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Solvation enthalpies of the proton and electron in polar and non-polar solvents

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Abstract

The importance of the proton and electron transfer processes in solution is well-known. Nonetheless, there is still no systematic theoretical study on the proton and electron solvation enthalpies. We investigated the solvation enthalpies of the proton and electron in different solvents of various polarities (water, DMSO, acetonitrile, methanol, ethanol, acetone, aniline, benzene, and penthylethanoate) using the SMD solvation model. All calculations were performed at the B3LYP-D2 and M052-X levels of theory with 6-311++G(d,p) basis set. On the basis of our calculations, it was found that the B3LYP-D2 and M05-2X functionals provide similar solvation enthalpies for the proton. Also, the results obtained for the proton solvation enthalpies are in good agreement with the published results. On the other hand, the electron solvation enthalpies calculated by means of B3LYP-D2, and especially using M05-2X, are significantly different from the reported results.

Keywords: Solvation enthalpies, proton, electron, B3LYP-D2, M05-2X

1. Introduction

Antioxidant properties of natural products, as well as synthetic compounds, have been intensively studied using different experimental methods and theoretical approaches. Theoretical studies of antioxidant action are usually based on thermodynamic properties, such as: bond dissociation enthalpy (BDE), electron transfer enthalpy (ETE), proton affinity (PA), proton dissociation enthalpy (PDA), and ionization potential (IP). Protective role of antioxidants can be described by at least three free radical mechanisms (Wright et al., 2001; Klein et al., 2007; Litwinienko et al., 2007): single-step (Hydrogen Atom Transfer – HAT), and double-step mechanisms (Single Electron Transfer followed by Proton Transfer – SET-PT, and Sequential Proton Loss Electron Transfer – SPLET).

The HAT mechanism is described as follows:

$$\mathrm{Ar}-\mathrm{OH} \rightarrow \mathrm{Ar}-\mathrm{O}^{\bullet} + \mathrm{H}^{\bullet} \tag{1}$$

HAT is characterized by the BDE value of the OH group. BDE can be calculated using the following equation:

$$\mathrm{BDE} = H(\mathrm{Ar{-}O}^{\bullet}) + H(\mathrm{H}^{\bullet}) - H(\mathrm{Ar{-}OH}) \tag{2}$$

$H(\mathrm{Ar{-}OH})$ is the enthalpy of the parent polyphenolic molecule, $H(\mathrm{Ar{-}O^{\bullet}})$ is the enthalpy of the radical generated after the hydrogen atom abstraction, and $H(\mathrm{H^{\bullet}})$ is the enthalpy of the hydrogen atom.

In the first step of the SET-PT mechanism the parent compound loses an electron, thus yielding the corresponding radical cation $\mathrm{Ar{-}OH^{\bullet+}}$.

$$\mathrm{Ar{-}OH} \rightarrow \mathrm{Ar{-}OH^{\bullet+}} + \mathrm{e^{-}} \qquad (3)$$

The IP value, which describes this step, can be calculated as follows:

$$\mathrm{IP} = H(\mathrm{Ar{-}OH^{\bullet+}}) + H(\mathrm{e^{-}}) - H(\mathrm{Ar{-}OH}) \qquad (4)$$

$H(\mathrm{Ar{-}OH{\bullet}{+}})$ is the enthalpy of the radical cation and $H(\mathrm{e{-}})$ is the enthalpy of the electron.

The second step in SET-PT is a deprotonation of $\mathrm{Ar{-}OH{\bullet}{+}}$:

$$\mathrm{Ar{-}OH^{\bullet+}} \rightarrow \mathrm{Ar{-}O^{\bullet}} + \mathrm{H^{+}} \qquad (5)$$

The PDE value describes this step, and can be calculated using the following equation:

$$\mathrm{PDE} = H(\mathrm{Ar{-}O^{\bullet}}) + H(\mathrm{H^{+}}) - H(\mathrm{Ar{-}OH^{\bullet+}}) \qquad (6)$$

$H(\mathrm{H+})$ is the enthalpy of the proton.

The first step in the SPLET mechanism is a deprotonation of the parent molecule where the phenoxide anion $\mathrm{Ar{-}O{-}}$ is formed (Foti et al., 2004; Litwinienko et al., 2009):

$$\mathrm{Ar{-}OH} \rightarrow \mathrm{Ar{-}O^{-}} + \mathrm{H^{+}} \qquad (7)$$

The PA value of the phenoxide anion $\mathrm{Ar{-}O{-}}$ can be calculated by means of the equation:

$$\mathrm{PA} = H(\mathrm{Ar{-}O{-}}) + H(\mathrm{H+}) - H(\mathrm{Ar{-}OH}) \qquad (8)$$

$H(\mathrm{Ar{-}O{-}})$ is the enthalpy of the phenoxide anion.

