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Computational Studies on Anthraquinone-2-sulfonic Acid, Electrochemistry and Electronic Investigation

Siavash Riahi [1,2,*] , *Solmaz Eynollahi*[2], *Mohammad Reza Ganjali*[2,3]

[1] Institute of Petroleum Engineering, Faculty of Engineering, University of Tehran
[2] Center of Excellence in Electrochemistry, Faculty of Chemistry, University of Tehran, P. O. Box 14155-6455, Tehran, Iran
[3] Endocrinology & Metabolism Research Center, Tehran University of Medical Sciences, Tehran, Iran
[*]E-mail: riahisv@khayam.ut.ac.ir

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This research presents calculations and computation of Anthraquinone-2-sulfonic acid (AQS) electrode potentials in water. For this purpose, the DFT and HF calculation with the 6-31G basis set were utilized. The calculated values were compared with the experimental values obtained by linear sweep voltammetry. The resulting data illustrated that the method was likely to be useful for the prediction of biomolecules electrode potentials in different aprotic solvents. The bond lengths, bond angles, dipole moment, electron affinity, ionization potential, electronegativity, absolute hardness, highest occupied molecular orbital (HOMO) and the energy of the lowest unoccupied molecular orbital (LUMO) were calculated in water.

Keywords: Redox reaction, Anthraquinone-2-sulfonic acid, DFT, HF, Solvent effect, Computational chemistry

1. INTRODUCTION

Quinone compounds are toxic substances, especially interesting for their capability to catalytically stimulate redox cycling of dioxygen to superoxide and other toxic forms of oxygen [l]. Anthraquinones are derivative of quinones, as the largest group of natural quinones and historically the most important ones [2], have been widely used in chemistry, biochemistry, pharmacology and industry, especially as useful nucleotidespecific ligands for the purification of proteins by affinity techniques [3,4]. We have chosen anthraquinone-2-sulfonic acid (AQS) as a model compound, due to its solubility in water.

The main activities of these compounds arise from their reversible electron transfer behaviour [5-7]. The electro-oxidation of the compound in this category is well documented and involves a transfer of two electrons and two protons to provide the associated quinones [8-9]. The electron transfer process constitutes the basic feature of chemical, biochemical and, especially, electrochemical reactions. Therefore, the ability to calculate redox potentials accurately using the theoretical methods would be advantageous in a number of different areas, particularly where the experimental measurements are difficult, due to the complex chemical equilibria and the reactions of the involved chemical species. Recently, a number of reports, dealing with the electrode potential calculation of several biomolecules, have been published in the literature [10-13]. Computational studies have been widely used in drug [14-17], anticancer derivatives [18], and toxic compounds [19-30].

In this paper, the vibrational frequencies for AQS and $AQSH_2$ were calculated using ab initio molecular orbital calculations (HF) and density function theory (DFT). Furthermore, standard electrode potential of half reaction, $E_{1/2}$, the electron affinity of the reduced species in the gas phase (EA), or the ionization potential for the reverse reaction (IP), the energy of the highest occupied molecular orbital (HOMO) or the energy of the lowest unoccupied molecular orbital (LUMO), bond lengths, bond angles and dipole moment of AQS and $AQSH_2$ was also calculated at the same level.

2. CALCULATION AND EXPERIMENTAL DETAILS

2.1. Calculations

Scheme 1 depicts the two-electron oxidation reaction of the (AQS). The oxidized form (AQS) can also be converted to its reduced form ($AQSH_2$) using catechol CAH_2 as a reference molecule, according to the following isodesmic reaction [31]:

$$AQS_{(sol)} + CAH_{2\,(sol)} \longrightarrow AQSH_{2\,(sol)} + CA_{(sol)} \qquad (1)$$

The difference between the electrode potential of the two species can be obtained from the change in the Gibbs free energy of reaction (1), in accordance with the equation (2):

$$E^{o\prime} = E^{o\prime}_{CA} - \frac{\Delta G^{\circ}}{2F} \qquad (2)$$

Where ΔG° is the free energy change for reaction (1), $E^{o\prime}_{CA}$ is the experimental formal electrode potential for a reference molecule, $E^{o\prime}$ is the calculated electrode potential and F is the Faraday constant. The Gibbs free energy change for reaction (1) can be computed by the thermodynamic cycle depicted in Figure 1, which is used in the case of transferring all the involved species in the reaction from the gas phase into the solution phase [32].

