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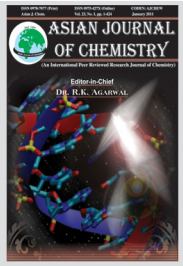

Ab initio Study of Interaction of Methanol with Water Molecule Clusters at Different Temperatures

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In this work, the interaction of one molecule of methanol with 9-16 molecules of water clusters in different temperatures (273.15-453.15 K) has been studied. The intermolecular hydrogen bonding and ΔG and ΔH of formation of $CH_3OH(H_2O)_n$ (n = 9-16) clusters are calculated at the different temperatures. The calculations are performed at the DFT methods and B3LYP/6-31G* level of theory. It was shown that in all cases both the ΔH and ΔG of the formation of each cluster from the free molecules increase with increasing the number of water molecules in the cluster. The ΔH values of the formation of all clusters are negative in all temperatures but the corresponding ΔG values change to a positive number after a defined temperature, depending on the type and the size of the clusters.

Key Words: *Ab initio*, Thermodynamic, Cluster Methanol-water, Temperature.

INTRODUCTION

Hydrogen bonding plays one of the most important roles in an arrangement of molecules in crystals[1,2]. A large number of papers appeared dealing with the Lewis acidity and basicity of functional groups involved in H-bonds as for example: nitro[3], formyl[4], carboxylic[5], carbonyl[6,7], hydroxyl[8], *etc.* Methanol generally forms three strong hydrogen bonds, two as proton acceptors (*via* the lone-pair electrons on oxygen) and one as a proton donor[9]. The methyl CH bonds may form weak hydrogen-bonding interactions. The bulky methyl group and the dipole produces give methanol a more complex and asymmetrical cluster compared with water. Much of the stabilization of water-methanol mixtures comes from the very sensitive electronic interaction of the hydrogen bond. Computational results indicate that the cyclic methanol clusters are the global minima when compared with chain, branched-cyclic and branched-chain arrangements[10,11]. Cyclic structures maximize the number of hydrogen bonds and display an increase in cooperatively, thus yielding more favourable interactions among the members of the mixture.

In this work, we reported the thermodynamic properties of $CH_3OH(H_2O)_n$ (n = 9-16) clusters in various temperatures. In the best of our knowledge, the CH_3OH-H_2O clusters with more than four molecules[12-17] have been never studied.

COMPUTATIONAL METHOD

Calculations were performed using the Gaussian 03 system of codes. The geometries of all components were fully optimized at DFT computational levels using the basis sets 6-31G*. Calculations were performed on a Pentium-PC computer with a 3000 MHz processor. A starting molecular-mechanics structure for the *ab initio* calculations was obtained using the HyperChem 5.02 program[18]. Vibrational frequency analyses, calculated at the same level of theory, at various tempreatures (273.15-403.15 K) indicate that optimized structures are at the stationary points corresponding to local minima without any imaginary frequency.

RESULTS AND DISCUSSION

The optimized structures of all 8 clusters studied here are shown in Fig. 1. As it can be seen in the Fig. 1, it is found that the most stable structure for $CH_3OH(H_2O)_n$ clusters with more than three H_2O molecules, is a structure with the maximum number of intermolecular hydrogen bonds.The ΔG and ΔH of formation of $CH_3OH(H_2O)_n$ clusters in various tempretures were calculated with considering following reaction:

$$CH_3OH(g) + nH_2O(g) \rightarrow CH_3OH(H_2O)_n\ (g) \qquad (1)$$

The results are given in Table-1. As it can be seen, the ΔH values of all clusters are negative in all studied temperatures. The data in Table-1 indicate that in $CH_3OH\ (H_2O)_n$ clusters with increasing the value of (n) the ΔH value increases. Obviously, with increasing the number of molecules, the ΔH of the formation of cluster increases only when the number of intermolecular hydrogen bonds increases. Thus increasing the ΔH value in the series of above clusters indicates that the number of intermolecular hydrogen bonds increases from a smaller

TABLE 1
CALCULATED ΔH (Kcal mol^{-1}) AND ΔG (Kcal mol^{-1}) VALUES FOR $CH_3OH(H_2O)_n$ CLUSTERS AT VARIOUS TEMPERATURES (K)