In the second step $\mathrm{Ar{-}O{-}}$ loses an electron yielding the corresponding free radical:

$$\mathrm{Ar{-}O^{-}} \rightarrow \mathrm{Ar{-}O^{\bullet}} + \mathrm{e^{-}} \qquad (9)$$

This step is characterized by the ETE value that can be calculated using the following equation:

$$\mathrm{ETE} = H(\mathrm{Ar{-}O^{\bullet}}) + H(\mathrm{e^{-}}) - H(\mathrm{Ar{-}O^{-}}) \qquad (10)$$

For complex studies of antioxidant mechanisms in solution-phase, knowing the proton and electron solvation enthalpies (eqs 4, 6, 8, and 10) in various non-polar and polar solvents is essential. With exception for valuable data for aqueous solution (Jortner et al., 1966, Atkins 1998, Donald et al., 2010), there are no other experimental data. In addition, a systematic theoretical study on the proton and electron solvation enthalpy has not been yet performed. Therefore, the main aim of this paper is to determine the proton and electron solvation enthalpies for some commonly used non-polar and polar solvents.

2. Computational details

All calculations were carried out by using the Gaussian 09 program package (Frisch et al., 2009). The equilibrium geometries of all species under investigation were calculated using two methods: M05-2X (Zhao et al., 2008; Zhao et al., 2005), and B3LYP-D2 (Grimme 2011). Since calculation results also depend on the basis set choice, the computations were performed with the 6-311++G** basis set (McLean et al., 1980; Wachters 1970), which includes diffuse and polarization functions on heavy and hydrogen atoms. In this manner the error resulting from not using a complete basis set is minimized.

The M05-2X functional proved to yield satisfactory overall performance for the main group thermochemistry and thermochemical kinetics, as well as organic, organometallic, biological, and noncovalent interactions. This functional has been successfully used by independent authors (Marković et al., 2012); Black et al., 2010; Galano et al., 2009; Galano et al., 2010; Marković et al., 2010; Zavala-Oseguera et al., 2009; Alberto et al., 2013). Another successful approach, originally developed by Grimme and called DFT-D (Grimme 2011), can be efficiently coupled with almost any existing DFT-based method. According to Grimme and Bayach (Grimme 2004; Grimme 2006; Bayach et al., 2013) an atom-atom additive damped empirical potential is used to include long-range dispersion contributions to the computed DFT total energy and gradients. In the case of B3LYP-D2 it holds:

$$\text{EB3LYP-D2} = \text{EB3LYP} - \text{EDisp} \tag{11}$$

where B3LYP (Becke 1993; Becke 1988; Lee et al., 1988) is a density functional, and E_{Disp} is the empirical term.

The geometries of all species obtained in this way were verified by normal mode analysis to be minima on the potential energy surface (no imaginary frequencies were obtained). The influence of solvents of various polarities: water, DMSO, acetonitrile, methanol, ethanol, acetone, aniline, benzene, and penthylethanoate, was approximated by the SMD solvation model (Marenich et al., 2009). SMD is based on the quantum mechanical charge density of a solute molecule interacting with a continuum description of the solvent. “D” in the model name stands for “density” and denotes that full solute electron density is used without defining partial atomic charges.

3. Results and Discussion

Before we present our results, we need to define the notation used in the present work. $X^{\pm}$ stands for charged specie (H^+ or e^-), whereas SOL-$X^{\pm}$ denotes a complex composed of a solvent molecule and the proton (SOL-X^+) or electron (SOL-X^-). Actually, SOL-X^+ is the protonated solvent molecule (Fig. 1), whereas SOL-X^- is the corresponding anion. Then, the solvation enthalpy of $X^{\pm}$ can be calculated by using the following equation (Mejías et al., 2000):

$$\Delta H_{sol}(X^{\pm}) = H(\text{SOL} - X^{\pm}_{sol}) - H(X^{\pm}_{gas}) - H(\text{SOL}_{sol}) \tag{12}$$

where $\Delta H_{sol}(X^{\pm})$ represents the solvation enthalpy of the proton or electron, $H(\text{SOL-} X^{\pm}_{sol})$ is the enthalpy of the SOL- $X^{\pm}_{sol}$ complex embedded in a dielectric continuum, and $H(\text{SOL}_{sol})$ is the enthalpy of a solvent molecule solvated with the molecules of the same kind. The gas-phase enthalpy of the proton, $H(H^+)$, is taken as that for an ideal gas (5/2 RT = 6.197 kJ mol^{-1} (Bartmess 1994)), while the gas-phase enthalpy of the electron, $H(e^-)$ amounts to 3.145 kJ mol^{-1} (Bartmess 1994).

