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Revisiting the solvation enthalpies and free energies of the proton and electron in various solvents

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ABSTRACT

In scientific literature there are only several values for solvation enthalpies and free energies of the proton and electron, the quantities from which the enthalpies and free energies of the solvated proton and electron can be issued. The latter quantities are of significance in thermodynamic modeling of antioxidative properties in the media where the reactions really occur. This work fills this gap in scientific literature. Namely, a systematic investigation of the solvation enthalpies and free energies of the proton and electron in twenty commonly used solvents of different polarities was performed. For this purpose eleven *ab initio* and DFT methods were used in combination with the 6-311++G(d,p) basis set and SMD solvation model. Due to very good overall performance, B3LYP was selected for further computations with larger basis sets. The thermodynamic values obtained at the B3LYP/Aug-cc-pVTZ level of theory are in very good agreement with the existing several values for solvation enthalpies of the proton and electron, and they are recommended for application in the examinations of antioxidative activity in different solvents.

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1. Introduction

Antioxidative activity of various classes of compounds has been the subject of numerous experimental and theoretical studies. Theoretical investigations are often focused on the elucidation of the mechanisms through which compounds exhibit their ability to trap reactive free radicals by yielding more stable and less harming radical species. There are three major antioxidative mechanisms: HAT (Hydrogen Atom Transfer), SET-PT (Single Electron Transfer-Proton Transfer) and SPLET (Sequential Proton-Loss Electron-Transfer). These processes are usually described by the following thermodynamic quantities: BDE (Bond Dissociation Enthalpy), IP and PDE (Ionisation Potential and Proton Dissociation Enthalpy), and PA and ETE (Proton Affinity and Electron Transfer Enthalpy). For an antioxidative compound ArOH these enthalpies are defined as follows:

$$\text{BDE} = H(\text{ArO}^\bullet) + H(\text{H}^\bullet) - H(\text{ArOH}) \quad (1)$$

$$\text{IP} = H(\text{ArOH}^{+\bullet}) + H(\text{e}^-) - H(\text{ArOH}) \quad (2)$$

$$\text{PDE} = H(\text{ArO}^\bullet) + H(\text{H}^+) - H(\text{ArOH}^{+\bullet}) \quad (3)$$

$$\text{PA} = H(\text{ArO}^-) + H(\text{H}^+) - H(\text{ArOH}) \quad (4)$$

$$\text{ETE} = H(\text{ArO}^\bullet) + H(\text{e}^-) - H(\text{ArO}^-) \quad (5)$$

In Eqs. (1)–(5) H denotes the enthalpy of the parent molecule (ArOH), its radical cation (ArOH⁺), radical (ArO[•]), and anion (ArO[−]). Certainly, the analogous equations can be written where the enthalpies are replaced with free energies (G). The enthalpies (free energies) of the hydrogen atom (H[•]), proton (H⁺), and electron (e[−]) also figure in these equations, where the enthalpies (free energies) of the proton and electron cannot be calculated. The thermodynamic quantities for the gas-phase can be easily attained by inserting the commonly accepted values of 6.197 kJ mol^{−1} for the proton enthalpy ($5/2RT$, the value for an ideal gas), 3.146 kJ mol^{−1} for the electron enthalpy, −26.255 kJ mol^{−1} for the proton free energy, and −3.633 kJ mol^{−1} for the electron free energy [1]. The gas-phase values for $H(\text{H}^+)$, $H(\text{e}^-)$, $G(\text{H}^+)$, and $G(\text{e}^-)$ have been recently revised [2,3]. Under an assumption that the proton does not behave as a classical particle at all temperatures (lower than 120 K), the values of 6.1398 and −26.3424 kJ mol^{−1} for $H(\text{H}^+)$ and $G(\text{H}^+)$ were obtained by using a procedure based on the Fermi–Dirac formalism at the standard pressure of 1 bar [2]. A procedure which determines the entropy of the electron in the gas-phase was used to calculate other thermodynamic quantities of the electron, and the values of 3.1351 and −3.6160 kJ mol^{−1} were obtained for $H(\text{e}^-)$ and $G(\text{e}^-)$ [3].

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Contemporary theoretical investigations are usually focused on the antioxidative action in different solvents, i.e. in the media where the reactions actually occur. The enthalpies and free energies of the proton and electron in different solvents can be issued from the corresponding solvation enthalpies and free energies. The solvation enthalpy (free energy) of the proton, $\Delta H_{\text{sol}}(\text{H}^+)$ or $\Delta G_{\text{sol}}(\text{H}^+)$, is the enthalpy (free energy) difference between a solvated proton and a proton at rest under vacuum. Similarly, the solvation enthalpy (free energy) of the electron, $\Delta H_{\text{sol}}(\text{e}^-)$ or $\Delta G_{\text{sol}}(\text{e}^-)$, is the enthalpy (free energy) difference between a solvated electron and an electron at rest under vacuum. Much effort has been devoted to attaining accurate hydration enthalpies of the proton and electron, $\Delta H_{\text{hyd}}(\text{H}^+)$ and $\Delta H_{\text{hyd}}(\text{e}^-)$. Some results for the hydration free energies of the proton and electron, $\Delta G_{\text{hyd}}(\text{H}^+)$ and $\Delta G_{\text{hyd}}(\text{e}^-)$, are also available in literature, whereas the data for other solvents are scarce.

Different values have been proposed for the hydration enthalpy of the proton. Among early results regarding this quantity, those suggested by Halliwell and Nyburg [4] and Conway [5] of -1091 and -1117 kJ mol^{-1} are worth mentioning. Later, Marcus obtained the value of -1103 kJ mol^{-1} by employing the TATB extrathermodynamic assumption [6], whereas Rashin et al. suggested an enthalpy range between -1087 and -1105 kJ mol^{-1} based on a macroscopic description of solvent which is averaged over its microscopic states [7]. The values of -1090 kJ mol^{-1} [8] and -1110 kJ mol^{-1} [9] were suggested in the books in the late 1990s. Tissandier et al. [10], Mejías and Lago [11], and Coe [12] reported the values of -1150.1 , ≈ -1150 , and -1151.0 kJ mol^{-1} on the basis of the sets of cluster-ion solvation data. These three mutually very similar results for the hydration enthalpy of the proton are notably lower than all previously reported values. In Refs. [10,12] the $\Delta G_{\text{hyd}}(\text{H}^+)$ values of -1104.5 and -1103.2 kJ mol^{-1} are also given. Using very similar procedure, but much larger set of ions, the $\Delta G_{\text{hyd}}(\text{H}^+)$ value of -1113.4 kJ mol^{-1} was suggested by Kelly et al. [13].