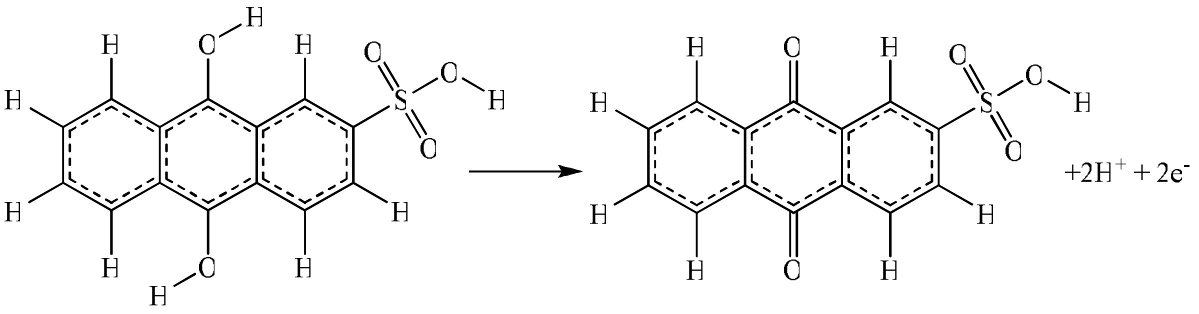
In order to calculate the standard Gibbs energy of reaction (1), ΔG^{o}, one should calculate the standard Gibbs energy of each component, ΔG_i^{o}, in reaction (1):

$$\Delta G^{\circ} = \sum \nu_i \Delta G_i^{\mathrm{o}} \qquad (3)$$

where ΔG_i^{o} the standard Gibbs energy of each component and ν_i is the stoichiometric coefficient. The standard Gibbs energy of each component is obtained using the following expression:

$$\Delta G_i^o = \Delta G_{i,gas}^o + \Delta G_{i,solv}^o \qquad (4)$$

where $\Delta G_{i,gas}^o$ is the gas-phase energy of each component and $\Delta G_{i,solv}^o$ is the solvation energy of the component. In the present work, the gas-phase contribution to the Gibbs energy, $\Delta G_{i,gas}^o$, was determined from ab initio calculation. These calculations have been performed at the HF and B3LYP using the 6-31G basis set [33-35]. The zero-point energies and thermal corrections together with entropies have been used to convert the internal energies to the Gibbs energies at 298.15 K. Solvation energies, $\Delta G_{i,solv}^o$, have been calculated using Polarisable Continuum Model (PCM) [36].



$AQSH_2$ AQS

Scheme 1. Electron oxidation reaction which is for AQS

$$\begin{tikzcd}
\mathrm{AQS}_{(g)} + \mathrm{CAH}_{2\,(g)} \arrow[r, leftrightarrow, "\Delta G_{(g)}"] \arrow[d, shift right=4ex, "\Delta G_{(solv,\ Ox)}"'] \arrow[d, shift left=4ex, "\Delta G_{(solv,\ CAH_2)}"] & \mathrm{AQSH}_{2\,(g)} + \mathrm{CA}_{(g)} \arrow[d, shift right=4ex, "\Delta G_{(solv,\ Red)}"'] \arrow[d, shift left=4ex, "\Delta G_{(solv,\ CA)}"] \\
\mathrm{AQS}_{(sol)} + \mathrm{CAH}_{2\,(sol)} \arrow[r, leftrightarrow, "\Delta G_{(tot)}"] & \mathrm{AQSH}_{2\,(sol)} + \mathrm{CA}_{(sol)}
\end{tikzcd}$$

Figure 1. The thermodynamic cycle, proposed to convert the standard Gibbs energy of the isodesmic redox reaction in the gas phase to the standard Gibbs energy of the reaction in solution.

2.2. Softwares and equipments

The formal potentials (E°´) were reported in reference 37 [37]. A Pentium IV personal computer (CPU at 3.06 GHz) with the Windows XP operating system was used. The initial geometry optimization was performed with HyperChem (Version 7.0 Hypercube, Inc., Alberta, Canada). For all the ab initio calculation, Gaussian 98 has been employed [38].

