Journal of Sol-Gel Science and Technology 8, 55–58 (1997)

Atomistic Modeling of Silica Based Sol-Gel Processes

J.C.G. PEREIRA AND C.R.A. CATLOW
The Royal Institution of Great Britain, 21 Albermale Street, London W1X 4BS, UK

G.D. PRICE
Dept. Geol. Sciences, University College London, Gower Street, London WC1E 6BT, UK

R.M. ALMEIDA
Dept. Eng. Materiais, Instituto Superior Técnico, Av. Rovisco Pais, 1000 Lisboa, Portugal

Abstract. Density Functional Theory is used to study water, methanol, ethanol, TMOS, and TEOS molecules and the most important silica clusters participating in sol-gel processes. Calculated bond lengths, bond angles and electric dipole moments compare well with experimental data. The energy of these molecules is reported and used to discuss the energetics of the hydrolysis and condensation reactions. Molecular Dynamics is employed to simulate liquid water, methanol, ethanol, TMOS, TEOS and experimental sol-gel solutions. Calculated densities and enthalpies of vaporisation compare well with experimental data. Preliminary results are presented for MD simulations of sol-gel solutions.

Keywords: Molecular Dynamics, Density Functional Theory, sol-gel solutions, silica clusters

1. Introduction

Computer simulation is used in this project to study, at a atomistic level, the chemistry and physics of SiO_2-based sol-gel processes [1]. Quantum mechanical methods [2, 3] are used to calculate the main properties of small atomic arrangements, including ground and transition states of molecules, and the information acquired in this way is subsequently applied, using classical methods [4], to simulate the corresponding liquid and solid systems.

First, we present several results obtained, after *ab*-initio geometry optimisation, for a molecule of water, methanol, ethanol, TMOS, TEOS and some of the most important silica clusters [5], with a maximum of 5 silicon atoms. Next, we describe some of the Molecular Dynamics results obtained for liquid water, methanol, ethanol, TMOS, TEOS and six liquid solutions aiming to simulate methanolic and ethanolic sol-gel solutions, (i) before the hydrolysis, (ii) after the hydrolysis, and (iii) after the first stage of the condensation.

2. Experimental

Each ab-initio geometry optimisation was preceded by both Molecular Dynamics and energy minimisations employing classical forcefields, to help to find the best possible initial conformation. For the most difficult cases, i.e., the large linear and branched silica clusters, semi-empirical quantum mechanical calculations were also performed. The conformations with lower energy were then submitted to full geometry ab-initio DFT optimisation until a given gradient was achieved.

All MD simulations of liquids were done using periodic boundary conditions, constant temperature and pressure, a Ewald sum for the Coulombic interactions and a long range correction for the Van der Waals interactions. Liquid water [6], methanol [7], and ethanol [8] were simulated with 408 molecules in the unit cell, while 51 molecules were used to simulate liquid TMOS and TEOS. Methanol and ethanol-based sol-gel solutions aiming to describe conditions (i) before hydrolysis, (ii) after hydrolysis, and (iii) after the first stage of condensation [9], were simulated with the following molecules per unit cell: (i) 30 alkoxide + 120 water + 240 alcohol (ii) 30 monomer + 360 alcohol and (iii) 15 dimer + 15 water + 360 alcohol, assuming molar ratios water/alkoxide = 4 and alcohol/alkoxide = 8, and the ideal completeness of both reactions.

3. Results and Discussion

The total energies, calculated after full ab-initio geometry optimisation, of water, methanol, ethanol, TMOS, TEOS and some important silica clusters, experimentally observed in SiO_2-based sol-gel processes, are presented in Table 1. Relevant structural data obtained for these molecules is shown in Table 2. Calculated and experimental electric dipole moments are presented in Table 3.

Table 2. Calculated and experimental [2, 11] bond lengths and bond angles.

	Structural data	
	Cal.	Exp.
O—H	0.98–0.99 Å	0.958 Å
C—H	1.10–1.11 Å	1.073–1.101 Å
C—O	1.42–1.43 Å	1.427–1.43 Å
C—C	1.50 Å	1.541 Å
Si—O	1.64–1.65 Å	1.61 Å
H—O—H	103.87°	104.45°
C—O—H	107.99°	108.9°

Table 3. Calculated and experimental [11] electric dipole moments, in liquid and gas phase (for ethanol, trans and gauche conformations).

