Solvation enthalpies of the electron in polar and non-polar solvents: Theoretical study

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Abstract: Although the electron transfer is a part of many important processes in biosystems that occur in the solution-phase, there is still no systematic theoretical study of the electron solvation enthalpies. The solvation enthalpies of the electron in different solvents of various polarities: benzene, toluene, acetone, methanol, ethanol, DMSO and water, are investigated. All calculations were performed by B3LYP, BHLYP and PBE approaches with aug-cc-pVDZ, aug-cc-pVTZ and aug-cc-pVQZ basis sets, using the Integral Equation Formalism Polarized Continuum Model (IEF-PCM). The calculations show that the B3LYP and PBE functionals provide similar results. With the exception of benzene, toluene and DMSO, the differences in values for all solvents are lower than 6 kJ mol^{-1}. The BHLYP solvation enthalpies are higher by 20—25 kJ mol^{-1} than the B3LYP ones.

**Keywords:** electron solvation enthalpy, solvent, DFT, IEF-PCM

Introduction

Oxidation including electron transfer is an important part of the aerobic life. For example, in mitochondria, water is formed by the reaction

$$4H^+ + 4e^- + O_2 \rightarrow 2H_2O \qquad (1)$$

during cell respiration. Two-step mechanisms of the primary antioxidants action also include electron transfer from the antioxidant to a scavenged free radical. In general, electron transfer represents a key elementary step in processes involving molecules, polymers, ions, electrochemical and biological systems. For the thermodynamic study of these reactions in the solution-phase, solvation enthalpy of the electron plays the crucial role. However, there is still the lack of experimental data. Although some theoretical values of electron solvation enthalpies are available, a systematic study is still missing.

The main aim of this paper is to compute the electron solvation enthalpies in commonly used solvents of various polarities and to compare them with available experimental as well as theoretical data.

The solvated electron has long been known as a metastable species in alkali metal solutions in ammonia, aliphatic amines and ethers. Its transient existence in water has been demonstrated by pulse radiolysis studies (Jortner and Noyes 1966). Available published hydration enthalpies of the electron are $\Delta H_{hydr}(e^-)$ = –153.1 kJ mol^{-1} (Jortner and Noyes 1966) and $\Delta H_{hydr}(e^-)$ = –129.3 kJ mol^{-1} (Donald et al. 2010). These data have been obtained as the enthalpy changes in the process

$$\text{solvent } (l) + e^- \ (solv) \rightarrow \text{solvent}^- \ (solv) \qquad (2)$$
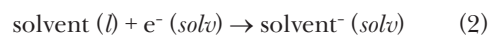
where the electron was "attached" to one molecule of the solvent placed in the cavity of the same solvent. The calculated gas-phase enthalpy of electron is 3.145 kJ mol^{-1} (Bartmess 1994).

Computational methods

All calculations were carried out using the Gaussian 03 program package (Frisch et al. 2003). The geometries of each compound or ionic structure were optimized using density functional theory (DFT) using B3LYP, BHLYP and PBE (PBE exchange functional and PBE correlation functional) functionals without any constraints (energy cut-off of 10^{-5} kJ mol^{-1}, final RMS energy gradient under 10^{-2} kJ mol^{-1} Å^{-1}). Dunning's correlation-consistent augmented basis sets (aug-cc-pVDZ, aug-cc-pVTZ and aug-cc-pVQZ) were applied (Dunning 1989). The optimized structures were confirmed to be real minima by vibrational analysis (no imaginary frequency). Solvent effect contributions to the total enthalpies were described by Integral Equation Formalism Polarized Continuum Model (IEF-PCM) (Cances et al. 1997). IEF-PCM calculations were carried out using default settings of Gaussian 03. In this paper, we have studied electron solvation enthalpies in seven solvents: benzene (C_6H_6), toluene ($CH_3C_6H_5$), acetone (CH_3COCH_3), ethanol (CH_3CH_2OH), methanol (CH_3OH), dimethylsulfoxide (CH_3SOCH_3) and water (H_2O). The total enthalpies of each molecule or ionic structure $H(X)$, at the

temperature T = 298.15 K, are estimated from the equation

$$H(X) = E_0 + \text{ZPE} + \Delta H_{\text{trans}} + \Delta H_{\text{rot}} + \Delta H_{\text{vib}} + RT \qquad (3)$$

where E_0 is the total electronic energy, ZPE represents zero-point energy, ΔH_{trans}, ΔH_{rot}, ΔH_{vib}, are the translation, rotation and vibration contributions to the enthalpy, respectively, and the RT term (R being the universal gas constant) is added to convert the energy to the enthalpy (Atkins 1998).

