The onset of ion solvation by ab initio calculations: Comparison between water and methanol

Eva Pluhařová and Pavel Jungwirth[*]

Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic and Center for Biomolecules and Complex Molecular Systems, Flemingovo nám. 2, 16610 Prague 6, Czech Republic

*Corresponding author. E-mail: pavel.jungwirth@uochb.cas.cz, FAX: +420-220 410 320

Summary

Optimal structures, as well as vertical and adiabatic desolvation energies for sodium, fluoride, and chloride in clusters with one to three water or methanol molecules are determined using converged ab initio methods (MP2/aug-cc-pvtz for geometries and CCSD(T) in the complete basis set limit for energetics). The results, which are in good agreement with previous calculations and experiments (whenever available), show that in small clusters interactions of ions with methanol are stronger than those with water. Only upon adding more solvent molecules the situation starts to reverse, approaching thus the bulk limit where water is a better solvent for alkali cations and halide anions than methanol.

Keywords: clusters, ion solvation, ab initio calculations.

Dedicated to Professor Rudolf Zahradník on the occasion of his 80th birthday.

I. INTRODUCTION

Microsolvation of ions in clusters is often viewed as a tool for approaching the bulk limit[1,2]. Indeed, extrapolation schemes have been applied to elucidate bulk information such as solvation enthalpies and free energies from data obtained for clusters of increasing size[1,2], despite possible pitfalls. These are for example the slow convergence with cluster size to the bulk limit and sizable differences in ion solvation in ambient temperature liquid vs. cryogenic clusters. Here, we turn this extrapolation approach upside down asking ourselves how relevant is the information about bulk ion solvation for the situation in small clusters. More precisely, we are posing the following question: If one has two solvents of different dielectric constants, such as water with $\varepsilon_r = 80$ and methanol with $\varepsilon_r = 33$, would favorable ion solvation in the bulk medium with the higher dielectric constant (i.e., water) translate to stronger interactions in the corresponding small clusters?

Small water clusters with a halide anion or alkali cation have been studied extensively in the last decades. A recent density functional theory (DFT) study compares microhydrated structures of these ions in aqueous clusters with up to six water molecules[3]. Alkali cations such as sodium or potassium typically exhibit a roughly symmetric water solvent shell[4]. Ab initio calculations of microhydration of halides show a gradual build-up of an asymmetric solvent shell around the anion with the exception of F$^-$ which exhibits a more symmetric mode of solvation[5-14]. Computational studies also exist concerning halide ion solvation in binary clusters with methanol and other short-chain alcohols[15]. Solvation of fluoride and chloride in small to medium sized methanol clusters was investigated by a combination of ab initio calculations and vibrational predissociation spectroscopy with the focus on surface vs. interior solvation of the anion[16-17]. Alkali cation microhydration was studied in methanol and other short chain alcohols and ion dissociation enthalpies were established[18,19]. In addition, sodium-water, sodium-methanol, and sodium-ethanol dimers were characterized using DFT calculations and IR spectroscopy[20]. Replacement of water by methanol was found to be exothermic in binary complexes with

sodium[21]. Similarly, small clusters of potassium with water, methanol, or acetonitrile were characterized[22] and preference of methanol over water as a microsolvent was established[23]. Nevertheless, to the best of our knowledge ion solvation processes in water and methanol in size selected clusters have not been systematically compared to each other with the aim to answer the question concerning transferability of bulk solvation preferences between the two solvents to small clusters. The goal of the present study is to address this issue by means of accurate ab initio calculations of small ion-water and ion-methanol clusters.

II. SYSTEMS AND COMPUTATIONAL METHODS

Ab initio calculations were performed for small aqueous and methanolic clusters containing a single sodium cation, or fluoride or chloride anion and one to three solvent molecules. Initial structures were chosen using chemical intuition and HF/3-21g pre-optimizations. Optimal structures were then obtained and frequency analysis was performed at the MP2/aug-cc-pVTZ level of theory. For each cluster we additionally evaluated the total electronic energy at MP2/aug-cc-pVTZ and CCSD(T)/aug-cc-pVDZ levels. This allowed for a complete basis set extrapolation (CBS)[24,25] of the form:

$$E_{MP2/CBS} = E_{MP2/aug-cc-pVDZ} + (E_{MP2/aug-cc-pVTZ} - E_{MP2/aug-cc-pVDZ})/0.703704 \qquad (1)$$

and

$$E_{CCSD(T)/CBS} = E_{MP2/CBS} + (E_{CCSD(T)/aug-cc-pVDZ} - E_{MP2/aug-cc-pVDZ}) . \qquad (2)$$

