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An Approach to Hydration of Model Silica Materials by Exploring Their Multiple Minima Hypersurfaces. The Role of Entropy of Association

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The influence of molecular water on the structure and formation of silica clusters is modeled with the use of the MMH (multiple minima hypersurfaces) approach. It combines quantum chemical Hamiltonians for the calculation of the internal energy with statistical modeling and formulas for the calculation of thermodynamic functions of association. The structures of the most probable clusters of hydration and some properties of the association with water are proposed. Different simple structures are calculated to consider the entropy of association in place of the simpler approach of a single “global minimum”. Ab initio, DFT, and semiempirical calculations of the structures and relevant reactions of silica fragments are also reported, confirming the reliability of the results on very different grounded quantum mechanical methods. Particularly, it has been shown that semiempirical PM3 Hamiltonian is reliable for silica cluster calculations of this kind, in comparison with accurate ab initio SCF and other DFT calculations. Apparently, the well-known systematic failures of this Hamiltonian are absent in this kind of structures and interactions. The increasing hydrophobic character of neutral silica clusters appears as a result of the free energies of association, and therefore, it originates on entropy. It is remarkable that the simple global minimum approach currently used in works of molecular modeling on this kind of compounds, where several hydrogen bridges have a place to exist with several different conformations, must be taken with caution given the remarkable entropy of association of such systems.

Introduction

The methods of quantum mechanical (QM) calculations are becoming a strong resource for theoretical modeling and research in physics, chemistry, and biology as “computer power” is becoming cheaper. By means of this tool, an approach to a qualitative and quantitative description of the phenomena at the atomic and molecular level is possible. However, attaining a scale in which molecular clusters could both be relevant to material sciences and also become fair objects for reliable QM calculations is a big problem. Therefore, calculations of silica materials have received attention mostly with methods based on empirical classical potentials, which can reach huge structures and quite good results. Previous attempts by one of the present authors of applying semiempirical and truly ab initio Hamiltonians have been certainly fruitful.[1] On the other hand, our experiences in QM calculations of silica had great success.[2]

The adsorption of water molecules on neutral silica and zeolites is a process of interest from both the empirical and theoretical points of view. Experimental techniques and theoretical methods (ab initio, DFT, and semiempirical) have been used to study these interactions.[3−5] There are two possible adsorption structures, a neutral complex in which the adsorbed molecule is attached to the acidic site via two hydrogen bonds and an ion pair complex in which the adsorbed molecule is protonated and coordinated via two protons to the negatively charged zeolite framework site. The solvation state of the silica clusters presented in this work is relevant for a better understanding of the role played by these clusters in the nucleation−crystallization process of zeolite hydrothermal synthesis.[2,6−10]

The multiple minima hypersurface (MMH) treatment to estimate association energies on the grounds of a combined semiempirical QM method and statistical thermodynamics formulas has been applied elsewhere to several objects,[11,12] including hydration clusters of drugs.[13] In the MMH framework, we sample local minima using quenching from random configurations using a quantum mechanical treatment. These minima are treated as a Maxwell−Boltzmann distribution and then employed to construct an appropriate partition function. The treatment of local minima in this way has also been named as the “superposition approximation”[14−16] and was developed in parallel to MMH, departing from earlier ideas of Burton.[17] MMH treats approximate quantum mechanical results after following gradient paths to reach minima and concentrates on association energies that serve to correct thermochemical equations for solvent effects and even find reactive or prereactive structures. A MMH study on the formation of small clusters and rings containing Si together with the study of the effects of hydration is an opportunity to apply it for material sciences. Condensation energies of different reactions in a range of relevant silica clusters can be estimated by this method. This point is particularly sensitive to the hydrothermal synthesis of zeolites and for understanding the behavior of silica toward ubiquitous solvents like water. The purpose of this work is to apply the MMH approach for the estimation of association properties in simple units of silica with water, also considering

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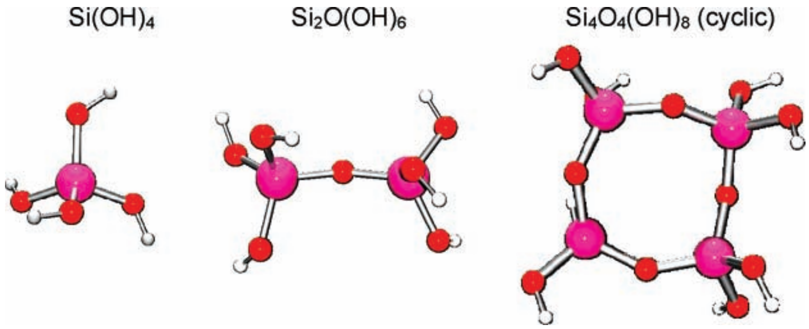

Figure 1. Formulas and structural graphics of molecules studied in the present work.

the role of the entropy of association in these processes. This point is particularly sensitive given the fact that the current methods based in QM for modeling reactions in microporous material environments cannot reach large systems in an affordable processing time, even with the very fast computers available nowadays.