	Electric dipole moments	
	Cal./Debye	Exp./Debye
Water	1.86	1.85 (g) 2.01–3.00 (l)
Methanol	1.59	1.70 (g)
Ethanol	1.51 tr	1.44 tr–1.68 ga (g)
TMOS	0.42	1.71 (l)
TEOS	0.28	1.63 (l)

The optimised bond lengths and bond angles compare well with the experimental values, as the error never exceeds 0.04 Å and 5°, respectively. The calculated dipole moments are also in good agreement with experiment. In the liquid phase, due to polarisability effects, they increase considerably, as can be seen for water, explaining why liquid TMOS and TEOS present such a large dipole moment, when the calculated value, for an isolated molecule, is very small, as expected from symmetry requirements. As the method and the atomic basis set used were the same throughout all the work, it can reasonably be expected that the same level of accuracy will be obtained for the silica clusters, where experimental data are presently not available. However, as the energy of a hydrogen bond is about 5–6 kcal mol^{-1}, the energy of silica clusters containing many hydroxyl groups depends in a critical way on the disposition of these OH groups and differences as big as 10 or even 15 kcal mol^{-1} can be found between different optimised conformations of a given cluster. A particularly careful optimisation process is thus required, in order to obtain reliable data. Furthermore, as all quantum mechanical calculations were done in gas phase, no solvation effects were considered, though these should be particularly significant in sol-gel solutions, where protonic solvents are usually used.

Table 1. Total energy of the clusters in Hartree (1 Ha = 627.51 kcal mol^{-1}). In q_n^m notation, n represents the number of silicons which are bonded to m bridging oxygens.

Cluster energies					
Water	−75.910391	Methanol	−114.85895	Ethanol	−153.83282
TMOS	−745.68760	TEOS	−901.58478	q_1^0	−589.89392
q_2^1	−1103.8924	$q_2^1 q_1^2$	−1617.8857	q_3^2	−1541.9430
$q_2^2 q_2^1$	−2131.9053	$q_3^1 q_1^3$	−2131.8933	$q_2^2 q_1^3 q_1^1$	−2055.9408
q_4^2	−2055.9751	$q_3^2 q_2^1$	−2645.8975	$q_3^1 q_1^3 q_1^2$	−2645.8921
$q_4^1 q_1^4$	−2645.8790	$q_3^2 q_1^3 q_1^1$	−2569.9496	q_5^2	−2569.9377

Table 4. Energy of the hydrolysis and condensation reactions, in kcal mol^{-1} (m is 0 for open chains and 1 for rings).

Reaction energies					
Hydrolysis: $Si(OR)_4 + 4H_2O + \triangle E \rightarrow Si(OH)_4 + 4ROH$					
TMOS	−0.351	TEOS	0.715		
Condensation: $n Si(OH)_4 + \triangle E \rightarrow Si_n O_{n-1+m}(OH)_{2(n+1-m)} + (n-1+m)\, H_2O$					
q_2^1	−9.381	$q_2^1 q_1^2$	−15.512	q_3^2	4.763
$q_2^2 q_2^1$	−38.146	$q_3^1 q_1^3$	−30.616	$q_2^2 q_1^3 q_1^1$	−4.192
q_4^2	−25.715	$q_3^2 q_2^1$	−43.587	$q_3^1 q_1^3 q_1^2$	−40.198
$q_4^1 q_1^4$	−31.978	$q_3^2 q_1^3 q_1^1$	−20.049	q_5^2	−12.582

The energies of the Hydrolysis and Condensation reactions, calculated from the cluster energies, are presented in Table 4. The energy of hydrolysis is very close to zero, whereas the condensation reaction is a highly exothermic process. As expected, cyclic clusters, q_3^2, q_4^2, q_5^2 and $q_2^2 q_1^3 q_1^1$ are considerably less Table than the equivalent open structures, $q_2^1 q_1^2$, $q_2^2 q_2^1$ and $q_3^2 q_2^1$. Linear clusters like $q_2^2 q_2^1$ and $q_3^2 q_2^1$ seem to be more stable than branched ones, like $q_3^1 q_1^3$, $q_3^1 q_1^3 q_1^2$ and $q_4^1 q_1^4$.