Using the above extrapolation we evaluated the ion and water or methanol desolvation energies. These were calculated as diferences between the cluster energies with and without the ion or a single solvent molecule, either allowing (adiabatic desolvation energy) or not allowing (vertical desolvation energy) for cluster relaxation upon removal of ion or solvent molecule. For each system, the adiabatic desolvation energy was corrected for the zero point vibrational energy

diference, while the vertical desolvation energy was corrected for the basis set superposition error using the counterpoise scheme[26].

For the smallest clusters containing an ion and a single solvent molecule we verified the employed CBS extrapolation against calculations employing large aug-cc-pVQZ and aug-cc-pV5Z basis sets. For these systems, we also checked the performance of density functional methods at the BLYP and B3LYP levels of theory, which we found to be almost quantitative. All calculations were performed using the Gaussian 03 program[27].

III. RESULTS AND DISCUSSION

The structures of the optimized ion-water clusters under study are presented in Figure 1, while those with methanol as a microsolvent are shown in Figure 2. In both cases we see a similar ion-solvent binding pattern – an anion forms a strong hydrogen bond with each of the solvent molecules, while a cation binds to water oxygens. For methanol clusters, the ion-solvent binding saturates all available OH-groups, while in water there remains the possibility for formation of additional solvent-solvent hydrogen bonds. For steric reasons dictated by the strong ion-water interactions these additional hydrogen bonds cannot develop for the sodium solute. For anions (chloride in particular) water-water hydrogen bonds do exist in the two- and three-water clusters, however, they are strained and, therefore, rather weak.

To further characterize the cluster we evaluated the following energetic properties: The vertical and adiabatic dissociation energies of the solvent molecule and the vertical and adiabatic dissociation energies of the ionic solute. The first two energies are connected with the process $X(Sol)_n \longrightarrow X(Sol)_{n-1} + Sol$, where X is the ion and Sol is the solvent molecule. For evaluation of the vertical dissociation energy the structure of $X(Sol)_{n-1}$ is assumed as unrelaxed after dissociation, while the adiabatic dissociation energy corresponds to a geometrically relaxed

fragment $X(Sol)_{n-1}$. Vertical and adiabatic dissociation energies of the ion are connected with the process $X(Sol)_n \longrightarrow (Sol)_n + X$. Similarly as in the previous case, for evaluation of the vertical dissociation energy we employ an unrelaxed structure of $(Sol)_n$, while for the adiabatic dissociation energy the geometry of $(Sol)_n$ is optimized after dissociation. For all systems under study these dissociation energies are presented in Figures 3-5. Since our values are obtained at the CCSD(T)/CBS level, they represent a benchmark to previous calculations (discussed in the introduction), with which they are in good agreement whenever available.

Figure 3 summarizes all the investigated dissociation energies for the chloride-containing clusters under study. While the vertical water binding decreases with cluster size (Figure 3a), the vertical ion binding increases almost linearly, which indicates a close contact of the ion with the first few solvent molecules. The adiabatic curves are less straightforward, since the relaxation of the remainder of the system after solvent or ion removal comes into play, too.

In the smallest cluster, i.e., the ion-solvent dimer, binding is stronger in methanol than in water. Also for two solvent molecules, binding remains stronger in the methanol case, albeit the difference between the two solvents decreases. The most interesting situation appears in clusters with three solvent molecules where binding of a water molecules (both vertical and adiabatic) becomes stronger than that of a methanol molecules. Nevertheless, ion binding remains stronger for methanol solute, however, the difference from water all but disappears in the adiabatic picture. These results indicate that although the smallest clusters exhibit a qualitatively opposite behavior from the bulk (where water is a better solvent for ions than methanol), the next solvent molecules help to restore the bulk order. This is primarily since water unlike methanol can form additional hydrogen bonds in small ion-solvent clusters, which leads to an additional stabilization of the aqueous clusters with more than a single solute molecule.