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

Methods and Procedures

The multiple minima hypersurface approach has been described previously in detail.[13,18] Therefore, we will only outline it briefly in this paper. Applications of this method were recently published.[19] Essentially, an approximate Hamiltonian is used to explore the potential hypersurfaces of molecular clusters by an exploration of possible structures in the configuration space. A convenient number of starting cluster geometries have been generated at random, and all of them are optimized at their time by the same gradient pathway procedure. Then, after visiting several different supermolecular geometries for each cluster, the collection of the most relevant local minima to the selected Hamiltonian hypersurface 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 formulas to calculate association energies and entropy.

Formulas for thermodynamic quantities regarding molecular associations are based on the partition function corresponding to the sum of each local minima structure, or ith state, with a degeneracy g_i, as obtained by

$$q^* = \sum_i g_i \mathrm{e}^{-\Delta\epsilon_i/RT} \tag{1}$$

where

$$\Delta\epsilon_i = \epsilon_i - \epsilon^{\text{ref}} \tag{2}$$

and

$$\epsilon^{\text{ref}} = \epsilon_{\text{tot(X)}} + n\epsilon_{\text{tot(H}_2\text{O)}} \tag{3}$$

(g_i can also be interpreted as the canonical partition function for minimum i, referred to an energy origin at ϵ^{ref}; this local partition function can be defined rigorously by restricting the integral in configuration space to the basin of attraction of the minimum in question, including degeneracy caused by molecular symmetry). Here, ϵ_i is the total HF energy of the optimized cluster i, and $\epsilon_{\text{tot(X)}}$ and $\epsilon_{\text{tot(H}_2\text{O)}}$ are the corresponding energies of the optimized isolated solute and of n water molecules, respectively. It means that $\Delta\epsilon_i$ is the energy of association of the ith cluster (each local minimum founded) calculated as a chemical reaction 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

$$E^{\text{assoc}} = RT^2 \frac{q^{*\prime}}{q^*} \tag{4}$$

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

$$A^{\text{assoc}} = -RT \ln q^* \tag{6}$$

where E^{assoc}, S^{assoc}, and A^{assoc} are the internal energy, entropy, and Helmholtz free energy of association, respectively, and $q^{*\prime} = \partial q^*/\partial T$. Optimized clusters having similar energies 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 the others, and consequently, it gives nothing new regarding the statistical information. Their statistical weight will be given by their energy in the Boltzmann distribution and not from this false multiplicity. It means that the clusters that sum in the partition function must be previously selected with respect to their structures to remove these redundancies.

In order to solve this problem, a similarity analysis between clusters must be introduced. The procedure uses the so-called Tanimoto analysis[20,21] to evaluate the similarity among molecular arrangements to discard redundant degeneracy. This procedure calculates the similarity between structures pair by pair. For this purpose, it first converts internal coordinates to Cartesians for all atoms in a given structure. Then, it obtains the matrix of the position vector modules with respect to an origin fixed at atom 1, called $[D]$

$$[D] \equiv [r_1, r_2, r_3, ..., r_N] \tag{7}$$

where N is the total number of atoms.

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

$$T = M/(A + B - M) \tag{8}$$

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

$$M = \sum_{i=1}^{N} r_i^{\text{A}} r_i^{\text{B}} \tag{9}$$

$$A = \sum_{i=1}^{N} r_i^{\mathrm{A}} r_i^{\mathrm{A}} \qquad (10)$$

$$B = \sum_{i=1}^{N} r_i^{\mathrm{B}} r_i^{\mathrm{B}} \qquad (11)$$

where r_i^{A} is an element of $[D_{\mathrm{A}}]$ and r_i^{B} is that of $[D_{\mathrm{B}}]$, both belonging to the A and B structures, respectively.