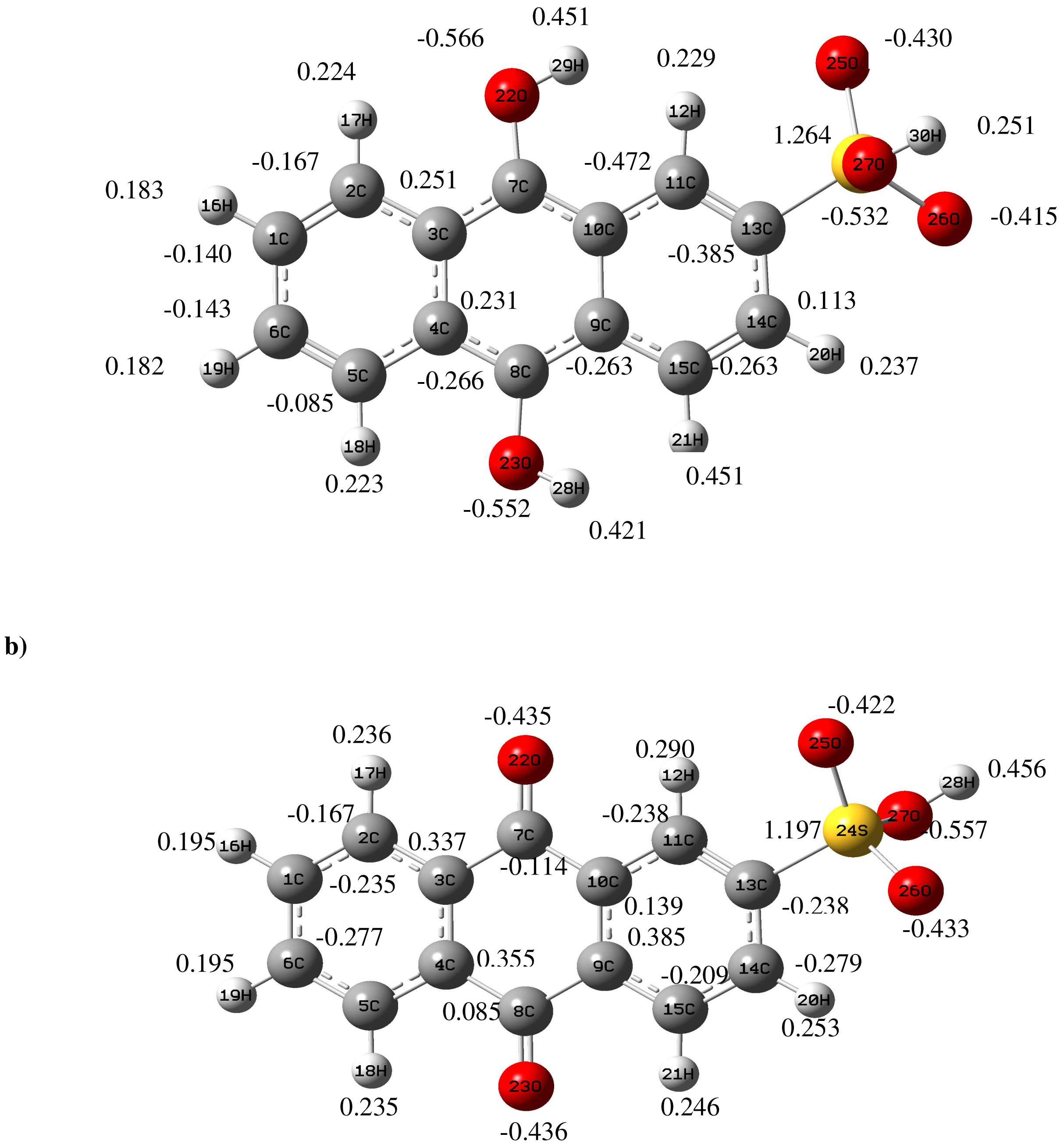


Figure 2. Optimized structures and atomic charges of (*a*) $AQSH_2$ and (*b*) AQS by DFT method.

3. RESULTS AND DISCUSSION

The geometrical optimization was the most significant step for the calculation of the formal electrode potential, on the grounds that the molecular parameters were controlled by the molecular geometry. The bond lengths and bond angles of the studied compounds were optimized by DFT and HF methods (Figures 2a, 2b and Table 1).