The corresponding results for fluoride are depicted in Figure 4. Although qualitatively the binding pattern is similar to that of chloride, fluoride interacts with solvent molecules more strongly due to its smaller size and, therefore, higher charge density. In addition, the crossover from preference for methanol to water does not occur within investigated system sizes (except for the vertical solvent binding which becomes practically equal for methanol and water in clusters with three solvent molecules).

Finally, Figure 5 shows the binding energies for small sodium-water and sodium-methanol clusters. The binding strength to sodium lies between those to fluoride and chloride, albeit closer to the former one. As for the anions, methanol wins as a preferred micro-solvent for sodium over water. As a matter of fact, there is no reversal of this pattern for the systems under study and larger clusters are needed for flipping the preference on the water side. This is due to the fact that the geometry of water binding to cations does not allow for creating stabilizing water-water hydrogen bonds in small clusters.

IV. CONCLUSIONS

We have presented optimal structures and vertical and adiabatic binding energies of ions and solvent molecules in clusters of sodium, fluoride, or chloride in clusters with one to three water or methanol molecules. These energies are based on CCSD(T) results at the complete basis set limit. We show that, contrary to expectations based on extrapolation from the bulk, in the smallest clusters interactions of ions with methanol are stronger than those with water. Only in larger clusters with more solvent molecules the situation is reversed, approaching eventually the bulk situation, where water is a better solvent than methanol for atomic cations and anions.

Acknowledgements

Supplementary material

All geometric parameters and absolute ab initio energies of the investigated systems are available from the authors upon request.

References:

1. Tissandier, M. D., Cowen K. A., Feng W. Y., Gundlach E., Cohen M. H., Earhart A. D., Coe J. V.: *J. Phys. Chem. A* **1998**, *102*, 7787.