All protonated solvent molecules studied in this paper are presented in Fig. 1, whereas the calculated solvation enthalpies for the proton and electron in different solvents are presented in Tables 1 and 2. It is worth pointing out that the experimental data on the proton and electron solvation enthalpies are scarce. The only available experimental values are those for the proton and electron in water. Their hydration enthalpies are: for the proton ΔHsol(H+) = –1090 kJ mol–1 (Atkins 1998), and for the electron ΔHsol(e–) = -153.1 kJ mol–1 (Jortner et al., 1966), and -129.3 kJ mol–1 (Donald et al., 2010). Thus, the validation of the obtained results will be based on the comparison to the available calculated values.

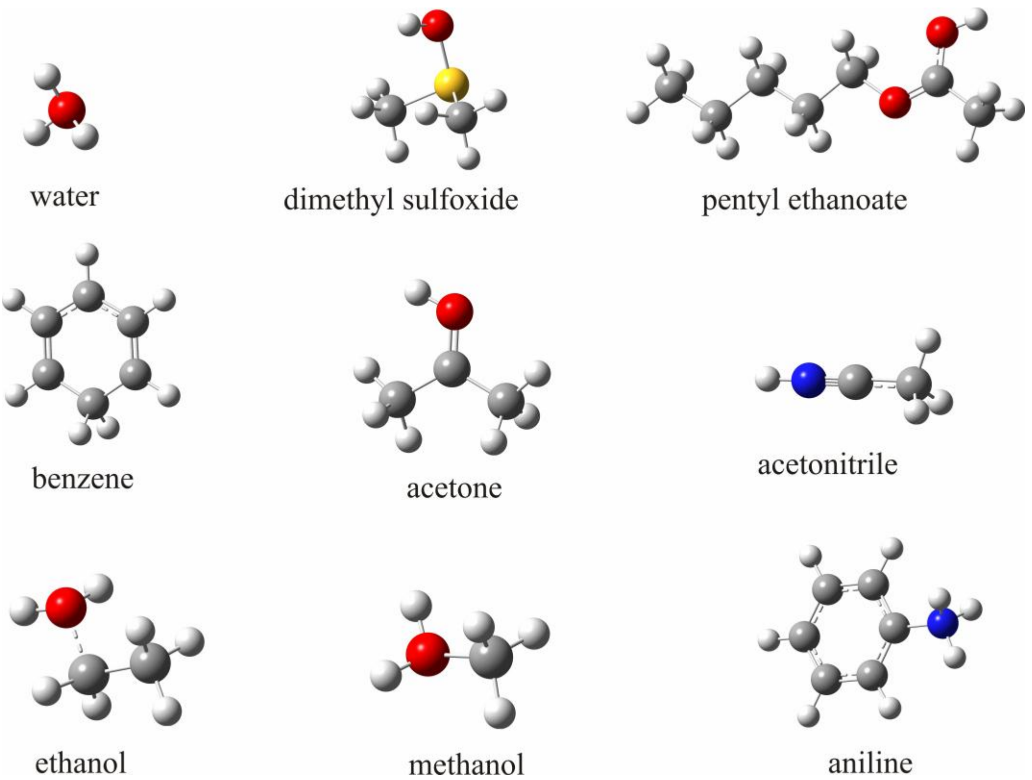

Fig. 1. The optimized geometries of the protonated solvent molecules under investigation.

3.1 Solvation enthalpies for the proton

Some calculated solvation enthalpies for proton have been reported by Rimarčík and Fifen (Rimarčík et al., 2010, Fifen et al., 2011). Their values are practically identical: -1022 and -1024 kJ mol^{-1}. To determine the proton hydration enthalpy, Mejías and Lago included in calculations 13 explicit water molecules that solvated H^{+}. They found the value of -1063 kJ mol^{-1} (Mejías et al., 2000). Tissandler and Coe obtained symilar values of -1150.1 and -1152.6 kJ mol^{-1} (Tissandler et al., 1998; Coe 1994). These values are very close to the experimental value.

Another theoretical study investigated the thermochemistry of the proton solvation in methanol within the cluster-continuum model. They used two DFT methods: B3LYP hybrid functional (ΔHsol(H+) = -1084 kJ mol–1) and M06-2X meta hybrid functional (ΔHsol(H+) = -1054 kJ mol–1) (Fifen et al., 2013).

Basis set	aug-cc-pVQZ		6-311++G**		
Functional	B3LYP[a]	BHLYP[a]	B3LYP[b]	M05-2X	B3LYP-D2
Benzene	-886	-885	-894	-877	-902
Penthylethanoate				-996	-1003
Aniline			-1092	-1102	-1108
Acetone	-1051	-1055	-1070	-1057	-1061
Ethanol	-1048	-1052	-1045	-1064	-1068
Methanol	-1039	-1044	-1038	-1065	-1069
Acetonitrile			-1031	-1031	-1043
DMSO	-1110	-1117	-1115	-1120	-1119
Water	-1022	-1026	-1022	-1052	-1055

Table 1. Solvation enthalpy of the proton (kJ mol^{-1}) in the studied solvents. [a](Rottmannova et al. 2013) and [b](Rimarčík et al., 2010).

