THE ONSET OF ION SOLVATION BY ab initio CALCULATIONS: COMPARISON OF WATER AND METHANOL

Eva PLUHAŘOVÁ[1] and Pavel JUNGWIRTH[2,*]

Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, v.v.i. and Center for Biomolecules and Complex Molecular Systems, Flemingovo nám. 2, 166 10 Prague 6, Czech Republic; e-mail: [1] eva.pluharova@marge.uochb.cas.cz, [2] pavel.jungwirth@uochb.cas.cz

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

Optimal structures as well as vertical and adiabatic desolvation energies for sodium cation and fluoride and chloride anions in clusters with one to three water or methanol molecules are determined using converging 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 (if available), show that in small clusters the interactions of ions with methanol are stronger than those with water. Only upon adding more solvent molecules the situation starts to revert, approaching thus the bulk limit where water is a better solvent for alkali metal cations and halide anions than methanol.
Keywords: Clusters; Ion solvation; Ab initio calculations; Salts; NaF; sodium fluoride.

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 a liquid at ambient temperature versus cryogenic clusters. Here, we turn this extrapolation approach upside down asking ourselves how relevant the information about bulk ion solvation is for the situation in small clusters. More precisely, we are posing the following question: If one has two solvents of different dielectric permittivities, such as water with $\varepsilon_r = 80$ and methanol with $\varepsilon_r = 33$, would favorable ion solvation in the bulk medium with a higher dielectric permittivity (i.e., water) translate to stronger interactions in the corresponding small clusters?

Small water clusters with a halide anion or alkali metal cation have been studied extensively in recent 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 metal 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 anions in small to medium-size methanol clusters was investigated by a combination of ab initio calculations and vibrational predissociation spectroscopy with the focus on surface versus interior solvation of the anion[16,17]. Microhydration of alkali metal cations was studied in methanol and other short-chain alcohols and dissociation enthalpies were established[18,19]. In addition, sodium cation–water, sodium cation–methanol, and sodium cation–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 a sodium cation[21]. Similarly, small clusters of potassium cation 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 with 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.

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 (the numerical constant coming from ref.[26]):

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

and

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

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[27].

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. Bionding energies obtained this way were within 1 kcal/mol of the values from the original extrapolation. 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[28].

RESULTS AND DISCUSSION

The structures of the optimized ion–water clusters under study are presented in Fig. 1, while those with methanol as a microsolvent are shown in Fig. 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 of formation of additional solvent–solvent hydrogen bonds. For steric reasons dictated by strong ion–water interactions these additional hydrogen bonds cannot develop for the sodium cation solute. For anions (in particular chloride), 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 associated with the process $X(Sol)_n \rightarrow X(Sol)_{n-1} + Sol$, 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 associated with the process $X(Sol)_n \rightarrow (Sol)_n + X$. Similarly as in the previous case, for evaluation of the vertical dissociation energy we employ an unrelaxed structure of

$Cl^-(H_2O)$ $Cl^-(H_2O)_2$ $Cl^-(H_2O)_3$

$F^-(H_2O)$ $F^-(H_2O)_2$ $F^-(H_2O)_3$
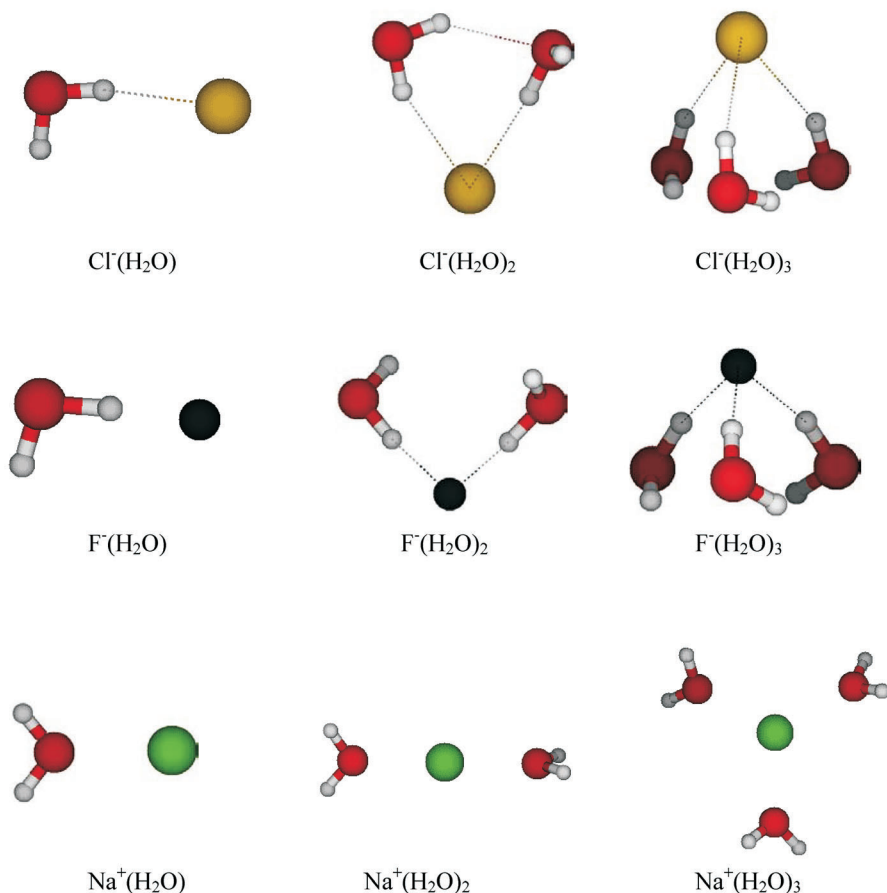
$Na^+(H_2O)$ $Na^+(H_2O)_2$ $Na^+(H_2O)_3$

Fig. 1
Structures of ion–water clusters for chloride, fluoride, and sodium with one to three water molecules

(Sol)$_n$, while for the adiabatic dissociation energy the geometry of (Sol)$_n$ is optimized after dissociation. For all the systems under study, these dissociation energies are presented in Figs 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. The vertical water binding gets stronger with increasing cluster size (Fig. 3a) and the vertical ion binding
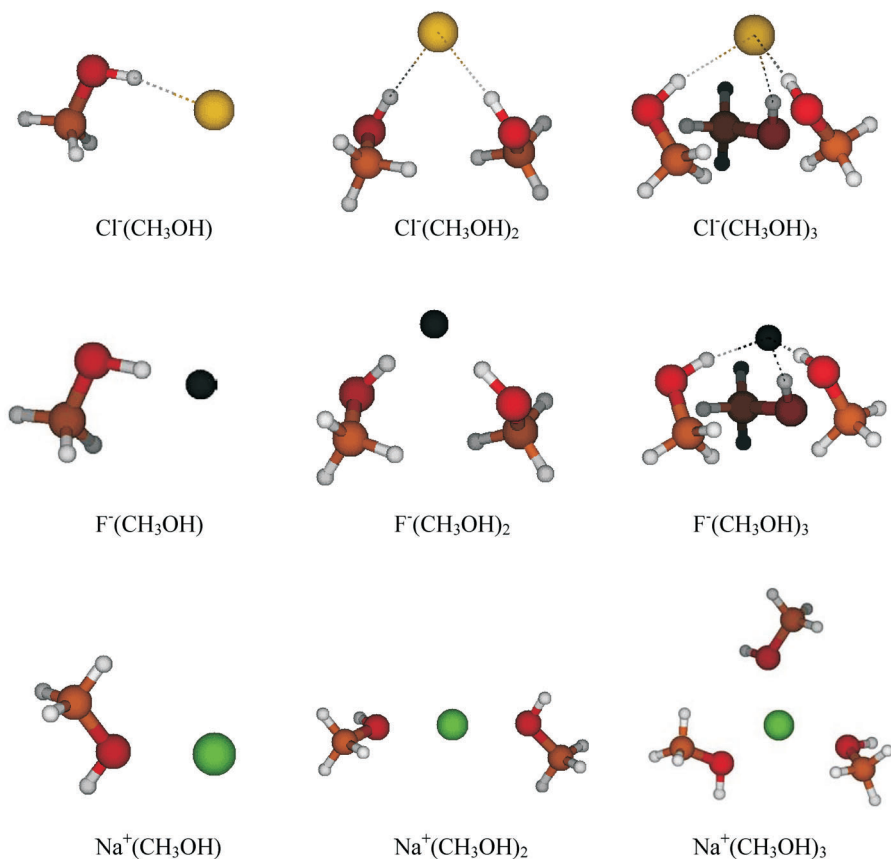

Cl⁻(CH₃OH) Cl⁻(CH₃OH)₂ Cl⁻(CH₃OH)₃

F⁻(CH₃OH) F⁻(CH₃OH)₂ F⁻(CH₃OH)₃

Na⁺(CH₃OH) Na⁺(CH₃OH)₂ Na⁺(CH₃OH)₃

Fɪɢ. 2
Structures of ion–methanol clusters for chloride, fluoride, and sodium with one to three water molecules

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 rest of the system after solvent or ion removal comes into play, too.
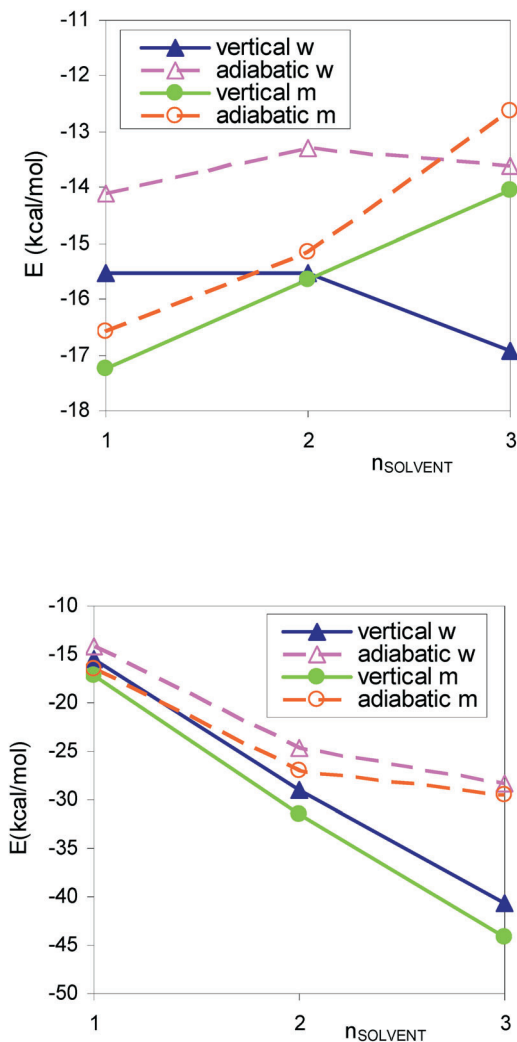
Vertical and adiabatic CCSD(T)/CBS binding energies of solvent (a) and chloride (b) in water (w) or methanol (m) clusters with one to three solvent molecules

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
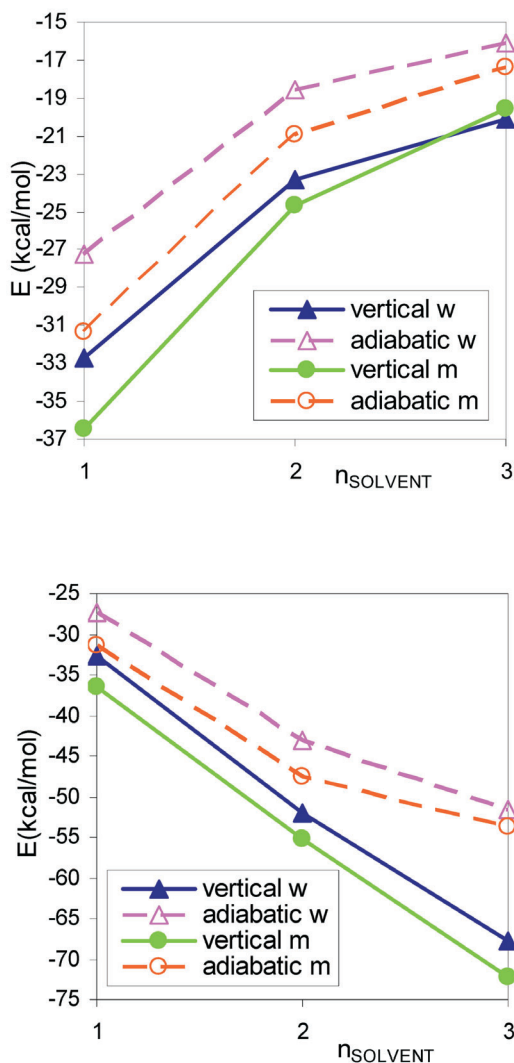