By investigating the thermochemistry of solvation of the proton in methyl alcohol within the cluster-continuum model Fifen et al. suggested the values of -1054.4 and -1075.3 kJ mol^{-1} for the solvation enthalpy and free energy of the proton in methanol [14].

Different properties of the hydrated electron, including structural, spectroscopic, kinetic, thermodynamic, and dynamic features, have been the subject of experimental and theoretical investigations [15–20]. As for the hydration enthalpy of the electron, the results obtained from the pulse radiolysis experiments should be emphasised [17–19]. This approach is based on measuring the enthalpies of the reactions (6)–(8), and uses the values for the hydration enthalpy of the proton and hydrogen atom.



Using the $\Delta H_{\text{hyd}}(\text{H}^+)$ value of -1117 kJ mol^{-1} [5], the values of -126 kJ mol^{-1} [17] and -145 kJ mol^{-1} [19] were suggested for the hydration enthalpy of the electron, 277 kJ mol^{-1} for the formation enthalpy of the hydrated electron [18], and -161 kJ mol^{-1} for the hydration free energy of the electron [17]. Bearing in mind that different $\Delta H_{\text{hyd}}(\text{H}^+)$ values can be employed in the calculations related to the pulse radiolysis experiments, it turns out that the hydration enthalpy of the electron spans in a very wide range. Using experimental and theoretical tools, Donald et al. showed that the ion–electron pairs are yielded when an electron is combined with a gaseous water cluster which involves different number of water molecules and a La^{3+} ion [21]. The value of -129.3 kJ mol^{-1} was obtained for $\Delta H_{\text{hyd}}(\text{e}^-)$ by extrapolating the experimentally

obtained recombination energies to infinite cluster size, thus avoiding any estimates for $\Delta H_{\text{hyd}}(\text{H}^+)$ or $\Delta H_{\text{hyd}}(\text{e}^-)$.

Some more comprehensive studies on the solvation enthalpies of the proton and electron in different solvents (in total: cyclohexane, benzene, chloroform, acetone, dichloromethane, methanol, ethanol, DMSO, and water) were performed by Fifen et al. [22], Rottmannová et al. [23], and Škorňa et al. [24]. These theoretical works were carried out by means of the B3LYP and BHLYP functionals in combination with few basis sets and the IEF-PCM solvation model. The aim of this work is to undertake a systematic investigation of the solvation enthalpies and free energies of the proton and electron in twenty commonly used solvents of different polarities. An additional goal is to examine the performance of various quantum mechanical methods employed in accomplishing this task.

2. Methodology section

It will be assumed that a proton or electron, when surrounded by the molecules of a certain solvent will bind to a solvent molecule solvated by the molecules of the same kind (S_{sol}), thus yielding a charged particle $(S-\text{H})_{\text{sol}}^+$ or $(S-\text{e})_{\text{sol}}^-$, which is embedded in a dielectric continuum [22–24]:



Then, the solvation enthalpies of the proton and electron are given by the following equations:

$$\Delta H_{\text{sol}}(\text{H}^+) = H(S-\text{H})_{\text{sol}}^+ - H(S_{\text{sol}}) - H(\text{H}_{\text{gas}}^+) \quad (11)$$

$$\Delta H_{\text{sol}}(\text{e}^-) = H(S-\text{e})_{\text{sol}}^- - H(S_{\text{sol}}) - H(\text{e}_{\text{gas}}^-) \quad (12)$$

The solvation free energies of the proton and electron, $\Delta G_{\text{sol}}(\text{H}^+)$ and $\Delta G_{\text{sol}}(\text{e}^-)$, are defined analogously:

$$\Delta G_{\text{sol}}(\text{H}^+) = G(S-\text{H})_{\text{sol}}^+ - G(S_{\text{sol}}) - G(\text{H}_{\text{gas}}^+) \quad (13)$$

$$\Delta G_{\text{sol}}(\text{e}^-) = G(S-\text{e})_{\text{sol}}^- - G(S_{\text{sol}}) - G(\text{e}_{\text{gas}}^-) \quad (14)$$

Using Eqs. (11)–(14) the solvation enthalpies and free energies of the proton and electron were calculated for the following solvents: 1-butanol (dielectric constant $\epsilon = 17.33$), acetic acid ($\epsilon = 6.25$), acetone ($\epsilon = 20.49$), acetonitrile ($\epsilon = 35.69$), aniline ($\epsilon = 6.89$), benzaldehyde ($\epsilon = 18.22$), benzene ($\epsilon = 2.27$), chlorobenzene ($\epsilon = 5.70$), cyclohexane ($\epsilon = 2.02$), diethylether ($\epsilon = 4.24$), dimethylformamide (DMF, $\epsilon = 37.22$), dimethyl sulfoxide (DMSO, $\epsilon = 46.83$), ethanol ($\epsilon = 24.85$), methanol ($\epsilon = 32.61$), nitrobenzene ($\epsilon = 34.81$), pentylethanoate ($\epsilon = 4.73$), quinoline ($\epsilon = 9.16$), tetrahydrofuran (THF, $\epsilon = 7.43$), toluene ($\epsilon = 2.37$), and water ($\epsilon = 78.35$). For this purpose, the geometries of the parent solvent molecules and corresponding protonated solvent molecules and radical anions were optimised by means of 11 quantum mechanical methods. A short overview of these methods (Supplementary material) reveals that, except for *ab initio* MP2 [25], and B2PLYP and B2PLYP-D3 [26,27], which can be considered as the mixtures between pure GGA-DFT and MP2, the methods used in this study are based on density functional theory: hybrid exchange–correlation functional (B3LYP [28]), dispersion-corrected functionals (B3LYP-D2 [29] and B3LYP-D3 [30]), and hybrid meta-GGA functionals (M05-2X [31], M06, M06-2X, M06-HF [32], and TPSS [33]). Such choice of the methods is based on the fact that the majority of them have been widely engaged in contemporary investigations devoted to antioxidative activity. Dispersion-corrected and hybrid meta-GGA functionals proved to describe short- and medium-range interatomic interactions more successfully than traditional DFT methods, while among hybrid functionals B3LYP showed the best overall performance.