Table 1. The significant changes of bond length and bond angel of AQS and $AQSH_2$

	AQS			$AQSH_2$	
	DFT	HF		DFT	HF
Bond length (Å)			Bond length (Å)		
C–C	1.476	1.489	C⎓C	1.384	1.432
C⎓C	1.403	1.386	C–H	1.082	1.072
C–H	1.085	1.071	C–O	1.395	1.377
C=O	1.255	1.222	O–H	0.989	0.962
O–H	1.000	0.965	S=O	1.646	1.642
S=O	1.632	1.639	S–O	1.623	1.709
S–O	1.791	1.698	C–S	1.887	1.857
C–S	1.906	1.849			
Bond angles(°)			Bond angles(°)		
C–C⎓C	119.203	119.285	C⎓C⎓C	121.021	121.488
C⎓C⎓C	120.183	120.183	C⎓C– O	122.314	120.374
C⎓C–H	119.794	118.687	C⎓C–H	119.919	118.687
C–C= O	121.409	120.509	C–O–H	115.524	115.716
C–S=O	109.360	105.876	C–S–O	96.576	97.685
S–O–H	109.913	109.913	O=S=O	117.661	117.559
O= S= O	119.682	118.587	O–S=O	105.156	104.760

The most negative charge is 22O because this electronegative atom was connected to (29H and 7C). The most positive charge is 24S because of was connected to three electronegative atoms (25O, 27O and 26O) (Fig.2a).

For both the reduced and oxidized forms in the gas and solution phases, the calculated Gibbs energies of the molecules are summarized in Table 2, using DFT/6-31G and HF/6-31G. For the selection of 6-31G basis set, the decisive factor was the size of the studied molecules. The computation of the solvation energies is considered an essential step, since these energy values are required for the conversion of the gas-phase energies to the energies in the solution phase. As a matter of fact, these solute–solvent interactions, calculated by the PCM solvation model [36], were added to the gas phase energies to give the Gibbs energy change of each component in the solution phase. Table 2 also lists the total Gibbs free energy of each component in the presence of water.

Table 2. The Gibbs free energy of the studied molecules for both reduced (red.) and oxidized (ox.) forms in the gas phase and the solution phase, along with the change of the Gibbs free energy of reaction (1), ΔG_i^o, in both gas and solution phases[a]

	Mol.	$\Delta G_{i,gas}^{o}$ [b]		$\Delta G_{i,solv}^{o}$ [b]		ΔG_i^o	
		Red.	Ox.	Red.	Ox.	Gas	Solution
DFT/6-31G	AQS	-1313.16770	-1311.99694	-1313.23529	-1312.01969	0.057808	0.013075
	CA	-380.95453	-379.77474	-380.98108	-379.78978	0	0
HF/6-31G	AQS	-1306.981862	-1305.854934	-1307.195537	-1305.868909	0.10164	-0.06795
	CA	-380.270371	-379.074527	-380.366967	-379.15704	0	0

[a] Solution result was obtained with the PCM model

[b] These energies are in atomic units, Hartree (1 Hartree = 2625.49975 kJ mol^{-1})

Table 3. Calculated thermochemistry values

Thermochemistry parameters	AQS	AQSH$_2$
	DFT	DFT
Zero-point correction	0.193301	0.214145
Thermal correction to Energy	0.209089	0.231240
Thermal correction to Enthalpy	0.210033	0.232184
Thermal correction to Gibbs Free Energy	0.150002	0.169444
Sum of electronic and zero-point Energies	-1311.953649	-1313.123002
Sum of electronic and thermal Energies	-1311.937861	-1313.105907
Sum of electronic and thermal Enthalpies	-1311.936917	-1313.104963
Sum of electronic and thermal Free Energies	-1311.996948	-1313.167703

The thermochemistry values were calculated and were shown in Table 3. The difference of the results of calculation using DFT and HF are not significant, that were shown the robustness and validity of the results.

The attainment of CAQ electrode potentials was achieved with the aid of the total Gibbs energies and the experimental value of the electrode potential of the reference molecule, catechol (CA), in water (Eq. (2)) 10-13[8-11]. Table 4 presents the electrode potentials of the molecules, studied in water at the DFT/6-31G and HF/6-31G level. According to this Table, the electrode potentials of the molecules at this method and those obtained through experiments were found to be in a satisfactory agreement.

