mathbf{A_D}$=2$\mathbf{A}$, $\mathbf{B_D}$= $\mathbf{B}$, and with two Al_{13}^{7+} cations, where the distance between the central aluminium atoms of Keggin cations Al(c)-Al(c)=A = 20.83(10^{-10} m). This double supercell model will be denoted as Model-I. Both Al_{13}^{7+} cations in anti-parallel arrangement were then moved from their original positions to bring them into closer contact (see fig. 5). Several initial models have been derived from the Model-I, with different initial parameters and with different mutual orientation of Keggin cations, i.e. with different mutual rotations around their 3-fold axis. The distance of central aluminium atoms Al(c)-Al(c) was lower than 12.0 (10^{-10} m) for all these models. Energy minimizations of all these models were performed with three rigid units in the double supercell: two Al_{13}^{7+} cations and the silicate layer.

The results of energy minimization for all models with the close contact of Al_{13}^{7+} cations in anti-parallel arrangement showed, that the values of Coulombic and consequently of the total crystal energy are sensitive to the starting mutual orientation of cations. This effect will be illustrated on two selected models:

• MODEL-IA, with the initial parameters: d_{001} = 19.63 (10^{-10} m), Al(c)-Al(c) = 10.20 (10^{-10} m), VDW = –1144.3 kJ/mol, COUL = –18833.4 kJ/mol, HB = –91.6 kJ/mol, and the total crystal energy E_c = –20069.3 kJ/mol.

• MODEL-IB, with the initial parameters: d_{001} = 19.53 (10^{-10} m), Al(c)-Al(c) = 11.80 (10^{-10} m), VDW = –1145.2 kJ/mol, COUL = –16902.9 kJ/mol, HB = –107.9 kJ/mol, and the total crystal energy E_c = –18156.0 kJ/mol.

The arrangement of Al_{13}^{7+} cations in minimized models IA and IB is shown in figures 6a and 6b. The parameters obtained after energy minimization for MODEL-IA and -IB are summarized in table 1, compared with the parameters for double supercell with Al(c)-Al(c) = 20.83 (10^{-10} m) (MODEL-I). As one can see in the table 1, two different mutual orientation of Keggin cations leads to the different values of energy. The value of basal spacing 19.73 (10^{-10} m) for MODEL-IA is higher, than the values 19.41 - 19.61 (10^{-10} m), obtained for all models in 8-MMT supercell with Al(c)-Al(c) = 20.83 (10^{-10} m). Due to the stronger Coulombic interaction between Keggin cations in case of MODEL-IA, one of the cations is slightly tilted with respect to the silicate layers, (the 3-fold axis is not perpendicular to the layers) and this tilting results in higher value of basal spacing 19.73 (10^{-10} m). Consequently the clustering of Keggin cations may lead to the higher basal spacing and to increase of d-values range.

Comparing the energy values for the three minimized models in table 1 , we can see nearly the same values of Coulombic and total crystal energy and basal spacing for

MODEL-IB with the close contact of Keggin cations and MODEL-I with the long distance of cations. MODEL-IA with the cations in close contact is even more stable, than the MODEL-I. That means, the interactions between Keggin cations can not guarantee a reasonable distance, allowing to create a channels for sorption between them.

Present results of molecular simulations confirmed the irregular dimensions of pores and the irregularity in the distribution of pores in the interlayer space. These structural features represent a serious obstruction in the development of selective sorbents, based on montmorillonites, intercalated with Al_{13}^{7+}-cations. Comparing the results of molecular simulations with the limited informations available from the diffraction data, we can conclude, that our results agree with the experiment in three main points:

• Inhomogeneity in Al_{13}^{7+}-cation distribution and clustering of cations leads to the lattice strain and diffraction line broadening of 001 reflections, which has been observed in diffraction patterns. (see for example Trillo et al);

• Irregularity in the stacking of layers, resulting in hk-bands in diffraction pattern;

• The values of basal spacing obtained in present work are in agreement with diffraction data reported in literature .

References

1. Johansson, G. *Acta Chem. Scand.* **1960**, *14*, 771.
2. Mayo, L. S.; Olafson, B. D. and GoddardIII, W.A. *J. Phys. Chem.* **1990**, *94*, 8897.
3. Figueras, F.; Klapyta, Z.; Massiani, P.; Mountassir, Z.; Tichit, D.; and Fajula, F. *Clays & Clay Minerals* **1990**, *38*, 257.
4. Jones W. *Catalysis Today*, **1988**, *2*, 357.
5. Tschipursky, S. I. and Drits, V. A. *Clay Minerals* **1984**, *19*, 177.
6. Méring, J. and Oberlin, A. *Clays & Clay Minerals* **1967** *27*, 3.
7. Hsu, P. H. *Clays & Clay Minerals* **1992**, *40*, 300.
8. Trillo, J. M.; Alba, M. D.; Castro, M. A.; Poyato, J.; and Tobias, M. M.; *Journal of Mat. Science* **1993**, *28*, 373.