Results and Discussion

The e$^-$ solvation enthalpies in studied solvents determined using IEF-PCM DFT calculations are summarized in the Table 1. B3LYP calculations of the solvation enthalpies of the electron in benzene (Table 1) are in the range from –7 kJ mol^{-1} (for aug-cc-pVTZ basis set) to –17 kJ mol^{-1} (aug-cc-pVDZ). In the Table 1 we can see that aug-cc-pVTZ basis set gives approximately the same results in comparison with aug-cc-pVQZ. Aug-cc-pVTZ basis set calculations of benzene are similar to published values of Rimarčík et al. (2010). Solvation enthalpies of electron reported by Marković et al. (2013) are lower by

ca 3–13 kJ mol^{-1} (B3LYP-D2 functional) and by ca 1–11 kJ mol^{-1} (M05-2X functional) in comparison with the B3LYP ones. BHLYP calculations for benzene are in the range from 5 to –1 kJ mol^{-1} and PBE in the range from –30 to –34 kJ mol^{-1} (see Table 1). In comparison with B3LYP, BHLYP values are higher by 20–22 kJ mol^{-1} and PBE results are lower by ca 20–25 kJ mol^{-1}.

Toluene B3LYP values are in the range from –23 kJ mol^{-1} to –27 kJ mol^{-1}. In comparison with Rimarčík (2010), these results are lower by 10–14 kJ mol^{-1}. PBE calculations are lower than the B3LYP ones by ca 10 kJ mol^{-1} (see Table 1). BHLYP solvation enthalpies have values from –1 (aug-cc-pVDZ) to –7 kJ mol^{-1} (aug-cc-pVTZ). In the case of BHLYP aug-cc-pVQZ calculations convergence problems appeared during the optimization of anions geometries.

Solvation enthalpies of the electron in acetone calculated with B3LYP and PBE functionals are very similar. The differences are lower than 6 kJ mol^{-1} (see Tables 1). In comparison with available published data, these values are lower by 25 kJ mol^{-1} (Rimarčík et al., 2010) and by 10–25 kJ mol^{-1} (Marković et al., 2013). BHLYP solvation enthalpies are higher by

Tab. 1. Solvation enthalpies (in kJ mol^{-1}) of electron, ΔH(e$^-$), in studied solvents.

Solvent	Aug-cc-pVDZ			Aug-cc-pVTZ			Aug-cc-pVQZ		
	B3LYP	BHLYP	PBE	B3LYP	BHLYP	PBE	B3LYP	BHLYP	PBE
Benzene	–17	5	–30	–7	–1	–32	–8	*	–34
Toluene	–23	–1	–33	–25	–7	–35	–27	*	–39
Acetone	–145	–120	–149	–141	–116	–147	–141	–115	–147
Ethanol	–90	–69	–96	–91	–70	–97	–91	–71	–98
Methanol	–100	–79	–105	–101	–81	–106	–102	–82	–107
DMSO	–90	–76	–103	–96	–79	–103	–96	–79	–103
Water	–119	–97	–120	–118	–97	–120	–118	–97	–120

*Convergence problems.