2. Meot-Ner M.: *Chem. Rev.* **2005**, *105*, 213.

3. Krekeler C., Hess B., Delle Site L.: *J. Chem. Phys.* **2006**, *125*, 054305.

4. Patwari G. N., Lisy J. M.: *J. Chem. Phys.* **2006**, *118*, 8555.

5. Combariza J. E., Kestner N. R.: *J. Phys. Chem.* **1994**, *98*, 3513.

6. S. S. Xantheas, L. X. Dang: *J. Phys. Chem.* **1996**, *100*, 3989.

7. Bryce R. A., Vincent M. A., Malcom N. O. J., Hiller I. H., Burton N. A.: *J. Chem. Phys.* **1998**, *109*, 1998.

8. Cabarcos O. M., Weinheimer C. J., Lisy J. M., Xantheas S. S.: *J. Chem. Phys.* **1999**, *110*, 5.

9. Baik J., Kim J., Majumdar D., Kim K. S.: *J. Chem. Phys.* **1999**, *110*, 9116.

10. Weis P., Kemper P. R., Bowers M. T., Xantheas S. S.: *J. Am. Chem. Soc.* **1999**, *121*, 3531.

11. Tobias D., Jungwirth P., Parrinello M.: *J. Chem. Phys.* **2001**, *114*, 7036.

12. Masamura M.: *J. Phys. Chem. A* **2002**, *106*, 8925.

13. Zhan C. G., Dixon D. A.: *J. Phys. Chem. A* **2004**, *108*, 2020.

14. Kemp D. D., Gordeon M. S.: *J. Phys. Chem. A* **2005**, *109*, 7688.

15. Bogdanov B., McMahon T. B.: *J. Phys. Chem. A* **2000**, *104*, 7871.

16. Cabarcos O. M., Weinheimer C. J., Martinez T. J., Lisy J. M.: *J. Chem. Phys.* **1999**, *110*, 9516.

17. Corbett C. A., Martinez T. J., Lisy J. M.: *J. Phys. Chem. A* **2002**, *106*, 10015.

18. Rodgers M. T., Armentrout P. B.: *J. Phys. Chem. A* **1999**, *103*, 4955.

19. Garcia-Muruais A., Cabaleiro-Lago E. M., Hermida-Ramon J. M., Rios M. A.: *Chem. Phys.* **2000**, *109*, 254.

20. Fridgen T. D., McMahon T. B., Maitre P., Lemaire J.: *Phys. Chem. Chem. Phys.* **2006**, *8*, 2483.

21. Nielsen S. B., Masella M., Kebarle P.: *J. Phys. Chem. A* **1999**, *103*, 9891.

22. Islam M. S., Pethrick R. A., Pugh D.: *J. Phys. Chem. A* **1998**, *102*, 2201.

23. Evans D. H., Keesee R. G., Castelman A. W. Jr.: *J. Phys. Chem.* **1991**, *95*, 3558.

24. Feller D.: *J. Chem. Phys.* **1992**, *96*, 6104.

25. Feyereisen M. M., Feller D., Dixon D. A.: *J. Phys. Chem.* **1996**, *100*, 2993.

26. Boys S. F., Bernardi F.: *Mol. Phys.* **1970**, *19*, 558.

27. Gaussian 03, Revision C.02, Frisch M. J., Trucks G. W., Schlegel H. B., Scuseria G. E., Robb M. A., Cheeseman J. R., Montgomery Jr. J. A., Vreven T., Kudin K. N., Burant J. C., Millam J. M., Iyengar S. S., Tomasi J., Barone V., Mennucci B., Cossi M., Scalmani G., Rega N., Petersson G. A., Nakatsuji H., Hada M., Ehara M., Toyota K., Fukuda R., Hasegawa J., Ishida M., Nakajima T., Honda Y., Kitao O., Nakai H., Klene M., Li X., Knox J. E., Hratchian H. P., Cross J. B., Bakken V., Adamo C., Jaramillo J., Gomperts R., Stratmann R. E., Yazyev O., Austin A. J., Cammi R., Pomelli C., Ochterski J. W., Ayala P. Y., Morokuma K., Voth G. A., Salvador P., Dannenberg J. J., Zakrzewski V. G., Dapprich S., Daniels A. D., Strain M. C., Farkas O., Malick D. K., Rabuck A. D., Raghavachari K., Foresman J. B., Ortiz J. V., Cui Q., Baboul A. G., Clifford S., Cioslowski J., Stefanov B. B., Liu G., Liashenko A., Piskorz P., Komaromi I., Martin R. L., Fox D. J., Keith T., Al-Laham M. A., Peng, C. Y., Nanayakkara, A., Challacombe M., Gill P. M. W., Johnson B., Chen W., Wong M. W., Gonzalez, C., Pople J. A.: Gaussian, Inc., Wallingford CT, 2004.

Figure Captions

Figure 1: Structures of ion-water clusters for chloride, fluoride, and sodium with one to three water molecules.

Figure 2: Structures of ion-methanol clusters for chloride, fluoride, and sodium with one to three water molecules.

Figure 3: Vertical and adiabatic CCSD(T)/CBS binding energies of a) solvent and b) chloride in water (w) or methanol (m) clusters with one to three solvent molecules.
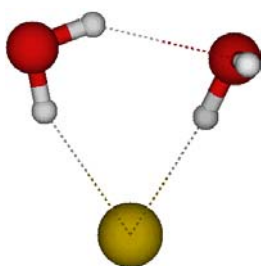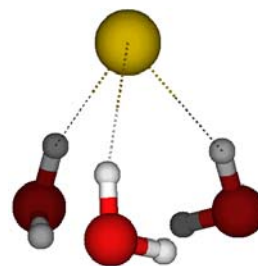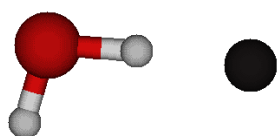
Figure 4: Vertical and adiabatic CCSD(T)/CBS binding energies of a) solvent and b) fluoride in water (w) or methanol (m) clusters with one to three solvent molecules.

Figure 5: Vertical and adiabatic CCSD(T)/CBS binding energies of a) solvent and b) sodium in water (w) or methanol (m) clusters with one to three solvent molecules.

Figure 1
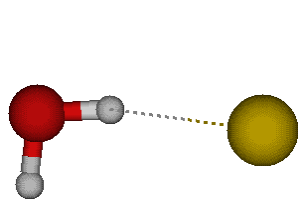
Cl⁻(H₂O)   Cl⁻(H₂O)₂   Cl⁻(H₂O)₃
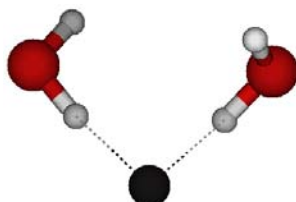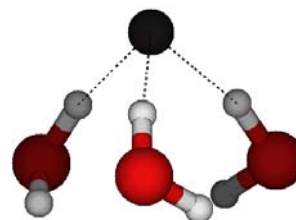
F⁻(H₂O)   F⁻(H₂O)₂   F⁻(H₂O)₃