Then, every cluster with an energy difference less than 0.096 kJ/mol 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, a limit value of discrimination must be fixed 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 that we are in 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.[22]

As discussed in the basic reference of our method,[13,18] 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, $E^{\mathrm{assoc}} = H^{\mathrm{assoc}} + \Delta nRT$, and consequently

$$H^{\mathrm{assoc}} = RT^2(q^{*\prime}/q^*) - \Delta nRT \qquad (12)$$

$$G^{\mathrm{assoc}} = -RT \ln q^* - \Delta nRT \qquad (13)$$

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

A choice for the calculation of molecules in this manner of serial procedure is the use of a semiempirical Hamiltonian. The principle disadvantage of this approach is the lack of ab initio theoretical rigor.[18] However, these calculations have important advantages that we should take into account, such as the lack of BSSE in these methods due to the orthogonality of the atomic orbital basis set, the implicit consideration of correlation effects during the parametrization procedures with respect to experimental values, and the quickness of computations in the case of large supermolecules. For these reasons, we have chosen a semiempirical SCF-MO Hamiltonian for our calculations. Also, Chatterjee et al. report that semiempirical QM methods can be successfully used to determine the interaction energy for several different templates within a cluster of the ZSM5.[23]

A minimum of 50 random molecular aggregates formed by solute and solvent molecules have been built in the present work in every case by using the Granada program. There is a web page where the procedure is explained in detail, and all programs for processing are available.[24] Geometries were then optimized at the PM3 semiempirical Hamiltonian[25] level to reach an equivalent number of local minimum structures. This, and not a larger 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". In some cases, when the convergences become delayed, up to 70 initial structures have been optimized. Gaussian 98 and 03[26] programs were used with the built-in basis sets and procedures for ab initio calculations. ORTEP 3 is the molecular graphics program for this paper[27] together with Accelrys DS Visualizer 1.5. Tests for hydration effects have been also performed with the well-known COSMO method.[28]

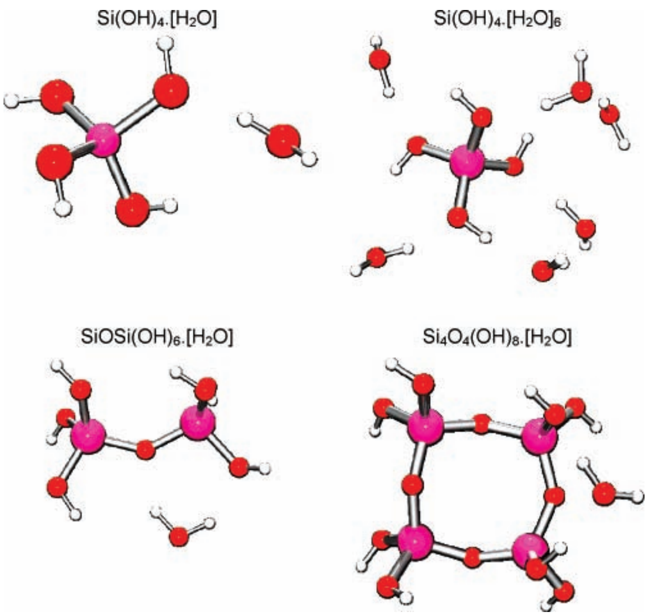

Figure 2. Ball and stick representation of some simple silicate hydrates at the lowest energies.

Results and Discussion

Geometries and Condensation Reactions in the Gas Phase. An important initial point is testing the ability of semiempirical Hamiltonians to deal with molecular silica systems. The PM3 Hamiltonian behavior toward DFT and accurate ab initio calculations of the simplest tetrahedra of oxygenated Si was investigated in a previous paper.[29] We demonstrated that the PM3 Hamiltonian is a compromise choice for considering, simultaneously, a reasonable fast computation and accuracy. The optimized bond length and bond angles at the PM3 level compare well with the experimental values, as the error never exceeds 0.07 Å and 6° respectively.

Our first calculations are reported for reactions in vacuo. They are shown in Table 1 for condensation reactions of isolated molecules and the relevant case of isomerization where the abilities to describe silica conformation are tested. Previous theoretical works including HF and DFT calculations show comparable energies. An overall good behavior is observed for the semiempirical Hamiltonian. The excellent agreement between the PM3 values for case 4 of isomerization and the accurate MP2/6-31+G**|MP2/6-31+G** basis set results must be pointed out.

Hydration by the MMH Procedure. We built molecular aggregates of clusters formed by growing quantities of water molecules and explored their respective hypersurfaces as described previously. After selecting molecular geometries of local energy minima influencing 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, as explained in the Introduction, to refine the statistical procedure.