	Temperature (K)													
	273	293	298	303	313	323	333	343	353	363	373	383	393	403
	ΔH (Kcal mol^{-1})													
9.1	-111.74	-111.70	-111.68	-111.66	-111.62	-111.55	-111.48	-111.40	-111.31	-111.21	-111.10	-110.99	-110.87	-110.74
10.1	-122.34	-122.27	-122.25	-122.23	-122.16	-122.08	-122.00	-121.90	-121.79	-121.67	-121.54	-121.40	-121.26	-121.11
11.1	-137.01	-136.96	-136.94	-136.91	-136.85	-136.77	-136.68	-136.58	-136.48	-136.35	-136.22	-136.07	-135.92	-135.76
12.1	-154.91	-154.86	-154.84	-154.82	-154.76	-154.68	-154.59	-154.48	-154.37	-154.24	-154.10	-153.95	-153.79	-153.62
13.1	-168.52	-168.49	-168.48	-168.46	-168.40	-168.32	-168.23	-168.13	-168.01	-167.88	-167.73	-167.58	-167.41	-167.24
14.1	-184.16	-184.14	-184.12	-184.11	-184.05	-183.97	-183.88	-183.78	-183.66	-183.52	-183.37	-183.21	-183.04	-182.85
15.1	-198.76	-198.74	-199.32	-198.71	-198.66	-198.58	-198.48	-198.37	-198.25	-198.10	-197.94	-197.77	-197.59	-197.39
16.1	-210.20	-210.16	-210.14	-210.12	-210.06	-209.96	-209.85	-209.72	-209.59	-209.42	-209.25	-209.05	-208.85	-208.63
	ΔG (Kcal mol^{-1})													
9.1	-26.99	-17.54	-19.23	-17.68	-14.59	-11.49	-8.39	-5.30	-2.20	0.88	3.97	7.05	10.13	13.20
10.1	-29.23	-18.86	-20.71	-19.00	-15.60	-12.20	-8.80	-5.41	-2.01	1.38	4.76	8.15	11.52	14.90
11.1	-33.94	-26.40	-24.51	-22.62	-18.86	-15.09	-11.32	-7.57	-3.80	-0.05	3.70	7.45	11.19	14.93
12.1	-40.80	-32.44	-30.35	-28.27	-24.10	-19.92	-15.75	-11.59	-7.42	-3.26	0.89	5.04	9.18	13.33
13.1	-45.26	-36.23	-33.98	-31.72	-27.22	-22.71	-18.20	-13.70	-9.20	-4.70	-0.21	4.27	8.75	13.24
14.1	-50.44	-36.39	-38.20	-35.75	-30.86	-25.97	-21.08	-16.20	-11.31	-6.43	-1.56	3.31	8.17	13.03
15.1	-54.87	-44.34	-41.70	-39.06	-33.81	-28.54	-23.28	-18.02	-12.76	-7.51	-2.27	2.97	8.20	13.44
16.1	-57.27	-41.38	-43.27	-40.47	-34.88	-29.29	-23.70	-18.12	-12.53	-6.95	-1.38	4.19	9.75	15.31

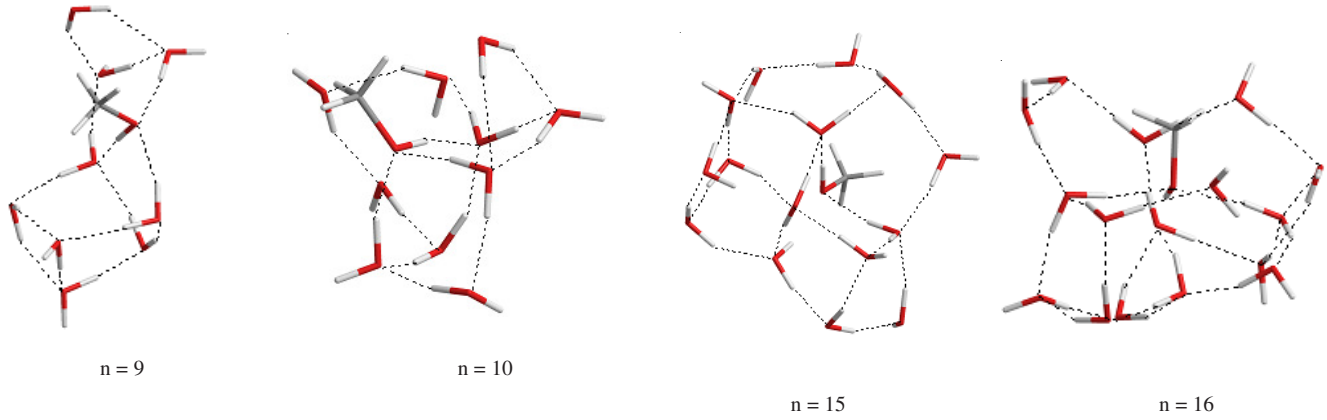

Fig. 1. Optimized structures for $CH_3OH(H_2O)_n$ clusters

cluster toward the bigger one. It is noted that the strength of intermolecular hydrogen bonding between water molecules is different with that between methanol molecules. The calculated ΔG values are given in Table-1. As it can be seen, the ΔG values of the clusters are negative only below of a critical temperature. It is observed that for the 1+1 cluster of the methanol-water in all temperatures the ΔG value is positive. The value 1.12 kcal/mol, indicating that the energy of an intermolecular hydrogen bond between these molecules is not enough to compensate the decreasing of the entropy of the system. Thus it seems that in all the cases the ΔG values of the clusters are negative below a defined temperature, if the number of intermolecular hydrogen bonds in the cluster is enough. Furthermore it is found that in $CH_3OH(H_2O)_n$ clusters, when move from smaller cluster to the bigger one, the ΔG value increases (becomes more negative), only if there are the maximum numbers of intermolecular hydrogen bonds. The ΔG values of $CH_3OH(H_2O)_n$ clusters at 273.15 K varies form -26.99 kcal/mol for n = 9 to -57.27 for n = 16, indicating that the number of intermolecular hydrogen bonds increases continuously with increasing the number of water molecules.

Conclusion

The ΔH and ΔG values of the formation of $CH_3OH(H_2O)_n$ clusters with up to 9-16 molecules of water, in various temperatures have been studied at the B3LYP/6-31G* level of theory. We optimized a structure with maximum number of intermolecular hydrogen bonds. The data show that in the $CH_3OH(H_2O)_n$ clusters with increasing the value of n the ΔH value increases. On the other hand, the results show that the ΔG value of the formation of one cluster from free molecules has a negative value only below of a critical temperature, depending on the type and the size of the cluster. The data show that in both series of above clusters with increasing the number of intermolecular hydrogen bonds, the ΔG value of system increases.

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