Na⁺(H₂O)   Na⁺(H₂O)₂   Na⁺(H₂O)₃

11

Figure 2

Cl⁻(CH₃OH)

$Cl^-(CH_3OH)$

$Cl^-(CH_3OH)_2$

$Cl^-(CH_3OH)_3$

$F^-(CH_3OH)$

$F^-(CH_3OH)_2$

$F^-(CH_3OH)_3$

$Na^+(CH_3OH)$

$Na^+(CH_3OH)_2$

$Na^+(CH_3OH)_3$
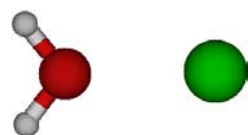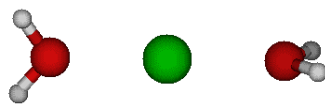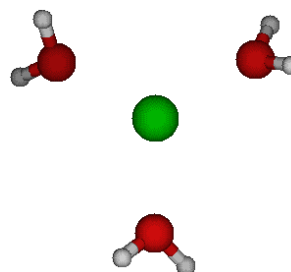
12
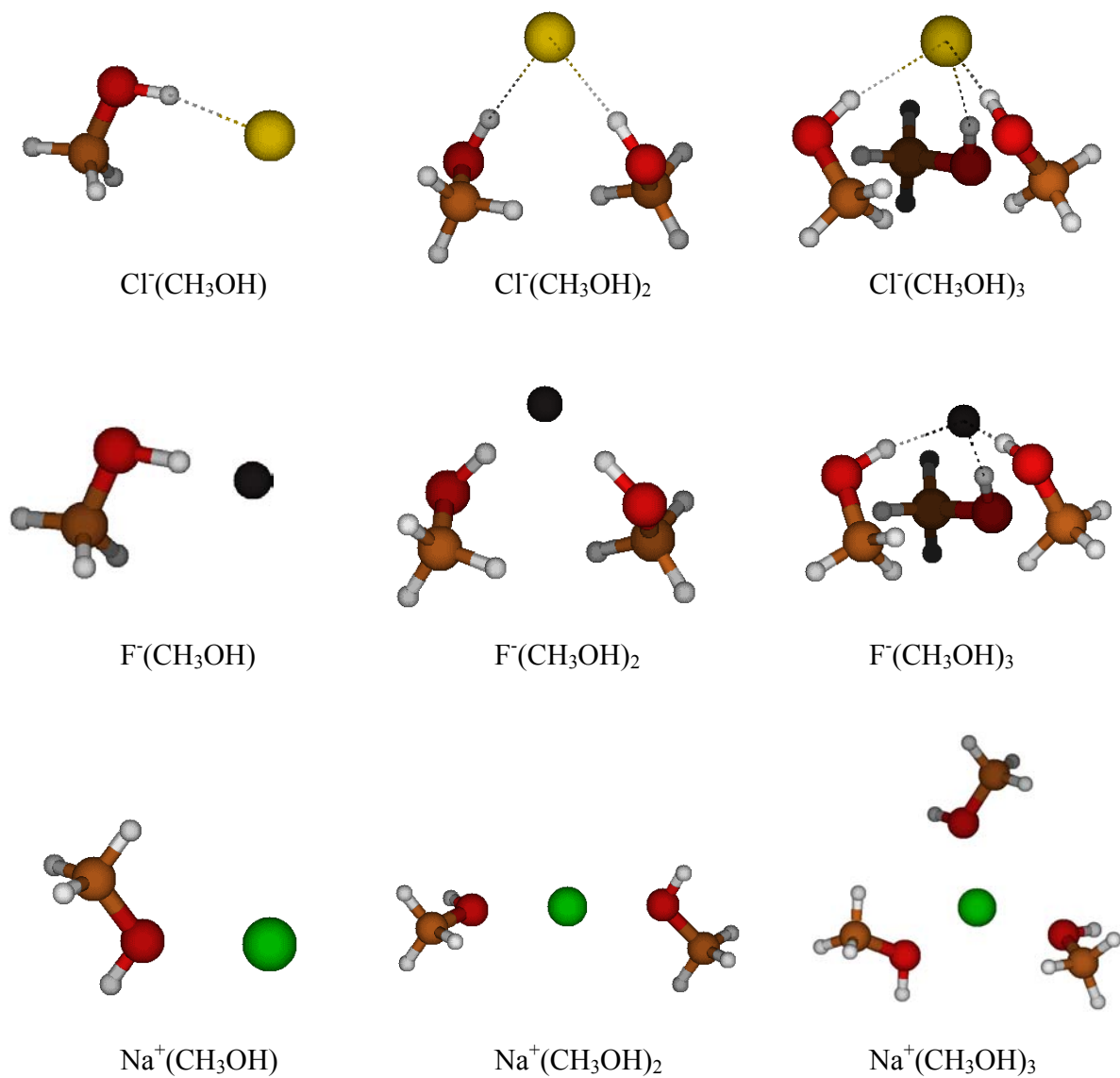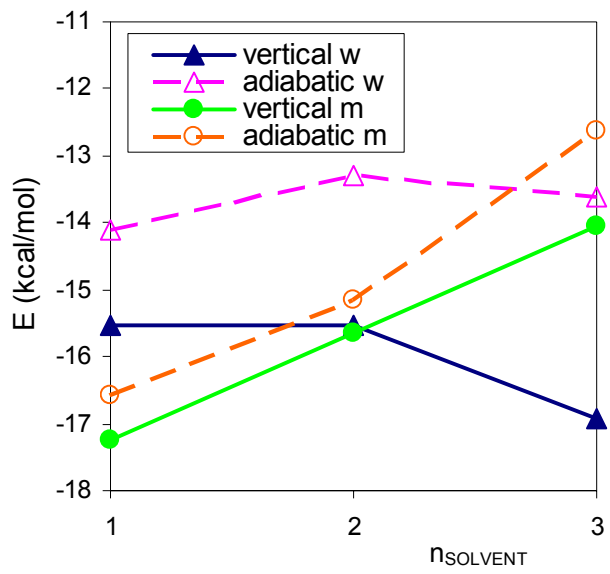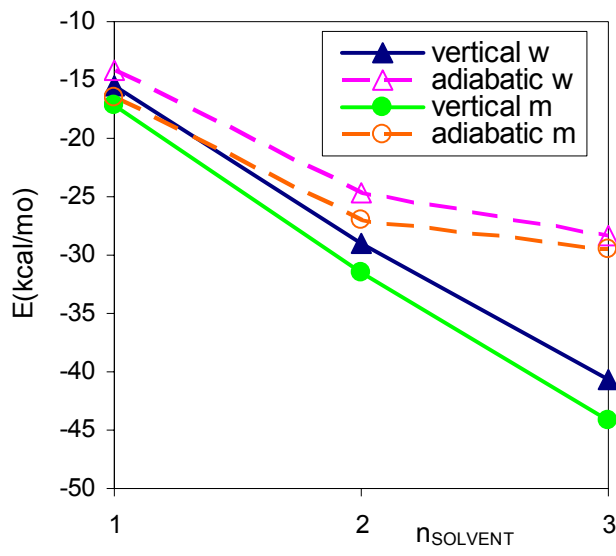
Figure 3a:

Figure 3b:

Figure 4a:
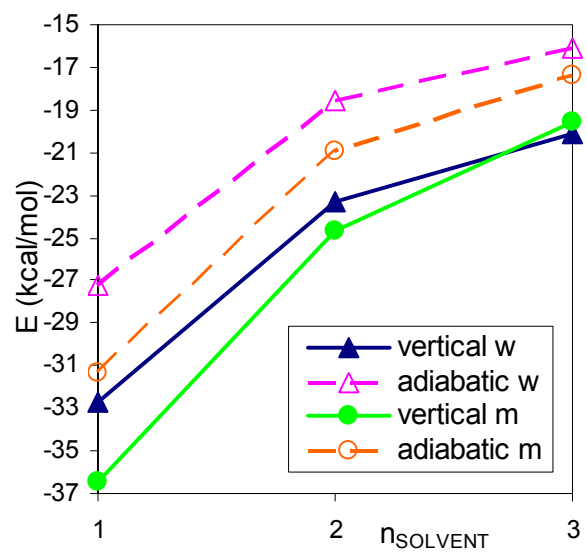
Figure 4b:

Figure 5a:

Figure 5b: