
Multiple Minima Hypersurfaces Studies of Aluminosilicate Hydration

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ABSTRACT: Hydrothermal zeolite synthesis is a complex process that is difficult to analyze experimentally. In this work, the role of water as solvent on the formation of aluminate and aluminosilicate clusters is described by quantum chemical calculations. The multiple minima hypersurfaces approach was used. It combines quantum chemical Hamiltonians for the calculation of the internal energy with statistical modeling and formulae for the calculation of thermodynamic functions of association. The structures of most probable hydration clusters are proposed and some of their association properties are calculated. Ab initio and semiempirical calculations of the structures and relevant reactions of aluminate and aluminosilicate fragments were reported. The results could be employed for an interpretation of the aluminosilicate synthesis. Calculations demonstrate the importance of considering other than the deepest minimum structures, giving a significant role to consider entropy of association. © 2009 Wiley Periodicals, Inc. *Int J Quantum Chem* 110: 586–594, 2010

Key words: semiempirical methods; zeolite; aluminosilicate; condensation reactions; water molecule

Introduction

Zeolites are aluminosilicate materials widely studied for their numerous applications. They contain pores and cavities of molecular dimensions. There are a variety of synthetic zeolites that have been used as catalysts and ion-exchange materials.

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In industrial chemistry, zeolites have an important role. Aluminosilicate zeolites are often synthesized under hydrothermal conditions [1]. Silicate and aluminosilicate varieties have been synthesized usually at moderate temperatures (25–150°C). These processes are still at an empirical stage or poorly understood. This kind of synthesis involves several species. It is a multiphase reaction (commonly involving at least two or more phases) and in some cases requires high temperature and pressure. In spite of the complexity of the system, the need for a careful observation and analysis is underlined. Al-

though these processes are very difficult to characterize experimentally, techniques of zeolites's modeling constitute an alternative for the detailed study of growth and nucleation of these materials and could help to understand it.

Condensation reactions play an important role in the chemistry of zeolites and have been studied by SCF calculations [2–6]. Mora-Fonz et al. [7] report that solvent and pH are factors that drive the condensation of silicates and that favor the cyclization of such species.

On the other hand, the adsorption of water molecule on acid zeolites is a process of interest from both empirical and theoretical points of view. Experimental techniques and theoretical methods have been used to study these interactions on zeolites [8–15].

The multiple minima hypersurfaces (MMH) approach estimate association energies of the molecular ground states combining semiempirical QM method and statistical thermodynamics formulae [16, 17]. Applications to several objects of this method are being recently published [18–20], including hydration clusters of silicates, drugs, and water [16, 17, 20].

Recently, a MMH study on the formation of small clusters and rings containing *Si* together with the study of the effects of hydration was developed by the authors [20]. Condensation energies of different reactions in a range of relevant silica clusters were estimated by this method.

In this article, a similar study is shown by considering the association behavior in the formation of aluminosilicate fragments with water. Therefore, the aim of the work is testing our approach for the estimation of association properties in simple units of aluminate and aluminosilicate models. A semiempirical Hamiltonian was used as the performance of semiempirical methods in zeolites studies has been tested in previous papers [21, 22]. It has been shown in this case that semiempirical AM1 Hamiltonian is reliable for aluminosilicate cluster calculations in comparison with accurate *ab initio* SCF and other DFT calculations. It means this is a chance to apply it for different kind of processes that occur in material sciences, where very complex and large molecular systems disallow more accurate molecular modeling.

Systems and Computational Details

Firstly, calculations of aluminosilicate reactions are reported in *vacuo* and compared with previous

and present results at higher levels of theory, including DFT and MP2/6-31+G** calculations. We also calculated these reaction energies with the Gaussian and Plane Waves (GPW) method [23], its implementation is in Quickstep which is part of the freely available program package CP2K [24]. The method uses an atom-centered Gaussian-type basis to describe the wave function, but uses an auxiliary plane wave basis to describe density. The geometry optimization of all molecules using the BLYP functional was done. The implementation requires that the nuclei are described using pseudopotential (GTH). TZ2P basis set was used for all valence electrons.