All calculations were performed by employing the Gaussian 09 program package [34]. All methods were combined with the split-valence triple-zeta 6-311++G(d,p) basis set. The calculations at the B3LYP/6-311++G(3df,3pd) and B3LYP/Aug-cc-pVTZ were also performed. In all used basis sets the diffuse and polarisation functions are added to all atoms. The structures of all investigated molecules in all solvents were fully optimised, and frequency calculations performed. For this purpose the SMD continuum solvation model was applied which is based on the charge density of a solute molecule interacting with dielectric medium [35]. It was proved, by analysing the results of the frequency calculations, that all revealed stationary points are equilibrium geometries (no imaginary vibrations). The enthalpy and free energy values were calculated at $P = 101,325$ Pa and $T = 298.15$ K. The relative standard deviation was calculated for all solvents, where the MP2, B2PLYP and B2PLYP-D3 results were excluded from calculations.

3. Results and discussion

Following the above described procedure, all molecules whose enthalpies and free energies need to be inserted into Eqs. (11)–(14) were calculated by using the 6-311++G(d,p) basis set in combination with eleven quantum mechanical methods. In the case of the parent solvent molecules where several isomeric forms are possible, all isomers were calculated, and the most stable structures were selected for further consideration. In those cases where there is not only one site suitable for protonation, all possible protonated molecules were calculated, and the most stable isomers kept. The obtained results are listed in Tables 1–4. These results were produced by using the $H(H_{\text{gas}}^+)$, $H(e_{\text{gas}}^-)$, $G(H_{\text{gas}}^+)$, and $G(e_{\text{gas}}^-)$ values suggested by Bartmess [1]. Our intention was to include chloroform and carbon tetrachloride into the list of solvents. The obtained $\Delta H_{\text{sol}}(H^+)$ and $\Delta H_{\text{sol}}(e^-)$ values for chloroform are comparable to those reported in Refs. [22–24]. However, optimisation of protonated chloroform and carbon tetrachloride by means of all methods used in this work resulted in the structures consisting of separated HCl and corresponding carbocation. For example, in the structures calculated at the B3LYP/6-311++G(d,p) level of theory, which were supposed to be protonated carbon tetrachloride and chloroform, the C–Cl distances are 362.2 and 335.1 pm, respectively. For this reason the results for these two solvents are not here presented. It should be noted that we experienced major problems with convergence failure

and imaginary vibrations, more often in the case of radical anions. This problem was particularly severe in the case of the MP2, B2PLYP and B2PLYP-D3 methods. Consequently, it was not possible to calculate the solvation enthalpy and free energy for the electron in quinoline using MP2 (Tables 2 and 4). In addition, our numerous attempts to optimise the radical anions of DMSO and chlorobenzene using M06 and TPSS, respectively, were unsuccessful. In this sense, B3LYP and M06-2X proved to be the most robust methods.

Careful inspection of Tables 1 and 3 reveals that, in general, all methods produce mutually consistent values for the solvation enthalpy and free energy of the proton in a certain solvent. The relative standard deviation (RSD) for these quantities takes small values, not larger than around 2%. On the other hand, Tables 2 and 4 show that the solvation enthalpy and free energy values of the electron in a certain solvent span in wide ranges, as well as the corresponding RSD values, thus confirming a well-known fact that negatively charged species and those containing unpaired electrons are far more demanding for calculations than neutral molecules and cations. This occurrence was particularly pronounced in the case of cyclohexane, diethylether, and THF, whose RSD values for solvation enthalpy amount 90.11%, 124.31%, and 53.29%, while the RSD values for solvation free energy amount 119.42%, 108.30%, and 49.84%. In addition, the values for benzene and toluene obtained with the MP2, B2PLYP and B2PLYP-D3 methods, as well as the value for pentylethanoate obtained with MP2, extremely deviate from those produced by using other methods. Surprisingly, the least negative (most positive) values were produced by the MP2 method, followed by B2PLYP and B2PLYP-D3. The most negative (least positive) values were most often obtained by the M06-HF functional, which, however, failed in reproducing the $\Delta H_{\text{hyd}}(e^-)$ and $\Delta G_{\text{hyd}}(e^-)$ values. The B3LYP, B3LYP-D2, and B3LYP-D3 also yielded notably low $\Delta H_{\text{sol}}(e^-)$ and $\Delta G_{\text{sol}}(e^-)$ values. In addition, the results from these three methods for the solvation enthalpies and free energies of the electron are mutually very similar. This finding is not surprising since dispersion interactions do not dominate in a single molecule. As there are no pure experimental data on the solvation enthalpies or free energies of the proton and electron, it is difficult to conclude which method provides the values which match best with the exact values.

Interestingly, a comparison of the results of this study obtained at the B3LYP/6-311++G(d,p) level of theory to those of Rimarčič et al. [36] obtained at the same level of theory but with different

Table 1

Solvation enthalpies of the proton (kJ mol^{-1}). The results were obtained in combination with the 6-311++G(d,p) basis set and SMD solvation model. RSD stands for relative standard deviation.

Solvents	MP2	B2PLYP	B2PLYP-D3	B3LYP	B3LYP-D2	B3LYP-D3	M05-2X	M06	M06-2X	M06-HF	TPSS	RSD (%)
1-Butanol	-1063.8	-1062.5	-1063.9	-1062.8	-1065.9	-1065.9	-1057.8	-1055.5	-1057.6	-1064.3	-1069.8	0.44
Acetic acid	-1022.1	-1022.9	-1023.9	-1025.7	-1028.7	-1028.2	-1021.0	-1023.8	-1022.4	-1019.0	-1031.8	0.39
Acetone	-1049.9	-1055.5	-1056.6	-1060.2	-1062.9	-1062.9	-1056.1	-1058.5	-1053.6	-1049.9	-1066.5	0.48
Acetonitrile	-1032.9	-1038.2	-1039.1	-1043.8	-1044.7	-1045.6	-1030.7	-1045.4	-1032.4	-1025.3	-1050.7	0.81
Aniline	-1115.7	-1109.5	-1111.2	-1108.5	-1111.6	-1112.5	-1101.7	-1097.8	-1100.5	-1102.0	-1115.2	0.55
Benzaldehyde	-1032.3	-1044.7	-1045.7	-1051.7	-1053.8	-1054.0	-1040.3	-1044.1	-1036.3	-1031.1	-1058.6	0.87
Benzene	-869.6	-893.4	-894.7	-903.9	-908.2	-906.4	-879.3	-901.9	-877.4	-852.1	-913.6	2.22
Chlorobenzene	-853.0	-850.4	-852.0	-853.6	-856.0	-856.9	-837.7	-850.3	-836.5	-829.1	-865.5	1.37
Cyclohexane	-755.0	-760.2	-762.2	-766.2	-770.4	-769.6	-759.1	-762.4	-757.3	-760.7	-780.0	0.91
Diethylether	-1012.1	-1013.2	-1015.1	-1014.3	-1020.0	-1018.7	-1011.6	-1001.7	-1007.7	-1019.8	-1022.1	0.65
DMF	-1109.1	-1105.5	-1106.5	-1105.5	-1108.0	-1107.8	-1105.8	-1095.0	-1104.7	-1114.9	-1109.3	0.47
DMSO	-1127.4	-1120.1	-1121.3	-1119.6	-1120.2	-1122.1	-1120.3	-1115.8	-1119.7	-1127.3	-1118.3	0.28
Ethanol	-1070.5	-1068.5	-1069.8	-1068.4	-1071.6	-1071.4	-1064.5	-1063.3	-1064.0	-1068.6	-1076.0	0.39
Methanol	-1073.4	-1069.2	-1070.2	-1067.9	-1070.3	-1070.3	-1065.2	-1064.4	-1065.4	-1070.6	-1074.5	0.30
Nitrobenzene	-991.4	-999.5	-1000.5	-1007.4	-1009.5	-1009.7	-986.3	-999.9	-990.3	-980.1	-1018.7	1.26
Pentylethanoate	-1004.1	-1008.6	-1009.6	-1012.3	-1015.5	-1015.0	-1005.9	-1005.7	-1004.5	-1005.1	-1018.5	0.52
Quinoline	-1136.9	-1148.7	-1150.3	-1154.4	-1158.9	-1158.0	-1141.0	-1143.9	-1138.2	-1133.4	-1159.0	0.85
THF	-1042.1	-1043.8	-1045.5	-1044.7	-1049.6	-1048.6	-1040.6	-1034.0	-1036.6	-1046.0	-1051.4	0.56
Toluene	-895.8	-926.1	-927.4	-937.9	-942.5	-940.5	-913.7	-935.9	-911.7	-884.3	-946.5	2.17
Water	-1062.5	-1056.9	-1057.4	-1055.4	-1055.9	-1056.6	-1052.0	-1056.6	-1055.7	-1054.9	-1064.0	0.30

Table 2
Solvation enthalpies of the electron (kJ mol^{-1}). The results were obtained in combination with the 6-311++G(d,p) basis set and SMD solvation model. RSD stands for relative standard deviation.

Solvents	MP2	B2PLYP	B2PLYP-D3	B3LYP	B3LYP-D2	B3LYP-D3	M05-2X	M06	M06-2X	M06-HF	TPSS	RSD (%)
1-Butanol	-11.0	-52.5	-52.4	-68.8	-68.5	-68.6	-40.1	-42.1	-52.3	-71.9	-64.0	20.18
Acetic acid	-74.3	-99.9	-99.9	-120.9	-120.9	-121.1	-112.7	-103.0	-104.8	-124.6	-117.9	6.53
Acetone	-89.2	-112.3	-112.3	-132.9	-133.2	-132.7	-119.8	-120.6	-116.6	-129.0	-131.6	5.07
Acetonitrile	-69.3	-108.4	-108.5	-132.2	-133.2	-132.6	-116.7	-114.6	-113.0	-122.1	-129.7	6.51
Aniline	-23.9	-34.5	-34.4	-78.9	-79.7	-78.4	-77.2	-83.2	-77.4	-90.8	-73.5	6.06
Benzaldehyde	-107.2	-209.8	-209.7	-236.6	-236.8	-236.3	-235.4	-235.7	-230.6	-238.5	-234.5	0.92
Benzene	38.0	5.0	4.7	-16.5	-17.5	-16.2	-8.7	-21.3	-10.5	-19.3	-13.5	25.99
Chlorobenzene	-39.4	-77.9	-77.7	-105.0	-105.8	-104.5	-103.1	-108.9	-102.2	-110.3	/	2.59
Cyclohexane	54.1	21.4	21.6	4.4	4.9	4.6	48.5	34.8	35.1	3.2	14.1	90.11
Diethylether	8.1	-6.7	-6.7	-24.4	-24.5	-24.3	15.3	3.6	-0.7	-34.4	-14.3	124.31
DMF	-19.0	-74.2	-74.4	-92.1	-94.0	-92.5	-85.4	-88.1	-88.0	-95.5	-89.0	3.58
DMSO	-33.1	-42.3	-42.2	-53.0	-52.3	-52.5	-25.6	/	-42.9	-66.5	-49.0	23.61
Ethanol	-45.1	-56.5	-56.4	-73.6	-73.5	-73.5	-43.6	-46.9	-56.3	-76.2	-68.8	19.22
Methanol	-49.0	-62.0	-62.0	-80.0	-80.0	-80.0	-48.7	-52.5	-61.4	-82.1	-74.6	18.24
Nitrobenzene	-134.6	-280.1	-280.0	-315.4	-315.6	-315.3	-320.7	-311.5	-313.5	-338.5	-300.9	3.13
Pentylethanoate	5.0	-44.3	-44.0	-66.0	-66.1	-65.7	-51.1	-51.1	-48.6	-61.1	-64.0	12.04
Quinoline	/	-183.5	-183.4	-205.0	-205.3	-204.6	-205.3	-209.9	-202.5	-207.8	-203.6	1.07
THF	-7.7	60.3	140.3	-42.2	-41.7	-41.9	1.3	-19.7	-16.2	-49.0	-32.0	53.29
Toluene	37.5	-0.5	0.1	-21.7	-22.5	-21.0	-13.9	-25.4	-15.2	-26.7	-18.5	20.56
Water	-62.5	-81.4	-81.4	-101.0	-101.0	-100.9	-66.8	-66.2	-77.5	-66.3	-90.8	18.28

Table 3
Solvation free energies of the proton (kJ mol^{-1}). The results were obtained in combination with the 6-311++G(d,p) basis set and SMD solvation model. RSD stands for relative standard deviation.

Solvents	MP2	B2PLYP	B2PLYP-D3	B3LYP	B3LYP-D2	B3LYP-D3	M05-2X	M06	M06-2X	M06-HF	TPSS	RSD (%)
1-Butanol	-1059.7	-1061.1	-1062.4	-1062.1	-1064.4	-1065.0	-1056.0	-1053.5	-1056.7	-1066.5	-1068.9	0.49
Acetic acid	-1023.0	-1025.1	-1026.6	-1027.5	-1029.7	-1028.3	-1020.0	-1022.4	-1020.5	-1017.8	-1031.7	0.47
Acetone	-1050.3	-1055.7	-1056.9	-1060.5	-1063.2	-1063.2	-1055.7	-1058.7	-1053.5	-1048.7	-1066.9	0.52
Acetonitrile	-1035.1	-1043.3	-1044.2	-1049.0	-1049.9	-1050.9	-1035.8	-1050.3	-1034.5	-1030.2	-1056.2	0.86
Aniline	-1118.1	-1110.4	-1112.2	-1109.4	-1112.5	-1113.4	-1103.1	-1098.6	-1101.5	-1101.9	-1115.9	0.55
Benzaldehyde	-1034.5	-1045.2	-1046.2	-1052.0	-1054.2	-1054.3	-1040.8	-1044.8	-1036.5	-1031.1	-1058.9	0.88
Benzene	-875.2	-896.6	-898.0	-907.0	-911.5	-909.7	-882.9	-905.4	-881.9	-856.6	-916.9	2.16
Chlorobenzene	-858.9	-858.7	-861.5	-861.1	-864.0	-864.6	-842.6	-855.7	-841.0	-832.6	-872.4	1.53
Cyclohexane	-761.1	-767.3	-773.0	-773.4	-777.2	-776.1	-765.1	-767.9	-763.8	-762.3	-786.4	1.00
Diethylether	-1013.7	-1015.3	-1017.0	-1016.8	-1022.2	-1020.7	-1012.5	-1003.4	-1009.7	-1020.7	-1023.1	0.65
DMF	-1109.1	-1106.1	-1107.0	-1106.5	-1108.6	-1108.7	-1107.1	-1097.3	-1106.3	-1115.9	-1111.3	0.44
DMSO	-1131.1	-1124.2	-1125.4	-1123.7	-1124.4	-1126.4	-1122.8	-1117.8	-1121.7	-1129.1	-1121.0	0.29
Ethanol	-1069.7	-1068.4	-1069.7	-1068.8	-1071.9	-1071.7	-1064.5	-1063.9	-1064.0	-1069.7	-1076.2	0.39
Methanol	-1074.0	-1069.9	-1070.9	-1069.0	-1071.3	-1071.4	-1067.9	-1069.2	-1068.4	-1072.7	-1075.3	0.22
Nitrobenzene	-992.1	-1001.0	-1002.1	-1008.2	-1010.5	-1010.4	-989.0	-1002.7	-993.3	-982.8	-1022.4	1.23
Pentylethanoate	-1004.3	-1011.3	-1010.4	-1013.7	-1017.6	-1018.3	-1007.4	-1006.8	-1004.7	-1008.7	-1020.0	0.55
Quinoline	-1137.4	-1149.7	-1151.3	-1155.4	-1159.8	-1159.0	-1141.8	-1144.6	-1139.1	-1134.1	-1159.7	0.85
THF	-1040.2	-1044.6	-1046.4	-1046.1	-1051.0	-1050.0	-1038.5	-1033.6	-1035.5	-1046.8	-1048.8	0.62
Toluene	-898.8	-926.7	-927.8	-942.6	-944.6	-941.1	-919.6	-938.9	-914.7	-891.3	-950.2	2.02
Water	-1066.5	-1060.8	-1061.3	-1059.3	-1059.8	-1060.6	-1056.0	-1060.6	-1059.7	-1058.9	-1067.9	0.30

solvation model (IEF-PCM) shows that the results are very similar. More precisely, SMD produced more negative values for both $\Delta H_{\text{sol}}(\text{H}^+)$ and $\Delta H_{\text{sol}}(\text{e}^-)$, with few exceptions. These findings point out that the choice of solvation model also plays role in estimating solvation energies of the proton and electron.

Bearing in mind the robustness of the B3LYP functional, as well as the fact that this method has already been used in similar investigations [22–24], B3LYP was selected for further computations with some larger basis sets. It has been shown that the differences between the results obtained with Aug-cc-pVTZ and Aug-cc-pVQZ are negligible [23]. Taking this fact into account the 6-311++G(3df,3pd) and Aug-cc-pVTZ basis sets were combined with B3LYP to calculate the solvation enthalpies and Gibbs energies of the proton and electron in the examined solvents. Then, the enthalpy of the solvated proton and electron, $\Delta H(\text{H}_{\text{sol}}^+)$ and $\Delta H(\text{e}_{\text{sol}}^-)$, can be obtained by adding the $H(\text{H}_{\text{gas}}^+)$ and $H(\text{e}_{\text{gas}}^-)$ values to $\Delta H_{\text{sol}}(\text{H}^+)$ and $\Delta H_{\text{sol}}(\text{e}^-)$, respectively. Similarly, the Gibbs energy of the solvated proton and electron, $\Delta G(\text{H}_{\text{sol}}^+)$ and $\Delta G(\text{e}_{\text{sol}}^-)$, can be obtained by adding the $G(\text{H}_{\text{gas}}^+)$ and $G(\text{e}_{\text{gas}}^-)$ values to $\Delta G_{\text{sol}}(\text{H}^+)$ and $\Delta G_{\text{sol}}(\text{e}^-)$, respectively. To put it simply, a set of equations similar to Eqs. (11)–(14),

where the $H(\text{H}_{\text{gas}}^+)$, $H(\text{e}_{\text{gas}}^-)$, $G(\text{H}_{\text{gas}}^+)$, and $G(\text{e}_{\text{gas}}^-)$ values are excluded, were used for this purpose. The results obtained at these two levels of theory are presented in Tables 5 and 6, whereas all relevant structures optimised by using B3LYP/Aug-cc-pVTZ level of theory are depicted in Supplementary material.

An inspection of Tables 5 and 6 reveals that in majority of cases the values for $\Delta H_{\text{sol}}(\text{H}^+)$, $\Delta H_{\text{sol}}(\text{e}^-)$, $\Delta G_{\text{sol}}(\text{H}^+)$ and $\Delta G_{\text{sol}}(\text{e}^-)$, as well as for $\Delta H(\text{H}_{\text{sol}}^+)$, $\Delta H(\text{e}_{\text{sol}}^-)$, $\Delta G(\text{H}_{\text{sol}}^+)$ and $\Delta G(\text{e}_{\text{sol}}^-)$, resulting from two theoretical models are in very good agreement, where the values obtained by means of the Aug-cc-pVTZ basis set are generally lower. The reason for such performance of the two basis sets is, certainly, the fact that the Pople's split-valence basis set contains fewer basis functions, with only s diffuse function on hydrogen and s and p diffuse functions on heavy atoms, whereas the correlation consistent basis set contains s, p, and d diffuse functions on hydrogen and s, p, d, and f diffuse functions on heavy atoms. Fair disagreement between the thermodynamic properties of the solvated electron was observed in the case of those solvents whose radical anions have poor ability to delocalise an excess electron. In the case of cyclohexane the 6-311++G(3df,3pd) basis set produced small positive values,

Table 4

Solvation free energies of the electron (kJ mol^{-1}). The results were obtained in combination with the 6-311++G(d,p) basis set and SMD solvation model. RSD stands for relative standard deviation.

Solvents	MP2	B2PLYP	B2PLYP-D3	B3LYP	B3LYP-D2	B3LYP-D3	M05-2X	M06	M06-2X	M06-HF	TPSS	RSD (%)
1-Butanol	-12.2	-53.0	-52.9	-69.6	-68.9	-69.2	-40.1	-41.7	-52.6	-71.9	-65.3	20.54
Acetic acid	-76.3	-102.1	-102.2	-123.5	-123.4	-123.7	-113.9	-103.8	-104.7	-125.9	-121.1	7.10
Acetone	-88.9	-112.2	-112.2	-133.1	-133.6	-132.9	-120.6	-121.3	-117.9	-130.7	-131.9	4.83
Acetonitrile	-73.4	-115.8	-115.8	-139.3	-140.9	-140.0	-123.9	-122.0	-117.4	-129.1	-136.7	6.60
Aniline	-28.7	-36.6	-36.6	-91.4	-90.7	-86.5	-84.8	-92.0	-85.8	-96.2	-81.3	5.07
Benzaldehyde	-107.9	-213.8	-213.7	-238.6	-238.9	-238.3	-237.3	-237.9	-232.5	-240.3	-236.8	0.91
Benzene	34.7	0.3	-0.2	-22.2	-23.2	-22.0	-15.6	-30.0	-17.6	-24.0	-18.9	19.19
Chlorobenzene	-43.4	-84.8	-84.5	-115.5	-116.5	-115.1	-118.4	-119.8	-114.8	-118.5	/	1.55
Cyclohexane	50.7	15.1	15.3	-1.8	-1.3	0.1	43.6	30.0	30.5	1.7	9.6	119.42
Diethylether	7.3	-8.7	-8.5	-27.0	-26.6	-26.6	13.7	1.7	-2.6	-37.4	-17.0	108.30
DMF	-21.8	-72.3	-72.3	-91.6	-93.4	-91.8	-85.3	-88.7	-88.0	-96.6	-89.8	3.60
DMSO	-36.1	-45.3	-45.2	-54.6	-53.9	-54.1	-25.6	/	-44.1	-69.1	-51.1	24.30
Ethanol	-46.0	-57.4	-57.4	-74.7	-74.6	-74.6	-44.1	-47.9	-57.0	-77.2	-70.2	19.20
Methanol	-50.4	-63.6	-63.6	-81.7	-81.6	-81.6	-50.2	-54.1	-62.9	-83.6	-76.5	17.89
Nitrobenzene	-135.9	-283.8	-283.7	-315.5	-315.3	-315.2	-323.8	-313.6	-316.6	-342.6	-303.5	3.32
Pentylethanoate	2.8	-42.8	-39.9	-63.9	-65.8	-64.3	-51.6	-52.9	-49.5	-63.1	-62.3	10.49
Quinoline	/	-188.3	-188.2	-208.4	-208.7	-208.0	-208.5	-213.2	-205.8	-211.0	-207.1	1.03
THF	-8.3	57.4	137.2	-46.8	-46.1	-46.9	0.0	-28.7	-18.2	-53.1	-31.3	49.84
Toluene	38.7	-5.7	-0.4	-23.9	-24.8	-22.5	-18.7	-30.2	-17.6	-26.5	-21.3	16.61
Water	-64.4	-83.4	-83.4	-102.9	-103.0	-102.9	-68.7	-68.2	-79.4	-68.3	-94.6	17.95

Table 5

Solvation enthalpies, $\Delta H_{\text{sol}}(\text{H}^+)$ and $\Delta H_{\text{sol}}(\text{e}^-)$, and enthalpies of the solvated proton and electron, $\Delta H(\text{H}_{\text{sol}}^+)$ and $\Delta H(\text{e}_{\text{sol}}^-)$, (kJ mol^{-1}) calculated with the B3LYP functional in combination with the 6-311++G(3df,3pd) and Aug-cc-pVTZ basis sets.

Solvents	6-311++G(3df,3pd)				Aug-cc-pVTZ			
	$\Delta H_{\text{sol}}(\text{H}^+)$	$\Delta H_{\text{sol}}(\text{e}^-)$	$\Delta H(\text{H}_{\text{sol}}^+)$	$\Delta H(\text{e}_{\text{sol}}^-)$	$\Delta H_{\text{sol}}(\text{H}^+)$	$\Delta H_{\text{sol}}(\text{e}^-)$	$\Delta H(\text{H}_{\text{sol}}^+)$	$\Delta H(\text{e}_{\text{sol}}^-)$
1-Butanol	-1065.3	-68.5	-1059.1	-65.3	-1065.9	-70.7	-1059.7	-67.6
Acetic acid	-1033.2	-115.3	-1027.0	-112.1	-1033.8	-115.8	-1027.6	-112.6
Acetone	-1065.8	-130.0	-1059.6	-126.9	-1066.4	-130.7	-1060.3	-127.6
Acetonitrile	-1048.7	-129.1	-1042.5	-126.0	-1049.3	-128.7	-1043.1	-125.6
Aniline	-1108.8	-77.9	-1102.6	-74.7	-1110.3	-76.9	-1104.1	-73.8
Benzaldehyde	-1056.8	-234.5	-1050.6	-231.3	-1057.7	-234.0	-1051.5	-230.8
Benzene	-904.1	-16.7	-897.9	-13.5	-904.9	-17.5	-898.7	-14.4
Chlorobenzene	-863.1	-104.7	-856.9	-101.6	-862.1	-103.9	-855.9	-100.8
Cyclohexane	-769.8	3.8	-763.7	6.9	-770.1	-6.0	-764.0	-2.9
Diethylether	-1015.4	-24.7	-1009.2	-21.5	-1015.8	-31.1	-1009.6	-28.0
DMF	-1110.7	-89.2	-1104.6	-86.1	-1111.2	-89.9	-1105.0	-86.7
DMSO	-1109.2	-54.5	-1103.0	-51.3	-1116.6	-62.5	-1110.4	-59.4
Ethanol	-1070.7	-73.6	-1064.5	-70.4	-1071.3	-75.3	-1065.1	-72.2
Methanol	-1069.9	-79.3	-1063.7	-76.2	-1070.8	-81.4	-1064.6	-78.3
Nitrobenzene	-1013.8	-309.4	-1007.6	-306.3	-1015.2	-309.2	-1009.0	-306.1
Pentylethanoate	-1019.7	-61.7	-1013.5	-58.6	-1020.0	-63.1	-1013.8	-59.9
Quinoline	-1158.3	-203.3	-1152.1	-200.2	-1159.6	-202.1	-1153.4	-199.0
THF	-1045.7	-42.2	-1039.5	-39.0	-1045.9	-48.2	-1039.7	-45.0
Toluene	-938.3	-21.5	-932.1	-18.3	-939.1	-22.7	-932.9	-19.5
Water	-1058.0	-100.1	-1051.8	-96.9	-1058.9	-102.0	-1052.7	-98.8

with exception of $\Delta G_{\text{sol}}(\text{e}^-)$ which amounts to -0.4 kJ mol^{-1} , while the Aug-cc-pVTZ basis set yielded small negative values. Less pronounced but similar discrepancy was observed in the case of two examined ethers, diethylether, and THF. More diffuse and polarisation functions on all atoms in the Aug-cc-pVTZ basis set allows for molecular orbitals to occupy larger parts of space and take the shapes suitable for delocalisation of the unpaired electron, which leads to the stabilisation of the corresponding radical anions. In the case of DMSO, the results for both solvated electron and proton are notably different. DMSO contains sulphur for which the People's basis set is significantly smaller than the correlation consistent basis set. Namely, the 6-311++G(3df,3pd) basis set for sulphur consists of 14s, 10p, 3d, and 1f functions, whereas the Aug-cc-pVTZ basis set consists of 42s, 17p, 3d, and 2f functions. In the radical anion of DMSO and protonated solvent molecule sulphur bears large spin density and partial positive charge values. Thus, it is reasonable to decide that these two charged species issued from DMSO will be differently described with two different basis set. In the cases where some disagreements between the thermodynamic properties were

observed the additional calculations were carried out with the B3LYP-D2 functional, but the discrepancy was not decreased.

Both cyclohexane and benzene consists of carbon and hydrogen, but in the case of benzene the two basis sets yielded very similar results. Furthermore, chlorobenzene contains chlorine for which Aug-cc-pVTZ is significantly larger than 6-311++G(3df,3pd), but both basis sets generated consistent results. These findings can be attributed to the strong ability of the aromatic ring to delocalise either excess or deficiency of electrons, even when described with smaller basis sets.

A comparison of our results presented in Table 5 with several reported values shows that the $\Delta H_{\text{hyd}}(\text{e}^-)$ and $\Delta H_{\text{hyd}}(\text{H}^+)$ values are less negative than those proposed by Donald et al. [21], Tissandier et al. [10], Mejías and Lago [11], and Coe [12], whereas $\Delta H_{\text{sol}}(\text{H}^+)$ in methanol is slightly more negative than the result of Fifen et al. [14]. This finding is not surprising because the investigations based on cluster-ion solvation data generate the most negative values for the solvation enthalpy of the proton and electron. As for the results obtained by applying similar methodology, our

Table 6
Solvation free energies, $\Delta G_{\text{sol}}(\text{H}^+)$ and $\Delta_{\text{sol}}G(\text{e}^-)$, and free energies of the solvated proton and electron, $\Delta G(\text{H}_{\text{sol}}^+)$ and $\Delta G(\text{e}_{\text{sol}}^-)$ (kJ mol^{-1}) calculated with the B3LYP functional in combination with the 6-311++G(3df,3pd) and Aug-cc-pVTZ basis sets.

Solvents	6-311++G(3df,3pd)				Aug-cc-pVTZ			
	$\Delta G_{\text{sol}}(\text{H}^+)$	$\Delta G_{\text{sol}}(\text{e}^-)$	$\Delta G(\text{H}_{\text{sol}}^+)$	$\Delta G(\text{e}_{\text{sol}}^-)$	$\Delta G_{\text{sol}}(\text{H}^+)$	$\Delta G_{\text{sol}}(\text{e}^-)$	$\Delta G(\text{H}_{\text{sol}}^+)$	$\Delta G(\text{e}_{\text{sol}}^-)$
1-Butanol	-1064.6	-69.1	-1058.4	-65.9	-1065.2	-71.5	-1059.0	-68.4
Acetic acid	-1033.7	-118.3	-1027.5	-115.2	-1034.0	-119.0	-1027.8	-115.9
Acetone	-1066.6	-130.6	-1060.4	-127.4	-1066.9	-131.2	-1060.7	-128.0
Acetonitrile	-1051.3	-133.4	-1045.1	-130.3	-1054.5	-135.9	-1048.3	-132.7
Aniline	-1109.8	-86.1	-1103.6	-83.0	-1111.4	-84.6	-1105.2	-81.4
Benzaldehyde	-1057.2	-236.4	-1051.0	-233.2	-1058.1	-235.8	-1051.9	-232.7
Benzene	-907.2	-22.3	-901.0	-19.1	-908.0	-24.9	-901.8	-21.8
Chlorobenzene	-869.6	-117.5	-863.4	-114.3	-869.4	-115.9	-863.2	-112.7
Cyclohexane	-775.4	-0.4	-769.2	2.7	-777.4	-12.2	-771.2	-9.1
Diethylether	-1017.1	-27.1	-1010.9	-23.9	-1017.7	-33.9	-1011.5	-30.7
DMF	-1111.7	-88.9	-1105.5	-85.8	-1112.0	-89.9	-1105.8	-86.7
DMSO	-1113.1	-56.5	-1106.9	-53.4	-1120.7	-66.0	-1114.6	-62.8
Ethanol	-1071.0	-75.7	-1064.9	-72.5	-1071.7	-76.4	-1065.5	-73.2
Methanol	-1070.7	-80.9	-1064.5	-77.8	-1071.9	-83.0	-1065.7	-79.9
Nitrobenzene	-1014.8	-309.6	-1008.6	-306.4	-1018.1	-309.4	-1011.9	-306.3
Pentylethanoate	-1021.5	-61.9	-1015.3	-58.7	-1021.7	-63.5	-1015.5	-60.3
Quinoline	-1159.3	-206.5	-1153.1	-203.4	-1160.5	-205.4	-1154.3	-202.2
THF	-1047.2	-45.7	-1041.0	-42.5	-1047.6	-51.7	-1041.4	-48.5
Toluene	-944.0	-23.7	-937.8	-20.5	-940.6	-22.9	-934.4	-19.8
Water	-1062.0	-103.8	-1055.8	-100.6	-1062.9	-103.9	-1056.7	-100.8

$\Delta H_{\text{sol}}(\text{e}^-)$ values are slightly less negative, whereas the $\Delta H_{\text{sol}}(\text{H}^+)$ values are slightly lower than those suggested by Škorňa et al. [24] and Rottmannová et al. [23]. In spite of the fact that different solvation model was used in this work, our results obtained at the B3LYP/Aug-cc-pVTZ level of theory are in very good agreement with the values reported by Fifen et al. [22], with an exception of the $\Delta H_{\text{sol}}(\text{H}^+)$ value for benzene, where our value is closer to that of Rottmannová et al. Taking this fact into account, as well as the fact that in some cases the B3LYP/Aug-cc-pVTZ model yielded notably more negative values (which are, hopefully, closer to the exact values) than the B3LYP/6-311++G(3df,3pd) level of theory, we recommend the B3LYP/Aug-cc-pVTZ results for application in the investigations of antioxidative activity in different solvents.

Unfortunately, there are so few reported values for $\Delta G_{\text{sol}}(\text{H}^+)$ and $\Delta G_{\text{sol}}(\text{e}^-)$, implying that any discussion of the results in Table 6 does not make sense. On the other hand, the lack of solvation free energies of the proton and electron in literature makes our results more valuable.

4. Conclusions

Solvation enthalpies and free energies of the proton and electron are the quantities of significance in thermodynamic modeling of various natural and engineering processes. The reactions where reactive free radicals are trapped by antioxidants certainly represent a class of such processes. Thermodynamic modeling of antioxidative activity is based on the BDE, IP and PDE, and PA and ETE values. To calculate these enthalpies for a reaction which occur in a certain solvent one has to know the $\Delta H(\text{H}_{\text{sol}}^+)$ and $\Delta H(\text{e}_{\text{sol}}^-)$ values for this particular solvent, which can be issued from the corresponding $\Delta H_{\text{sol}}(\text{H}^+)$ and $\Delta H_{\text{sol}}(\text{e}^-)$ values. So far, there are only several such values in scientific literature, and even fewer $\Delta G_{\text{sol}}(\text{H}^+)$ and $\Delta G_{\text{sol}}(\text{e}^-)$ values. This work provides the $\Delta H_{\text{sol}}(\text{H}^+)$, $\Delta H_{\text{sol}}(\text{e}^-)$, $\Delta G_{\text{sol}}(\text{H}^+)$ and $\Delta G_{\text{sol}}(\text{e}^-)$ values, as well as the corresponding $\Delta H(\text{H}_{\text{sol}}^+)$, $\Delta H(\text{e}_{\text{sol}}^-)$, $\Delta G(\text{H}_{\text{sol}}^+)$ and $\Delta G(\text{e}_{\text{sol}}^-)$ values, for twenty solvents of different polarities. For this purpose eleven quantum mechanical methods were used in combination with the SMD solvation model. All methods produced mutually consistent $\Delta H_{\text{sol}}(\text{H}^+)$ and $\Delta G_{\text{sol}}(\text{H}^+)$ values for a certain solvent, whereas the $\Delta H_{\text{sol}}(\text{e}^-)$ and $\Delta G_{\text{sol}}(\text{e}^-)$ values span in wide ranges. Surprisingly, the MP2, B2PLYP and B2PLYP-D3 methods showed extremely bad performance in

reproducing $\Delta H_{\text{sol}}(\text{e}^-)$ and $\Delta G_{\text{sol}}(\text{e}^-)$, whereas B3LYP, B3LYP-D2, and B3LYP-D3 yielded notably low, mutually consistent results which are comparable with the reported literature data. The thermodynamic values obtained at the B3LYP/Aug-cc-pVTZ level of theory are in very good agreement with the existing several values for $\Delta H_{\text{sol}}(\text{H}^+)$ and $\Delta H_{\text{sol}}(\text{e}^-)$, and they are recommended for application in the examinations of antioxidative activity in different solvents.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.comptc.2015.09.007>.

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