Tab. 2. Theoretical solvation enthalpies (in kJ mol^{-1}) of electron, ΔH(e$^-$) in studied solvents and their relative permitivities, ε_r. All approaches used 6-311++G** basis set.

solvent	ε_r[a]	B3LYP[b]	B3LYP–D2[c]	M05–2X[d]
Benzene	2.271	–7	–20	–18
Toluene	2.374	–13	–	–
Acetone	20.493	–119	–133	–120
Ethanol	24.852	–76	–74	–44
Methanol	32.613	–86	–80	–49
DMSO	46.826	–84	–56	–29
Water	78.355	–105	–101	–66

[a]From the Ref. (Wilhelm and Battino 1973), and references therein.
[b]From the Ref. (Rimarčík et al. 2010).
[c]From the Ref. (Marković et al. 2013).
[d]From the Ref. (Marković et al. 2013).

25—30 kJ mol^{-1} with the values being from –115 to –120 kJ mol^{-1}.

Similarly as in the case of acetone, calculated solvation enthalpies of the electron in ethanol found with B3LYP and PBE functionals are very close. B3LYP calculations of ethanol are in a narrow range from –90 to –91 kJ mol^{-1}. These values are considerably lower in comparison with Rimarčík et al. (2010) and Marković et al. (2013) by 15—45 kJ mol^{-1} (Table 2). BHLYP results are also in a narrow range from –69 to –71 kJ mol^{-1}. These values are higher by ca 20—25 kJ mol^{-1} in comparison with B3LYP and PBE calculations.

B3LYP solvation enthalpies of the electron in methanol reached values in a narrow range (from –100 to –102 kJ mol^{-1}). Rimarčík et al. (2010) published B3LYP/6-311++G** value of –86 kJ mol^{-1}. In Marković et al. (2013), the electron solvation enthalpy reached values of –80 kJ mol^{-1} (B3LYP-D2 functional) and –49 kJ mol^{-1} (M05-2X functional). BHLYP calculations are lower by ca 20 kJ mol^{-1} with respect to the B3LYP ones. On the other hand, PBE solvation enthalpies are in a good agreement with B3LYP values, they are in a narrow range from –105 to –107 kJ mol^{-1}.

B3LYP calculations for DMSO are in the range from –90 to –96 kJ mol^{-1}. It is by about 6—12 kJ mol^{-1} lower than the published data (Rimarčík et al., 2010). Marković et al. (2013) data are higher, –56 kJ mol^{-1} for B3LYP-D2 functional and –29 kJ mol^{-1} for M05-2X functional. BHLYP values are by ca 20 kJ mol^{-1} higher in comparison with B3LYP, they are in a narrow range from –76 to –79 kJ mol^{-1}. PBE calculations give the value of –103 kJ mol^{-1}.

B3LYP and PBE solvation enthalpies of the electron in water (ca –120 kJ mol^{-1}) are in a good agreement with experimental data of Donald et al. (2010) (see Table 1). Differences are lower than 10 kJ mol^{-1}. Published calculations are lower by 15 kJ mol^{-1} (Rimarčík et al., 2010) and by 20—55 kJ mol^{-1} (Marković et al., 2013). BHLYP calculations provide the value of –97 kJ mol^{-1}.

As we can see in the Table 1, the solvation enthalpies obtained using various functionals exhibit the same trends. For B3LYP and PBE functionals, with the exception of benzene, toluene and DMSO, the differences of values for all remaining solvents are lower than 6 kJ mol^{-1} (Table 1). All BHLYP values are higher by 20—25 kJ mol^{-1} in comparison with the B3LYP ones. Interesting results provide BHLYP calculations for benzene predicting positive solvation enthalpies, in the range from 5 to –1 kJ mol^{-1} (Table 1).

Conclusion

In this paper, quantum chemical calculations of electron solvation enthalpies were presented. Solvents of various polarities were subjects of IEF-PCM DFT calculations. B3LYP and PBE functionals provide similar results. With the exception of benzene, toluene and DMSO, the differences of values for all solvents are lower than 6 kJ mol^{-1}. Obtained electron solvation enthalpies are in some cases significantly different from previously published data. The PBE solvation enthalpy of the electron in water is in a good agreement with experimental data of Donald et al. (2010). The calculated electron solvation enthalpies, $\Delta_{solv}H(e^-)$, can be utilized in the evaluation of reaction enthalpies of various electron transfer processes in a solution phase.

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