For hydration effects, the MMH approach was used. It has been described previously in detail [16, 17]. A minimum of 50 random molecular clusters formed by solute and solvent molecules have been built in every case. Such aggregates have been generated using a program called GRANADA. There is a web page where the procedure is explained in detail and all programs for processing are available [25]. The number of starting random molecular arrangements is justified because the convergence of the statistically averaged energy of association upon optimization is attained in all series since the first 20 or 25 minima are “weighted.” However, if the convergences became delayed, up to 70 initial structures have been optimized. We have checked even more configurations and we arrived to the same results that proof ergodicity. More structures only add redundant structures and rarely a change in the statistically averaged internal energy. It has also been published earlier [16, 19, 26].

An alternative for the calculation of molecules in the manner of serial procedures is the use of a semiempirical Hamiltonian. The cancellations of systematic errors in statistical weighting and the calculation of relative association energies produce averaging hydration energies rather similar to those of more accurate *ab initio* SCF and DFT calculations. Semiempirical calculations have important advantages that we should take into account, such as: BSSE do not appear in these methods due to the orthogonality of the atomic orbital basis set, correlation effects are implicitly considered during the parameterization procedures with respect to experimental values and the computations are much faster and even the only possible in the case of very large supermolecules. For these reasons, we have chosen a semiempirical SCF-MO Hamiltonian for our calculations. Chatterjee et al. reports that semiempirical QM methods can be successfully

used to determine the interaction energy for several different templates within a cluster of the ZSM5 [27]. The AM1 Hamiltonian is used to explore the potential hypersurfaces of molecular clusters by a random search of possible aggregates in the configuration space. Apparently, the well-known systematic failures of this Hamiltonian are absent in this kind of structures and interactions. All of them are optimized at their time by the same gradient pathway procedure. The Eigenvector Following (EF) routine for searching minima was used in all cases. All convergence criteria were increased 100 times with respect to defaults using Mopac v6 program [28]. In some cases, different arrangements converged to the same minimum and the Tanimoto similarity index was used to eliminate the redundant structures. Then, after visiting thousands of different supermolecular geometries for each cluster, the collection of most relevant local minima to the selected Hamiltonian is obtained. It corresponds to molecular arrangements to form a canonical ensemble (NVT) that must be significant to the state of the system. All of them are local minima of energy and the results can then be treated by statistical thermodynamic formulae to calculate association energies and entropy.

Gaussian 98 and 03 [29] programs were used for appropriate cases with the built-in basis sets and procedures. Figures shown here were made with ORTEP v. 3.0 [30].

THE STATISTICAL APPROACH

Formulae for thermodynamic quantities regarding association are developed from the partition function of association obtained by:

$$q^* = \sum_i g_i e^{-\frac{\Delta \varepsilon_i}{RT}} \quad (1)$$

where

$$\Delta \varepsilon_i = \varepsilon_i - \varepsilon^{\text{ref}} \quad (2)$$

and:

$$\varepsilon^{\text{ref}} = \varepsilon_{\text{tot}(X)} + n\varepsilon_{\text{tot}(\text{H}_2\text{O})} \quad (3)$$

being ε_i the total HF-SCF energy of the optimized cluster i , and $\varepsilon_{\text{tot}(X)}$ and $\varepsilon_{\text{tot}(\text{H}_2\text{O})}$ the corresponding energy of the optimized isolated solute and that of n water molecules, respectively. It means that $\Delta \varepsilon_i$ is

the energy of association of each cluster i (each local minimum founded) calculated as a chemical reaction equation for the association of the free molecules to clusters, in order to cancel systematic errors of Hamiltonians, and also translational, rotational, and most of the vibrational energy terms involved in molecular associations. Then, the statistical thermodynamic quantities are as follows:

$$E^{\text{assoc}} = RT^2 \frac{q^*}{q^{*'}} \quad (4)$$

$$S^{\text{assoc}} = R \ln q^* + \frac{E^{\text{assoc}}}{T} \quad (5)$$

$$A^{\text{assoc}} = -RT \ln q^* \quad (6)$$

where E^{assoc} , S^{assoc} , and A^{assoc} are the internal energy, entropy, and Helmholtz free energy of association, respectively, and $q^{*'} = \partial q^* / \partial T$. Optimized clusters having similar energy and different molecular arrangements are relevant to the ensemble and contribute in a significant way to the entropy.