TABLE 1: Calculated Energies (ΔE) of Condensation and Other Relevant Reactions (Isolated Molecules)[a]

reactions	PM3	PM3|MP2/6-31+G**[b]	MP2/6-31+G**|MP2/6-31+G**	DF-LDF/DN[c]	HF/6-31G**[d]	DF-BLYP/TNP[e]
Monomer to Dimer						
1. $2Si(OH)_4 \rightarrow [Si_2O(OH)_6] + H_2O$	−22.6	−22.6	−28.0	−20.5	−32.6	−9.2
Monomer to Cyclic Tetramer						
4. $Si(OH)_4 \rightarrow [Si_4O_4(OH)_8] + 4H_2O$	−95.4	−95.4	−99.6			
Dimer to Cyclic Tetramer						
3. $2[Si_2O(OH)_6] \rightarrow [Si_4O_4(OH)_8] + 2H_2O$	−50.2	−50.2	−43.5	−11.7		
Isomerization						
4. $Si(OH)_4\ [S_4] \rightarrow Si(OH)_4\ [D_{2d}]$	11.7		10.9		13.4	7.5

[a] In kJ mol^{-1}. [b] Energies calculated at the PM3 level with MP2/6-31+G** geometries. [c] DN basis set with LDF (DMOL) from ref 7. [d] Ref 31. [e] Ref 8.

TABLE 2: Hydration Energies of Silicates as Obtained by MMH-PM3 in kJ mol^{-1} of Water

	$Si(OH)_4[H_2O]_n$		$SiOSi(OH)_6[H_2O]_n$		$Si_4O_4(OH)_8[H_2O]_n$	
n	E^{assoc}	A^{assoc}	E^{assoc}	A^{assoc}	E^{assoc}	A^{assoc}
1	−20.4	−25.7	−25.4	−30.1	−28.3	−35.4
2	−18.6	−27.1	−22.1	−29.2	−26.2	−34.4
3	−17.8	−27.5	−19.7	−27.9	−25.0	−33.5
4	−18.8	−28.0	−19.2	−27.9	−24.6	−33.3
5	−18.6	−28.4	−19.5	−28.6	−25.1	−34.0
6	−19.7	−27.6				

Table 2 shows the behavior of selected simple silica in water at different degrees of hydration by the MMH approach. This case appears as a neutral system, and it produces interactions that mainly originated in hydrogen bonds. A single water molecule causes most of the perturbation on silica, as a general rule from the point of view of energy. Those single water molecule cases always show the lowest energy of association E^{assoc} and quite always the lowest free energy A^{assoc}. However, in the case of $Si(OH)_4$, it is observed that the free energy has a minimum in the pentrahydrate because the increase in entropy derived from the fact that this system shows several different nearly isoenergetic configurations in the surroundings of the global minimum. This could be expected due to the tetrahedral distribution of hydroxyl groups. Relevant cases are shown in Table 2

Figure 2 shows some simple silica hydrates of the lowest energies. The case of structures representing around 25% of the population of hydrates of the monomer and cyclic tetramer are shown in Figures 3 and 4, respectively. One of the relevant motifs that gives stability to several of the most populated structures is a water molecule with a double hydrogen bridge, one as the H donor and the other as the acceptor, although there are also cases where a single water molecule is double-bridged as the H donor in both cases. It can also be observed that water−water associations increase with the number of water molecules, mostly from the tetrahydrate, even in these lowest-energy clusters. Clustering of water with itself is a major contribution to convergence in association energies when the number of water molecules rises above four. It means that the most populated structures of four and five water molecules show some of them as noninteracting with silicates. It is also an indication that our results point toward the hydrophobicity of silicates, as occurs in reality.

Table 3 shows the same data but expressed in units of energy per silicon atom. The most relevant conclusion is that up to the association with four water molecules, the cyclic compound shows that the association energy with water (either internal or free energies) is a clear indication of the increasing hydrophobic character of silica upon self−clustering. The case of association with five water molecules deviates from the tendency because of the strong self-clustering of water itself in the tetrahydrate. It means that more stabilizing interactions occur among water molecules than between the silica "solute" and them. According to the structures corresponding to the energy of association minima, the most stable interaction is that corresponding to the hydrogen of water and oxygen atoms of silica in the cluster. Distances are around 2.0 Å, and the literature reports it around 1.8 Å.[5]

To test the reliability of our numerical values, we performed further calculations with more consistent Hamiltonians. Table 4 shows the results of thermodynamic function calculations using the simplest cluster of the silica model with one water molecule. Single-point energy calculations at the B3LYP/6-31G**|PM3 and MP2/6-31G**|PM3 levels have been carried out using a large set of 75 cells optimized with the PM3 Hamiltonian, with only 20 of them remaining as nonredundant after the similarity analysis. As the basis set superposition error is important in PES, the counterpoise procedure (CP) proposed by Boys and Bernardi[30] was applied in both post-HF and Kohn−Sham DFT cases to correct the obtained values. This table demonstrates that the average hydration energies calculated with several Hamiltonians are rather similar. This interesting result must be due to cancellations of systematic errors arising from both the calculation of the energies of reaction in eq 2 and the partition function calculated from a Boltzmann distribution. The latest point becomes significant in the case of free energies that are all quite equivalent.