Fig. 4

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

three solvent molecules where binding of a water molecule (both vertical and adiabatic) becomes stronger than that of a methanol molecule. Nevertheless, ion binding remains stronger for methanol solvent; however, the difference from water all but disappears in the adiabatic picture. These re-
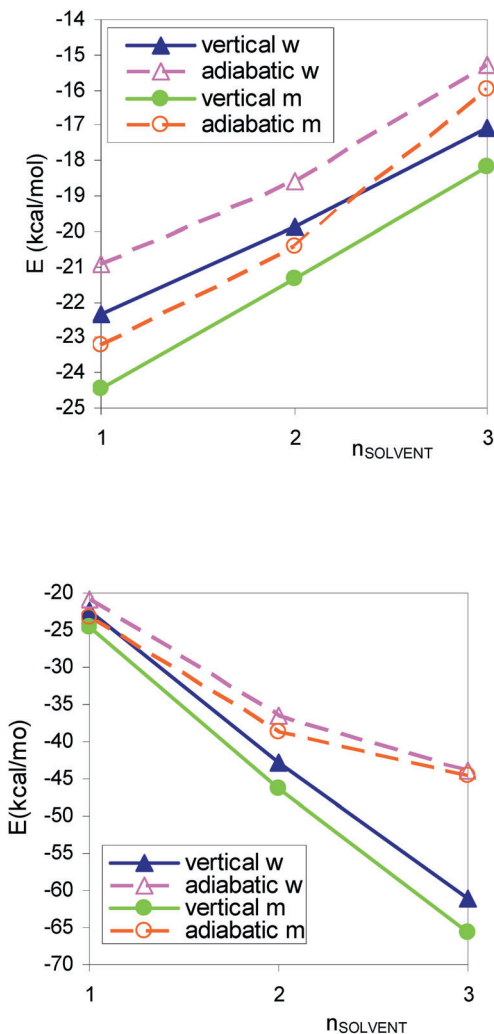

FIG. 5

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

TABLE I

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

	n	E, kcal/mol			
		vertical w	adiabatic w	vertical m	adiabatic m
(a)					
	1	−15.53	−14.10	−17.24	−16.58
	2	−15.53	−13.28	−15.65	−15.16
	3	−16.94	−13.61	−14.04	−12.62
(b)					
	1	−15.53	−14.10	−17.24	−16.58
	2	−28.99	−24.72	−31.48	−27.01
	3	−40.66	−28.39	−44.24	−29.54

TABLE II

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

	n	E, kcal/mol			
		vertical w	adiabatic w	vertical m	adiabatic m
(a)					
	1	−32.67	−27.27	−36.42	−31.31
	2	−23.29	−18.59	−24.68	−20.96
	3	−20.10	−16.13	−19.55	−16.33
(b)					
	1	−32.67	−27.27	−36.42	−31.31
	2	−52.04	−43.16	−55.32	−47.47
	3	−67.75	−51.55	−72.15	−53.70

sults indicate that although the smallest clusters exhibit a qualitatively opposite behavior to that of the bulk (where water is a better solvent for ions than methanol), further 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 additional stabilization of aqueous clusters with more than a single solute molecule.

The corresponding results for fluoride are depicted in Fig. 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 the investigated system sizes (except for the vertical solvent binding energies which become practically equal for methanol and water in clusters with three solvent molecules).

Finally, Fig. 5 shows the binding energies for small sodium cation–water and sodium cation–methanol clusters. The strength of binding to sodium cation lies between those to fluoride and chloride, albeit closer to the former. As is the case for the anions, methanol wins as a preferred microsolvent for Na^+ 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 flip-

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

	n	E, kcal/mol			
		vertical w	adiabatic w	vertical m	adiabatic m
(a)					
	1	−22.36	−20.92	−24.46	−23.22
	2	−19.87	−18.59	−21.35	−20.40
	3	−17.06	−15.29	−18.04	−16.38
(b)					
	1	−22.36	−20.92	−24.46	−23.22
	2	−42.76	−36.44	−46.29	−38.62
	3	−61.17	−44.00	−65.17	−44.91

ping the preference to the water side. This is due to the fact that the geometry of water binding to cations does not allow for formation of stabilizing water–water hydrogen bonds in small clusters.

For clarity and easy comparison with previous studies, all the above binding energies are also summarized numerically in Tables I–III.

CONCLUSIONS

We have presented optimal structures and vertical and adiabatic binding energies of ions and solvent molecules in clusters of sodium cation, 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.

SUPPLEMENTARY MATERIAL

All geometric parameters and absolute ab initio energies of the investigated systems are available online (doi:10.1135/cccc20080733).

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