However, in this process some redundant information can also be generated. It comes from clusters when the final structure after optimization is the same or nearly the same with respect to others, and consequently gives nothing new regarding the statistical information. Their statistical weight will be given by their energy in the Boltzmann distribution. It means that the clusters that sum in the partition function must be previously selected with respect to their structures, to remove these redundancies.

To solve this problem, a similarity analysis between clusters must be introduced. The procedure uses the so-called Tanimoto analysis [31, 32] to evaluate similarity among molecular arrangements to discard redundant degeneracy. This procedure calculates similarity between structures pair by pair. For this purpose it first converts internal coordinates to Cartesians for all atoms in a given structure.

The Tanimoto similarity index T corresponding to a comparison of cluster A with B is determined by the expression:

$$T = \frac{M}{(A + B - M)} \quad (7)$$

where A , B , M are calculated according the following expressions:

$$M = \sum_{i=1}^N r_i^A r_i^B \quad (8)$$

$$A = \sum_{i=1}^N r_i^A r_i^A \quad (9)$$

$$B = \sum_{i=1}^N r_i^B r_i^B \quad (10)$$

where r_i^A is an element of $[D_A]$ and r_i^B of $[D_B]$ both belonging to A and B structures, respectively.

Then, every cluster with an energy difference of less than $0.096 \text{ kJ mol}^{-1}$ is compared with respect to any previous one. This is equivalent to an arbitrarily chosen limit of 10^{-3} eV to consider that these clusters have the same energy in the present work, by far below the expected accuracy of semiempirical Hamiltonians. Then, it must be fixed a limit value of discrimination to consider the clusters equal or not from a geometrical point of view. For example, if the calculated value of T is greater than $T' = 0.85$, we can generally consider that these molecular arrangements are absolutely equivalent and it indicates the presence of redundant degenerate clusters. Therefore, if T is less than 0.85 the clusters are different, even when they can have the same energy, and this is the case where degeneracy is important to validate the partition function. In this case we work with a value of $T = 0.85$, following previous experiences with other systems [26].

As it is discussed in the basic reference of our method, to compare the experimental enthalpy and Gibbs free energy values, defined at constant pressure with the calculated association energies, we can introduce ideal gas corrections. Then, $E^{\text{assoc}} = H^{\text{assoc}} + \Delta nRT$, and consequently

$$H^{\text{assoc}} = RT^2(q^{*'} / q^*) - \Delta nRT \quad (11)$$

$$G^{\text{assoc}} = -RT \ln q^* - \Delta nRT \quad (12)$$

According to the deduced equations in that article, the ΔnRT term cancels when we are dealing with chemical reactions and consequently $\Delta H^{\text{assoc}} = \Delta E^{\text{assoc}}$ and $\Delta G^{\text{assoc}} = \Delta A^{\text{assoc}}$ in such cases. Therefore, we will express here when appropriate the most common quantities at constant pressure, in place of those at constant volume.

In a previous work [20], the reliability of our numerical values was tested by performing calculations with higher level of theory. The results demonstrated that averaging hydration energies calculated is rather similar. This interesting result must be due to cancellations of systematic errors arising from both the calculation of energies of reaction in Eq. (2) and the partition function calculated from a Boltzmann distribution. Another interesting testing was done comparing energetic consequences of environmental effects by different methods. MMH results with COSMO simulations were compared and an excellent agreement of those essentially different methods toward a very similar object was also observed.

Formulae and ball and stick representations of the main compounds studied in this article are shown in Figure 1.

Results and Discussion

ALUMINOSILICATE CONDENSATION REACTIONS IN GAS PHASE

Firstly, calculations are reported on clusters in vacuo. The condensation reactions give rise to primary aluminosilicate blocks. Regarding the energies, the condensation reactions of isolated molecules that accomplish with the Lowenstein rule [33] are favored (see Table I). Semiempirical results are compared with previous and also present values at higher levels of theory. In a previous article [22], the semiempirical Hamiltonian behavior toward DFT and accurate ab initio calculations of the simplest tetrahedra of oxygenated Si and Al was investigated. We demonstrated that a semiempirical Hamiltonian is a compromise choice for considering, simultaneously, a reasonable fast computation and accuracy. In the present results including Al, AM1 Hamiltonian reproduces correctly the condensation energies when compared with MP2/6-31+G**. Previous theoretical works includes DFT calculations also show comparable energies. Besides, we obtained also a satisfactory agreement with GPW method. All reactions have good agreement while using AM1 Hamiltonian and do not behave too well with PM3 when the formation of aluminosilicate clusters is taken into account (see Reactions 1, 2, 6, and 7).

Considering these results, clusters show strong energetic preference for the formation of Si-O-Al bridges. We find that, Al-O-Al bridges are energet-

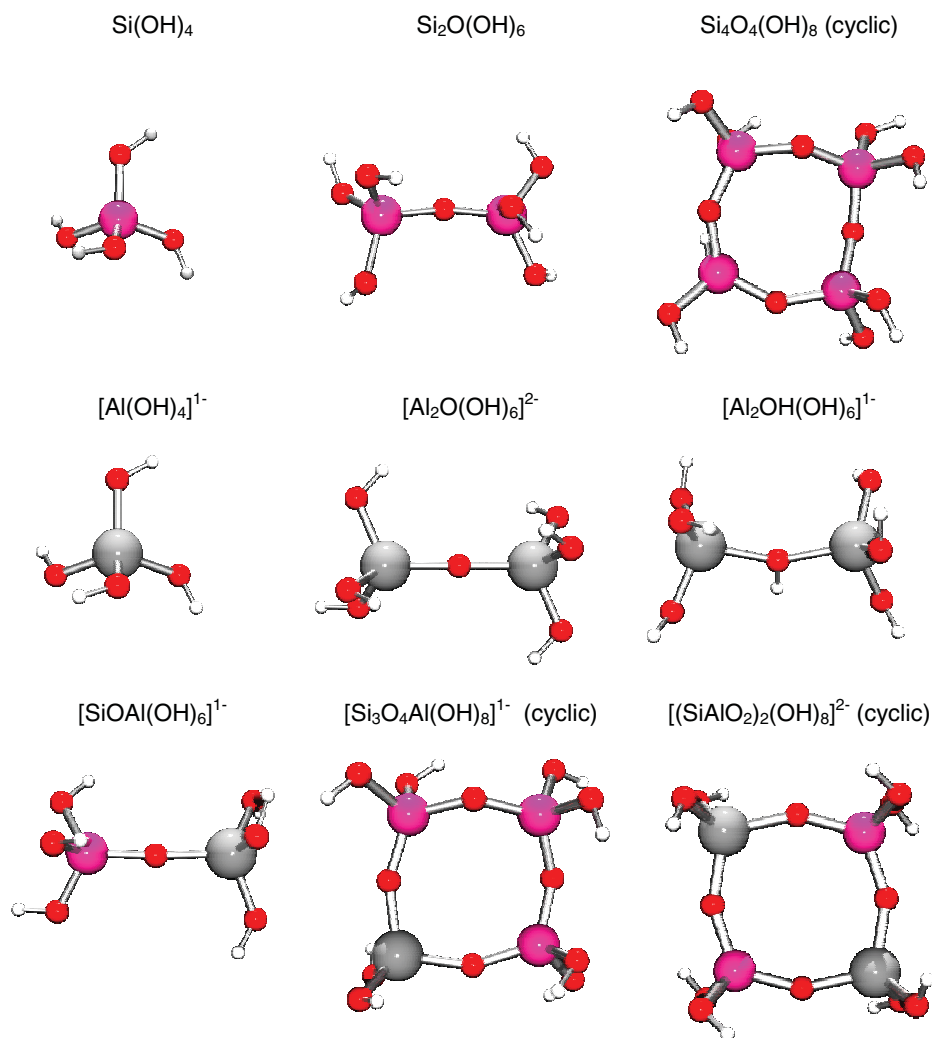


FIGURE 1. Formulas and structural graphics of molecules studied in the recent work. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

ically unfavorable by 50–80 kcal mol⁻¹. It is commonly accepted that “Lowenstein rule” controls the distribution of Al in aluminosilicate frameworks. The rule excludes the existence of Al-O-Al pairs and our results agree with it.

The results also show that forming $[\text{Si}_3\text{O}_4\text{Al}(\text{OH})_8]^-$ rings tetramer is more favorable if we take their monomers than their dimers. In general, the cluster condensation that contains one Al is energetically favorable.

ALUMINOSILICATE HYDRATION BY THE MMH APPROACH

We built molecular aggregates formed by growing quantities of water molecules and their hyper-

surfaces were explored. After selecting the molecular geometries of minimum energy in the group of all those that have probabilities of influencing in the macroscopic state of the system, the thermodynamic functions were calculated. Similarity calculations were introduced among the molecular structures obtained to eliminate undesirable redundancies in the calculation of partition functions and, consequently, to refine the statistical procedure.

The behavior about the selection of simple aluminate and aluminosilicate-water complexes at temperature of 298 and 423 K of hydration by the MMH approach were calculated. No significant differences in thermodynamical association properties were obtained. On the other hand, experimentally,

TABLE I

Calculated energies (ΔE) of condensation and other relevant reactions (isolated molecules).^a

Reactions	PM3	AM1	MP2/6-31+G**	GPW-BLYP/TZV2P	DF-LDF/DN ^b
Monomer to dimer					
1. $\text{Si}(\text{OH})_4 + [\text{Al}(\text{OH})_4]^- \rightarrow [\text{SiAl}(\text{OH})_6]^- + \text{H}_2\text{O}$	2.3	-14.5	-25.7	-20.9	-27.0
2. $2 [\text{Al}(\text{OH})_4]^- \rightarrow [\text{Al}_2\text{OH}(\text{OH})_6]^- + \text{OH}^-$	59.8	57.7	37.6	43.0	41.1
3. $2 [\text{Al}(\text{OH})_4]^- \rightarrow [\text{Al}_2\text{O}(\text{OH})_6]^{2-} + \text{H}_2\text{O}$	84.8	77.5	65.0	48.0	53.0
Monomer to cyclic tetramer					
4. $3 \text{Si}(\text{OH})_4 + [\text{Al}(\text{OH})_4]^- \rightarrow [\text{Si}_3\text{O}_4\text{Al}(\text{OH})_8]^- + 4 \text{H}_2\text{O}$	0.5	-43.2	-51.1	-33.7	—
Dimer to cyclic tetramer					
5. $2 [\text{SiAl}(\text{OH})_6]^- \rightarrow [(\text{SiAlO}_2)_2(\text{OH})_8]^{2-} + 2 \text{H}_2\text{O}$	81.8 ^c	55.8 ^c	49.8 ^c	56.9 ^c	56.0 ^c
6. $[\text{Si}_2\text{O}(\text{OH})_6] + [\text{SiAl}(\text{OH})_6]^- \rightarrow [\text{Si}_3\text{O}_4\text{Al}(\text{OH})_8]^- + 2 \text{H}_2\text{O}$	3.6	-17.7	-19.4	-10.7	-11.3
Lowensteinian to non-Lowensteinian					
7. $[(\text{SiAlO}_2)_2(\text{OH})_8]^{2-} \rightarrow [(\text{SiO})_2(\text{AlO})_2(\text{OH})_8]^{2-}$	3.0	8.7	8.9	—	18.0

^a In kcal mol⁻¹.^b DN basis set with LDF (DMOL) by Ref. [3].^c Assumes formation of Lowensteinian cluster.

the effect of temperature is mainly to increase the growth rate of the structure and do not affect the thermodynamical behavior [1].

We also obtained an interesting neutral complex structure in which the adsorbed molecule is attached to the acidic site via two hydrogen bonds. Tables II and III show the behavior of the aluminates and aluminosilicate clusters in water at different degrees of hydration by the MMH approach.

A single water molecule mostly perturbs all models, as a general rule, and always shows the lowest energy of association E^{assoc} and the lowest free energy A^{assoc} . These energies are in the order of very weak hydrogen bonds (4–16 kJ mol⁻¹). The negative value of Helmholtz free energy ($A^{\text{assoc}} < 0$) implies that the

association processes are favorable from the thermodynamical point of view. The clusters are likely to interact with water because they are ions, and this fact match with the previously obtained results in this field. According to the minimum of the association energies, the most stable interaction is that corresponding to the H of water and an O atom of the zeolite cluster. It is around 2.0 Å, and agrees with data in literature that is reported around 1.8 Å [15].

In general, the interactions with charged aluminate and aluminosilicate clusters are the strongest and consequently, water stabilizes the charged anions. Besides, the interaction energies per mol of solvent decrease in all cases when the number of molecules of water increases. We observed changes when

TABLE II

Hydration energies of aluminates as obtained by MMH-AM1 (kcal mol⁻¹) of water.

n	$[\text{Al}(\text{OH})_4]^{1-}$		$[\text{AlOAl}(\text{OH})_6]^{2-}$		$[\text{AlOAlH}(\text{OH})_6]^{1-}$	
	E^{assoc}	A^{assoc}	E^{assoc}	A^{assoc}	E^{assoc}	A^{assoc}
1	-11.8	-13.4	-16.8	-18.5	-10.1	-11.6
2	-11.5	-13.2	-16.4	-18.3	-10.0	-12.0
3	-11.3	-12.9	-15.9	-18.1	-9.8	-12.0
4	-11.2	-12.7	-15.6	-17.8	-9.5	-11.8
5	-11.0	-12.5	-15.3	-17.5	-9.4	-11.7

TABLE III

Hydration energies of aluminosilicates as obtained by MMH-AM1 (kcal mol⁻¹) of water.

n	$[\text{SiAl}(\text{OH})_6]^-$		$[(\text{SiAlO}_2)_2(\text{OH})_8]^{2-}$		$[(\text{SiO})_3\text{AlO}(\text{OH})_8]^-$	
	E^{assoc}	A^{assoc}	E^{assoc}	A^{assoc}	E^{assoc}	A^{assoc}
1	-10.8	-12.0	-15.5	-17.0	-13.0	-14.2
2	-9.8	-11.5	-13.7	-15.5	-11.2	-13.1
3	-9.8	-12.0	-13.4	-15.3	-10.7	-12.7
4	-9.7	-12.0	-12.7	-14.7	-10.9	-12.8
5	-9.7	-11.7	-12.4	-14.5	-9.8	-12.0

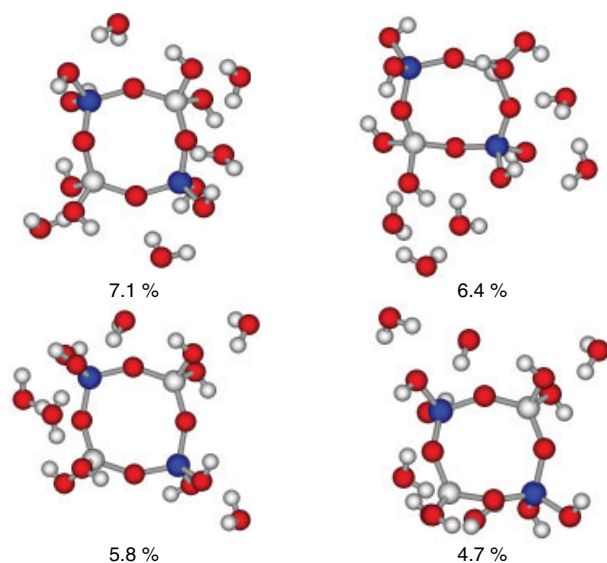


FIGURE 2. Molecular graphics representing about the 25% of the $[(\text{SiAlO}_2)_2(\text{OH})_8]^{2-} [\text{H}_2\text{O}]_5$ structures with their respective calculated populations. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

three molecules of water are included in the structure and then the interaction energies keep almost constant up to five molecules of water in the structure.

Figure 2 shows the cluster $[(\text{SiAlO}_2)_2(\text{OH})_8]^{2-} [\text{H}_2\text{O}]_5$ representing about the 25% of the population of hydrates of the cyclic tetramer. As we obtained in a previous work [20] based on hydration of silicates, one of the relevant motifs that give stability to several of the most populated structures is a water molecule with double hydrogen bridge, one as H donor and the other as acceptor, although there are also cases where a single water molecule is double-bridged as H donor in both cases.

The entropy of association (S^{assoc}) is positive in all cases showing an increase in the degrees of freedom for the interacting molecules. The value of such entropy of association would not be accurate due to the several approximations used in the Hamiltonian. However, it has an undeniable qualitative importance due to the fact that several cluster geometries are possible near to the global minimum, and this is a determining factor favoring solvation.

These models are showing several conformations for molecular interactions as hydrogen bonds. As we can see in the previous silicate MMH study, the reactions are hardly represented when a single global minimum is used. Only monohydrates models can be represented with certain reliability with 1 or 2 local minima and consequently, the entropy is low in comparison with pentahydrates clusters. The 50% of cluster populations can be represented with 2 or 3 structures (see Table IV). On the other hand, pentahydrate clusters show higher entropy than the monohydrate ones, as could be expected. In these cases, the 50% of cluster population can be represented with 10 or 15 structures.

Table IV also shows entropies at 423 K, which is a temperature more near to that used for hydrothermal zeolite synthesis. An increase of the entropy is observed as a general trend and hence, an increase of the structures to represent the 50% of population. The S^{423}/S^{298} rate was reported and means that in the cases of monohydrate structures, the effect of the temperature (from 298 to 423 K) in the entropy of association is higher than in the case of pentahydrates.

Condensation energies obtained for these reactions by MMH methods are reported in Table V. We find a crucial influence on the structures and stability of these clusters regarding the sole effect of hydration in the cases of cyclic tetramer formation.

TABLE IV
Population analysis of some relevant clusters.^a

Cluster	$N_{25\%}$	$N_{50\%}$	$N_{75\%}$	S^{assoc}	S^{assoc}	S^{423}/S^{298}
				(J K ⁻¹ mol ⁻¹)	(J K ⁻¹ mol ⁻¹)	
Temperature (K)	298	298	298	298	423	
$[\text{Al}(\text{OH})_4]^{1-} [\text{H}_2\text{O}]$	2	4	8	22.6	22.9	1.01
$[(\text{SiO})_3\text{AlO}(\text{OH})_8]^- [\text{H}_2\text{O}]$	1	2	4	16.4	20.5	1.25
$[(\text{SiAlO}_2)_2(\text{OH})_8]^{2-} [\text{H}_2\text{O}]$	1	3	7	20.7	23.2	1.12
$[\text{Al}(\text{OH})_4]^{1-} [\text{H}_2\text{O}]_5$	11	28	47	35.2	35.4	1.01
$[(\text{SiO})_3\text{AlO}(\text{OH})_8]^- [\text{H}_2\text{O}]_5$	4	12	26	30.5	31.5	1.03
$[(\text{SiAlO}_2)_2(\text{OH})_8]^{2-} [\text{H}_2\text{O}]_5$	4	11	20	29.5	30.7	1.04

^a $N_{X\%}$ means the number of clusters appearing to populate up to X% of the system.

TABLE V

Enthalpies and Gibb's free energies of condensation reactions considering the effect of the solvent (water) by MMH procedure (kcal mol⁻¹).