Another interesting test is comparing the energetic consequences of environmental effects by different methods. The COSMO method has proved efficient for this purpose in a previous paper.[2] In Table 5, we compare some of the MMH results with COSMO simulations. They have been performed after finding a single minimum, presumably the lowest, of n H_2O molecule clusters with the BLYP/DNP Hamiltonian and then correcting the environment with a dielectric constant of water by COSMO. The overall excellent agreement of those essentially different methods toward a very similar object can be observed and shown in the case of E^{assoc} by both methods with a single and pair of water molecules with the silica monomer.

Condensation energies obtained for key reactions in water by MMH methods are reported in Table 6 following the conventions of Table 1. They have been calculated after correcting the energies of reaction of the global minima with association terms, as described in ref 13. We find a crucial influence of hydration on the structures and stability of these clusters. Figure 4 shows these results in a more illustrative graphical form. As the number of water molecules increases, the influence of water solvent bodies on solute reactivity must be understood from the thermodynamic point of view, as a

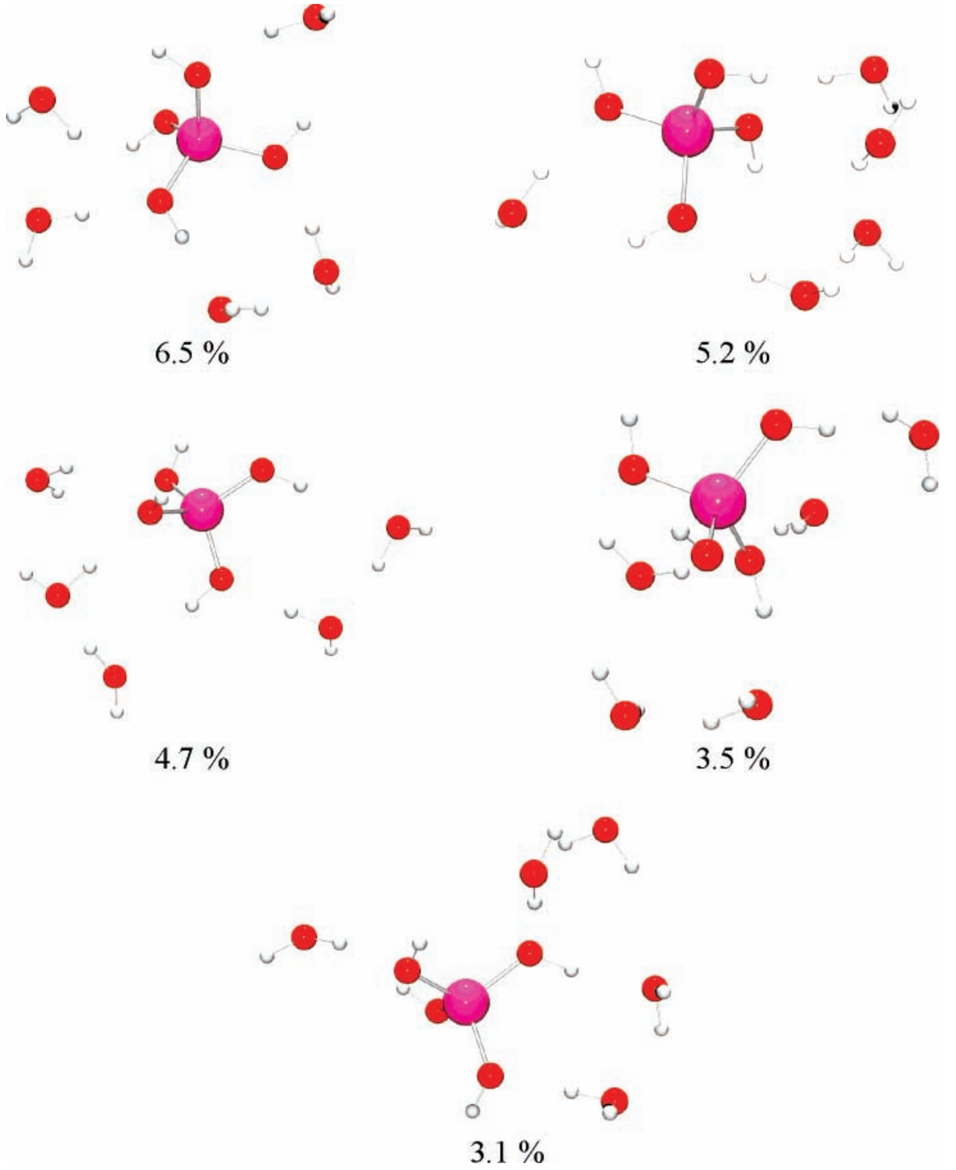

Figure 3. Molecular graphics representing about 25% of the silicate monomer pentahydrate structures with their respective calculated populations.

statistical average, accounting for the variety of possible conformations. Detailed reactivity studies must be carried out from the relevant lowest-energy clusters, which could model the kinetics of the reaction process. This study is, of course, beyond the scope of this work, although it could be a wealthy field for modeling chemical reactions accounting for all possible mechanisms in future research.