Table 4. Electrode potentials of the studied molecules, compared with the experimental values[a].

Mol.[b]	Exp.($E^{o\prime}$(mV)) [c]	$E^{o\prime}$ (mV)[d] (DFT/6-31G)	$E^{o\prime}$ (mV)[d] (HF/6-31G)
AQS	-64	-58.9	-83
CAH_2	375	375	375

[a] Calculated by Equation 2 ($E^{o\prime} = E^{o\prime}_{CA} - \frac{\Delta G^{\circ}}{2F}$)

[b] Studied Molecules

[c] Experimental values.

[d] Electrode potentials calculated by Eq. (2) as explained in the text

Table 5. The calculated amounts of HOMO and LUMO energies, dipole moment (μ), ionization potential (I), electron affinity (A), absolute electronegativity (χ) and absolute hardness (η) with the DFT/6-31G basis set

	AQS	$AQSH_2$	CA	CAH_2
E_{HOMO} (eV)	-7.80(-7.66)*	-5.46 (-5.41)	-6.36	-7.62
E_{LUMO} (eV)	-3.97 (-3.76)	-2.67 (-2.25)	7.19	3.96
E_{LUMO}- E_{HOMO} (eV)	2.33 (2.25)	1.30 (1.51)	13.55	11.58
μ	8.17 (11.63)	5.55(11.16)	1.49	4.00
I	7.80(7.66)	5.46 (5.41)	6.36	7.62
A	3.97 (3.76)	2.67 (2.25)	-7.19	-3.96
χ	5.88 (5.71)	4.06 (3.83)	-0.4	1.83
η	1.91 (1.95)	1.39 (1.58)	6.775	5.79

* The calculated parameters in water are presented in parenthesis

Table 5 summarizes the highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO) and HOMO and LUMO energy gaps for $CAQH_2$ calculated at DFT level in the 6-31G basis set. Results of the DFT methods are more accurate than HF method, so only results of DFT method are presented in table 5. The eigenvalues of LUMO and HOMO and their energy gap reflect the chemical activity of the molecule. LUMO as an electron acceptor represents the ability to obtain an electron, while HOMO as an electron donor represents the ability to donate an electron. The smaller the LUMO and HOMO energy gaps, the easier it is for the HOMO electrons to be excited; the higher the HOMO energies, the easier it is for HOMO to donate electrons; the lower the LUMO energies, the easier it is for LUMO to accept electrons. From the resulting data shown in table 5, it is obvious that the LUMO energies of $CAQH_2$ are lower than those of CAH_2 and the energy gap of $CAQH_2$ is smaller than that of CAH_2. Consequently, the electrons transfer from HOMO to LUMO in $CAQH_2$ is relatively easier than that in CAH_2. With the decrease of the LUMO energies, LUMO in

$CAQH_2$ accepts electrons easily. The same methods were employed to study $CAQH_2$, also leading to the above stated conclusions and confirming the obtained results. Furthermore, dipole moment was calculated in the solvent and is shown in Table 5.

Two important properties of any molecule (M) are its gas-phase ionization potential (I) and its electron affinity (A).

$$M(g) \rightleftarrows M^+(g) + e^- \quad I \qquad (5)$$

$$M(g) + e^- \rightleftarrows M^-(g) \quad A \qquad (6)$$

The determination of I and A allows the absolute electronegativity (χ) and absolute hardness (η) parameters for M to be calculated.

These quantities are defined as:

$$\chi = \frac{I + A}{2} \qquad (7)$$

$$\eta = \frac{I - A}{2} \qquad (8)$$

In the most common case, I and A are related to the one-electron orbital energies of the HOMO and LUMO, respectively.

$$-I = E_{HOMO} \quad \text{and} \quad -A = E_{LUMO}$$

Then (I–A) is simply the difference in energy between the HOMO and the LUMO. Soft molecules have a small energy gap. Low ‘I’ creates a better electron donor and large ‘A’ makes a better electron acceptor.

4. CONCLUSIONS

For $AQSH_2$ the formal electrode potentials were predicted with the help of DFT and HF with the 6-31G basis set. It was revealed that the data from the experiments coincided with the predicted formal electrode potentials for the $AQSH_2$ half reactions. This theoretical method is very effective for the prediction of an unknown formal electrode potential of any compound involved in biochemistry.

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