The results for the proton solvation enthalpies obtained in this paper (Table 1) are generally in good agreement with the published values (Rimarčík et al., 2010; Rottmannova et al., 2013). The differences for M05-2X and B3LYP-D2 do not exceed 30 and 33 and kJ mol–1 in regard to the published values (Rimarčík et al., 2010, Rottmannova et al., 2013). The most notable deviations were found for water, ethanol, and methanol (Table 1). The calculated values for the proton solvation enthalpy in water are in better agreement with the experimental value than those of Rimarčík, Fifen and Rottmannova (Rimarčík et al., 2010; Fifen et al., 2011, Rottmannova et al., 2013). These values are very close to the Mejías's value obtained on the basis of a cluster with 13 water molecules (Mejías et al., 2000).

The values for the proton solvation enthalpy in methanol obtained by using M05-2X and B3LYP-D2 are in better agreement with the values of Fifen than with those of Rimarčík. As for the other solvents, the proton solvation enthalpies calculated in the present work agree well with the reported values (Rimarčík et al., 2010; Rottmannova et al., 2013).

3.2 Solvation enthalpies for the electron

As discussed above, the only experimental results for the solvation enthalpy of electron are those for aqueous solution (Jortner et al., 1966; Donald et al., 2010). The calculated values do not agree with the experimental results. The B3LYP-D2 value is close to that of Rimarčík et al. 2010, but it is about 30 and 50 kJ mol^{-1} higher than the experimental values. On the other hand, the result obtained using the M05-2X functional is higher than the experimental ones by about 65 and 85 kJ mol^{-1}.

Basis set	ε_r	6-311++G**		
Functional		B3LYP[b]	M05-2X	B3LYP-D2
Benzene	2.271	-7	-18	-20
Pentylethanoate	4.73		-43	-57
Aniline	6.89	-51	-80	-81
Acetone	20.7	-119	-120	-133
Ethanol	24.55	-76	-44	-74
Methanol	32.63	-86	-49	-80
Acetonitrile	36.64	-95	-117	-132
DMSO	46.7	-84	-29	-56
Water	78.39	105	-66	-101

Table 2. Solvation enthalpies of the electron (kJ mol^{-1}) in the studied solvents and relative permitivities $\varepsilon_r.\varepsilon_r$ taken from the ref. (Wilhelm et al., 1973), and references therein. [b](Rimarčík et al., 2010).

The calculated values for the electron solvation enthalpies do not agree so well with the literature data (Rimarčík et al., 2010) as the proton solvation enthalpies (Tables 1 and 2). The M05-2X functional provides a very high value for the electron solvation enthalpies in water, DMSO, methanol, and ethanol in comparison to other two methods. On the other hand, the B3LYP-D2 values are in good accord with the results of Rimarčík et al., 2010. The only exception is acetonitrile. Obviously, it is not easy to decide which of the obtained results are more reliable due to the lack of the experimental results.

4. Conclusions

This paper reports the results of the comparative study on the proton and electron solvation enthalpies for commonly used solvents of various polarities. The B3LYP-D2 and M05-2X functionals produce mutually similar results for the proton solvation enthalpies, while the results for the electron solvation enthalpies mutually differ. The proton solvation enthalpies obtained in this work are in accordance with previously published data. On the other hand, electron solvation enthalpies calculated by B3LYP-D2, and especially by M05-2X, are significantly different in comparison to the published results. The calculated proton and electron solvation enthalpies can be utilized in evaluation of reaction enthalpies of various proton and electron transfer processes in corresponding solvents.

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Извод

Енталпије солватације протона и електрона у поларним и неполарним растварачима

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Резиме

Добро је познат утицај растварача на процес преноса електрона и протона. Ипак, још увек не постоје систематична теоријска испитивања енталпија солватисаног протона и електрона. Испитане су енталпије солватације протона и електона у растварачима различите поларности (вода, DMSO, ацетонитрил, метанол, етанол, анилин, бензен, и пентилетаноат) користећи SMD солватациони модел. Сви прорачуни су изведени на B3LYP-D2 и M05-2X нивоима теорије са базним скупом 6-311++G(d,p). На основу извршених прорачуна, утврђено је да B3LYP-D2 и M05-2X функционали показују сличне вредности за енталпије солватације протона. Такође, добијени резултати енталпија солватације протона су у сагласности са објављеним резултатима. Са друге стране, вредности енталпија електрона израчунате са B3LYP-D2 методом, а нарочито резултати добијени помоћу M05-2X методе, значајно се разликују од објављених резултата.

Кључне речи: Енталпија солватације, протон, електрон, B3LYP-D2, M05-2X

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