The equation of dimer formation from the simple monomer is hardly favored with hydration. It also resulted as antientropic, being disfavored upon hydration from the point of view of free energies. It is easily explained if we take into account that the number of water-associated silica molecules is reduced to half (two monomers giving a single dimer) in this case of condensation. It reduces the partition function values of products with respect to reactants. “Hydrated water” as a product of reaction 1 in the table is much more stable than hydrated silica, giving well-known low-energy structures with lower entropy.[18] The contrary occurs when the reaction gives vapor water, whose values have been obtained after subtracting the calculated energies of clustering in the lowest-energy case in reaction 2. These reactions are generally disfavored because energy is required for water cluster dissociation, but all of them remain less favored when the free energy is taken into account as compared to the enthalpies because the evident increase of entropy originates in the formation of more molecular entities.

On the contrary, the formation of the cyclic tetramer is generally favored by hydration, both from the point of view of the heat of reaction and the free energy. The general feature of the reactions is that a single water molecule disfavors the reaction, and only after further hydrations, they are improved. It means that several hydrogen bridges of silica with water appear to be necessary to carry out condensation. As expected, it is more antientropic for conducting to the cyclic tetramer from the monomers and less for that from the dimers. This is also less energetic.

The case of hydration with three water molecules is generally perturbed by a common effect, and it does not originate from the silica, but a water clustering is the consequence. With our method with a single water tetramer $[H_2O]_4$, we found a very deep minimum in the hypersurface, giving a H-bonded cyclic structure with more than 60% of the total cluster population. It dramatically changes the purely thermochemical reaction because one of the products is very favored, although it is the one of our main interest. It also brings an important antientropic character to reactions that involve units of four water molecules.

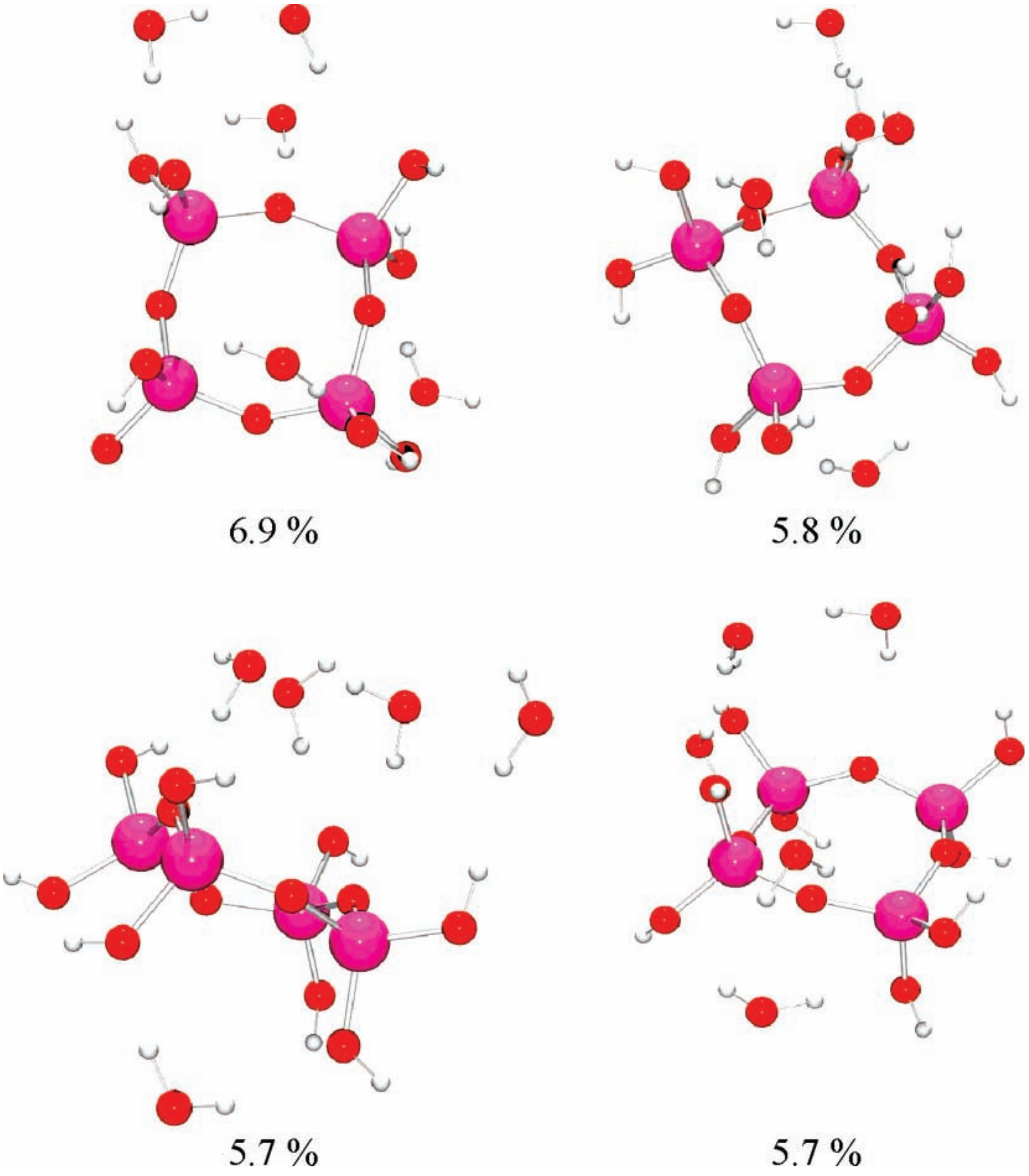

Figure 4. Molecular graphics representing about 25% of the silicate cyclic tetramer pentahydrate structures with their respective calculated populations.

TABLE 3: Hydration Energies of Silicates as Obtained by MMH-PM3 in kJ mol^{-1} of Silicon

	$Si(OH)_4[H_2O]_n$		$SiOSi(OH)_6[H_2O]_n$		$Si_4O_4(OH)_8[H_2O]_n$	
n	E^{assoc}	A^{assoc}	E^{assoc}	A^{assoc}	E^{assoc}	A^{assoc}
1	−20.1	−25.5	−12.8	−15.1	−7.1	−8.9
2	−37.6	−54.4	−22.2	−29.3	−13.2	−17.2
3	−54.0	−82.8	−29.6	−42.0	−18.8	−25.1
4	−75.2	−112.0	−38.4	−56.0	−24.7	−33.5
5	−92.0	−142.5	−49.3	−71.3	−31.4	−42.5

TABLE 4: Comparison of MMH Hydration Energies of Single Tetrahedra with Those of Different Hamiltonians (in kJ mol^{-1})

$Si(OH)_4[H_2O]$	E^{assoc}	A^{assoc}
PM3|PM3	−20.4	−25.7
B3LYP/6-31G**|PM3	−18.8	−24.3
MP2/6-31G**|PM3	−15.9	−23.0

One of the relevant points of this statistical approach is the fact that modeling reactions on such complex structures, showing several conformations and places for molecular interactions as hydrogen bonds, hardly represents when a single global minimum is used. As shown in Table 7, only the case of monohydrates of the monomer and dimer can be represented with certain reliability with a single local minimum because the entropy of association is low (see that 50% of the cluster population can be represented with only two structures in the case of the monomer and one in the case of dimer). However, cases of pentahydrates show a significantly higher entropy of hydration, and consequently, the lowest-energy structures are much more abundant, 15 cluster geometries being needed to represent 50% of the population for the monomer and cyclic tetramer. It is very interesting that there are fewer hydrated dimer structures that appear very stable, and in this case, only 10 of them represent 50% of the population.