To simulate the liquid solutions used in experimental sol-gel work, with different compositions, pressure and temperature, transferable potentials and a systematic procedure had to be devised, allowing an accurate description in a wide range of conditions without a significant loss in accuracy. This methodology has been tested in water, methanol, ethanol, TMOS and TEOS, and calculated and experimental densities and enthalpies of vaporisation are reported in Tables 5 and 6. The agreement seems to be good for the densities, though only reasonable for $\triangle H_V$, where the calculated values are typically 0.5–0.8 kcal mol^{-1} smaller than the experimental evidence. Results of similar quality were obtained for different temperatures and pressures.

Table 5. Calculated and experimental [10, 11] densities at 20°C and 1 atm, in gcm^{-3}.

	Densities	
	Cal.	Exp.
H_2O	1.013	0.998
D_2O	1.139	1.105
Methanol	0.765	0.791
Ethanol	0.770	0.789
TMOS	1.042	1.02
TEOS	0.935	0.93

Table 6. Calculated and experimental [10] enthalpies of vaporisation, in kcal mol^{-1}, at the boiling temperature T_b, and 1 atm.

	Enthalpies of vaporisation		
	Cal.	T_b/°C	Exp.
H_2O	9.0	(1000)	9.72
Methanol	7.8	(64.5)	8.42
Ethanol	9.2	(78.3)	9.41

Table 7. Densities (g/cm^3) and RDF first peaks (height/distance) for some key pair functions (O_{hh} in water; O_{sh} in silica clusters), before hydrolysis, after hydrolysis, and after the first stage of condensation.

	Sol-gel solutions							
	30 $Si(OR)_4$ + 120 H_2O + 240 ROH			30 $Si(OH)_4$ + 360 ROH		15 $Si_2O(OH)_6$ + 15 H_2O + 360 ROH	
	ρ_{ideal}	ρ	gO_{hh}—Si	ρ	gO_{sh}—Si	ρ	gO_{sh}—Si
Methanol-based R=CH_3	0.869	0.869	1.63/3.96 Å	0.871	1.06/3.34 Å	0.867	1.01/4.05 Å
Ethanol-based R=CH_2CH_3	0.838	0.802	1.14/3.59 Å	0.804	1.65/3.48 Å	0.825	1.43/3.92 Å

Preliminary results for the sol-gel solutions are presented in Table 7. The methanolic solution is almost ideal, whereas the ethanolic, which is more complex, has a significant decrease in density, compared with the ideal solution value. The crucial interactions between the oxygen and silicon atoms that lead to the hydrolysis and condensation reactions seem to be favoured by the relatively small distances that separates these atoms in solution.

4. Conclusions

Density Functional Theory can be used to calculate, with high accuracy, the structure, charge distribution and energy of the important clusters participating in sol-gel processes, though the presence of multiple hydroxyl groups make it difficult to find the geometry corresponding to the global minimum of energy. Using this data, a systematic procedure can be devised to simulate, via Molecular Dynamics, the liquid systems involved in sol-gel processes, for different conditions of pressure and temperature. The results presented here are a preliminary account of a continuing study of these systems.

Acknowledgments

We want to acknowledge JNICT and Instituto Superior Tecnico, Lisboa, for their financial support, and Biosym Technologies, San Diego, for their technical support.

References

1. C.J. Brinker and G.W. Scherer, *Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing* (Academic Press, San Diego, 1990).
2. W.J. Hehre, L. Radom, P. Schleyer, and J.A. Pople, *Ab Initio Molecular Orbital Theory* (John Wiley & Sons, 1986).
3. R.G. Parr and W. Yang, *Density-Functional Theory of Atoms and Molecules* (Oxford University Press, 1989).
4. M.P. Allen and D.J. Tildesley, *Computer Simulation of Liquids* (Oxford Science Publications, 1992).
5. J. Sauer, Chem. Rev. **89**, 199 (1989).
6. W.L. Jorgensen, J. Chandrasekhar, and J.D. Madura, J. Chem. Phys. **79**(2), 926 (1983).
7. W.L. Jorgensen, J. Chem. Phys. **103**, 341 (1981).
8. W.L. Jorgensen, J. Chem. Phys. **103**, 345 (1981).
9. S.H. Garofalini and G. Martin, J. Phys. Chem. **98**, 1311 (1994).
10. *International Critical Tables*, III and V (1st. Edition, 1928).
11. *CRC Handbook of Chemistry and Physics* (CRC Press, London, 1994).