Reactions	Number of molecules of water around the solute (<i>n</i>)						
		0	1	2	3	4	5
Monomer to dimer							
1. Si(OH) ₄ [H ₂ O] _{<i>n</i>} + [Al(OH) ₄] [−] [H ₂ O] _{<i>n</i>} → [SiOAl(OH) ₆] [−] [H ₂ O] _{<i>n</i>} + H ₂ O(l)	ΔH^0	−14.5	−10.2	−11.2	−11.9	−10.8	−12.8
	ΔG^0		−8.6	−9.4	−10.3	−10.3	−10.9
2. 2[Al(OH) ₄] [−] .[H ₂ O] _{<i>n</i>} → [Al ₂ OH(OH) ₆] [−] [H ₂ O] _{<i>n</i>} + OH [−] [H ₂ O] _{<i>n</i>}	ΔH^0	57.7	49.2	49.0	50.5	51.4	51.4
	ΔG^0		50.9	51.1	51.4	52.1	52.2
3. 2 [Al(OH) ₄] [−] [H ₂ O] _{<i>n</i>} → [Al ₂ O(OH) ₆] ^{2−} [H ₂ O] _{<i>n</i>} + H ₂ O(l)	ΔH^0	77.5	81.6	79.2	78.4	77.9	77.4
	ΔG^0		83.1	80.7	79.4	78.4	78.2
Monomer to cyclic tetramer							
4. 3 Si(OH) ₄ [H ₂ O] _{<i>n</i>} + [Al(OH) ₄] [−] [H ₂ O] _{<i>n</i>} → [Si ₃ O ₄ Al(OH) ₈] [−] [H ₂ O] _{<i>n</i>} + 4 H ₂ O(l)	ΔH^0	−43.2	−37.2	−43.0	−45.1	−42.7	−47.6
	ΔG^0		−33.2	−37.8	−38.9	−39.2	−41.1
Dimer to cyclic tetramer							
5. 2[SiOAl(OH) ₆] [−] [H ₂ O] _{<i>n</i>} → [(SiAlO ₂) ₂ (OH) ₈] ^{2−} [H ₂ O] _{<i>n</i>} + 2 H ₂ O(l)	ΔH^0	55.8	56.5	51.9	50.7	49.7	49.2
	ΔG^0		57.4	53.5	52.9	52.3	51.1
6. [Si ₂ O(OH) ₆] [H ₂ O] _{<i>n</i>} + [SiOAl(OH) ₆] [−] .[H ₂ O] _{<i>n</i>} → Si ₃ O ₄ Al (OH) ₈] [−] [H ₂ O] _{<i>n</i>} + 2 H ₂ O (l)	ΔH^0	−17.7	−11.2	−17.2	−21.6	−23.3	−24.6
	ΔG^0		−11.2	−17.2	−20.5	−21.9	−22.7

These favorable reactions continue this behavior when the solvent effect is included. In general, the greatest stabilization is obtained with five molecules of water around the solute.

The reaction of formation of [(SiAlO₂)₂(OH)₈]²⁻ from a dimer is hardly favored by hydration from the point of view of the heat of reaction (like in the gas phase). It also resulted antientropic, being disfavored upon hydration from the point of view of free energies. One and two water molecule disfavors the reaction in all cases. It means that several hydrogen bridges of silicates with water appear necessary to carry out condensations.

Conclusions

Systematic optimization processes of aluminosilicates were carried out at AM1 semiempirical level. A set of condensation reactions of isolated molecules in gas phase were calculated and the results were compared with MP2 calculations and GPW method. These calculations show that AM1 Hamiltonian reproduces correctly these energies.

The MMH methodology allows us to obtain a group of significant minima for each interacting system and to calculate the association properties. It must be remarked that several conformations or molecular arrangements of water around each aluminosilicate clusters have similar populations and they contribute significantly to the ensemble properties, giving a significant place to entropy of association when this kind of clusters are to be modeled.

This approach can be used to calculate the properties of hydration in the structure and formation of aluminate and aluminosilicate clusters. Results show in general, how hydration allows the syntheses of relevant aluminosilicate fragments. Solvent effects in the formation of zeolite chains were calculated and we found the following order of influence: Si-O-Al > Al-O-Al.

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