Table 7 also shows entropies at 423 K. This temperature is nearer to that used in hydrothermal silicate syntheses. The general trend, as expected, is an increase of the entropy in all cases. The S^{423}/S^{298} rate is also reported. Our model shows that in the cases of simple monohydrated structures (monomer and dimer), the increase of temperature (from 298 to 423 K) favors the interaction with water by the entropy of association to a higher extent than that in cases of cyclic monohydrated and all

TABLE 5: Comparison of Hydration Values with DFT Results (in kJ mol^{-1})[a]

n	E^{assoc}(MMH)	E^{min}(MMH)	E(BLYP/DNP)	E^{assoc}(COSMO)
		$Si(OH)_4[H_2O]_n$		
1	−20.4	−21.3	−33.5	−19.4
2	−18.6	−21.3	−33.4	−19.8
3	−17.8	−21.2	−35.5	−21.4
4	−18.8	−22.9	−36.2	−22.0
		$SiOSi(OH)_6[H_2O]_n$		
1	−25.4	−27.1	−34.5	−21.3
2	−22.1	−25.8	−33.4	−21.8

[a] E^{assoc}(MMH) is the statistical association energy described by eq 4, as in Table 2. E^{min}(MMH) is the result of eq 2 for the minimum-energy cluster of each series. E(BLYP/DNP) is the energy of the minimum-energy cluster as obtained from the equation $M + [H_2O]_n \rightarrow M[H_2O]_n$, and E^{assoc}(COSMO) is the results of this kind of cluster formation in the environment of the water dielectric constant.

TABLE 6: Enthalpies and Gibb's Free Energies of Condensation Considering the Effect of Association with Water by the MMH Procedure (kJ/mol of Product Molecule)[a]

		surrounding H_2O molecules (n)					
reactions		0	1	2	3	4	5
Monomer to Dimer							
1. $2Si(OH)_4[H_2O]_n \rightarrow [Si_2O(OH)_6][H_2O]_n + H_2O[H_2O]_n$	ΔH^0	−22.7	−15.2	−20.8	−41.8	−24.7	−27.1
	ΔG^0	−22.7	−14.8	−11.2	−22.2	−17.1	−16.7
Monomer to Cyclic Tetramer							
2. $4Si(OH)_4[H_2O]_n + [H_2O]_n \rightarrow [Si_4O_4(OH)_8][H_2O]_n + 4H_2O[H_2O]_n$	ΔH^0	−97.8	−76.2	−98.9	−184.2	−108.3	−127.0
	ΔG^0	−97.8	−83.8	−77.0	−133.5	−102.9	−107.1
Dimer to Cyclic Tetramer							
3. $2[Si_2O(OH)_6][H_2O]_n + [H_2O]_n \rightarrow [Si_4O_4(OH)_8][H_2O]_n + 2H_2O[H_2O]_n$	ΔH^0	−52.5	−45.8	−57.5	−100.7	−59.0	−72.8
	ΔG^0	−52.5	−54.3	−54.6	−89.0	−68.7	−73.8

TABLE 7: Population Analysis of Some Relevant Clusters[a]

	$N_{25\%}$ 298	$N_{50\%}$ 298	$N_{75\%}$ 298	S^{assoc} (J K^{-1} mol^{-1}) 298	S^{assoc} (J K^{-1} mol^{-1}) 423	S^{423}/S^{298}
$Si(OH)_4[H_2O]$	1	3	4	17.7	20.1	1.14
$[Si_2O(OH)_6][H_2O]$	1	1	3	15.8	18.3	1.16
$[Si_4O_4(OH)_8][H_2O]$	2	5	10	23.9	25.2	1.05
$Si(OH)_4[H_2O]_5$	5	15	32	33.0	34.3	1.04
$[Si_2O(OH)_6][H_2O]_5$	3	10	23	30.3	31.4	1.04
$[Si_4O_4(OH)_8][H_2O]_5$	4	15	32	29.9	31.1	1.04

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

pentahydrated structures. This analysis is quite impossible when global minima are only modeled.

Conclusions

The MMH approach can be used to calculate the properties of hydration in the structure and formation of silica clusters. Results show, in general, how hydration favors thermodynamic properties of syntheses pathways of relevant simple silica compounds and how the entropy of association explores a generally forgotten place in the understanding of these processes by theoretical modeling.

We could establish that the PM3 semiempirical Hamiltonian reproduces good results on the relevant molecular geometry data of silica by means of comparison with previous and present results at higher levels of theory. It provides a very important point, given the higher cost of these calculations at the DFT or any other more sophisticated QM level.

From our results, it remain clear that entropy plays a key role in the increasing hydrophobic character of neutral silica clusters, as well as facilitating the hydration of simple silicate molecules at higher temperatures. Therefore, the use of MMH allows one to obtain new knowledge and experiences in this field. It is remarkable that the simple global minimum idea of most molecular modeling on this kind of compound, where several hydrogen bridges have a place to exist with several different conformations, must be taken with caution.

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