

Calculation of Standard Electrode Potential and Study of Solvent Effect on Electronic Parameters of Anthraquinone-1-carboxylic Acid

S. Riahi^{1,2,*}, S. Eynollahi² and M.R. Ganjali^{2,3}

¹ Institute of Petroleum Engineering, Faculty of Engineering, University of Tehran, P. O. Box 14399-57131, Tehran, Iran

² Center of Excellence in Electrochemistry, Faculty of Chemistry, University of Tehran, Tehran, Iran

³ Endocrinology & Metabolism Research Center, Medical Sciences/University of Tehran, Tehran, Iran

*E-mail: riahisv@khayam.ut.ac.ir

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This research presents calculations and computation of Anthraquinone-1-carboxylic acid (CAQ) electrode potentials in water. For this purpose, the DFT calculations with the 6-31G basis set were utilized. The calculated values were compared with the experimental values obtained by linear sweep voltammetry. The observed and the calculated changes in the reduction potential of the CAQ differed from those of the reference compound (catechol), being less than 20 mV. In this way, a method was provided, by which the reduction potentials of the related molecules could be predicted very accurately. Actually, 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) of the studied compounds were calculated in water.

Keywords: Redox reaction, Anthraquinone-1-carboxylic acid, DFT, Solvent effect, Chemometrics, Computational chemistry

1. INTRODUCTION

Quinones are a series of widespread compounds found in the living organisms performing a variety of biochemical and physiological functions and constitute a broad range of organic compounds with various interesting properties such as antitumor, antibacterial, antifungal and antibiotoxic activities [1-2]. Anthraquinones are derivative of quinones, as the largest group of natural quinones and historically the most important ones [3], have been widely used in chemistry, biochemistry,

pharmacology and industry, especially as useful nucleotidespecific ligands for the purification of proteins by affinity techniques [4]. 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]. In recent years, our research group has been involved in the different branch of chemical and electrochemical sciences [14-30].

In this paper are calculated the half-wave potential, $E_{1/2}$, 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) on Anthraquinone-1-carboxylic acid (CAQ). In addition, the bond lengths, bond angles and dipole moment of AH_2 in water were calculated with the employment of ab initio molecular orbital calculations with 6-31G basis set. Additionally, comparison of the resulting data with the experimental values is presented. Since the solvation energy of the organic molecules plays a critical role in their reactivity, the solvation energy calculations of the studied molecules in water are also of interest. Furthermore, solvent effects on geometry and also dipole moment were studied.

2. EXPERIMENTAL PART

2.1. Calculations

Scheme 1 depicts the two-electron oxidation reaction of the (CAQ). The oxidized form (CAQ) can also be converted to its reduced form ($CAQH_2$) using catechol CAH_2 as a reference molecule, according to the following isodesmic reaction [31]:

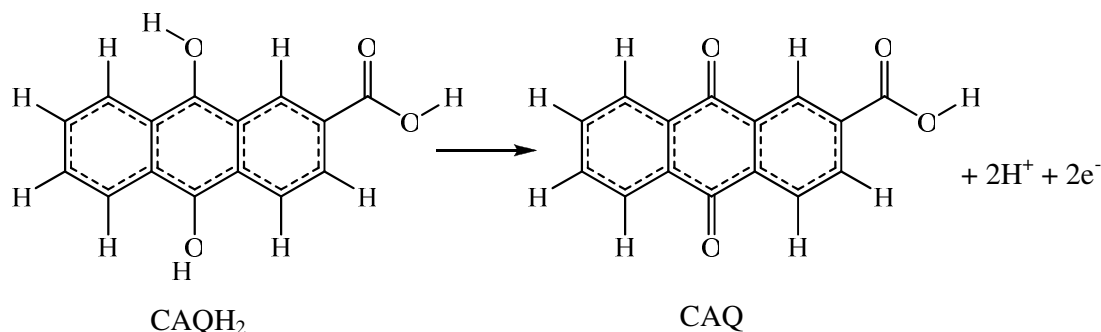


The difference between the electrode potential of the two species can be obtained from the change in the Gibbs free energy of reaction (1), in accordance with the equation (2):

$$E^{\circ'} = E_{CA}^{\circ} - \frac{\Delta G^{\circ}}{2F} \quad (2)$$

Where ΔG° is the free energy change for reaction (1), E_{CA}° is the experimental formal electrode potential for a reference molecule, $E^{\circ'}$ 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].



Scheme (1): Electron oxidation reaction which is for CAQ

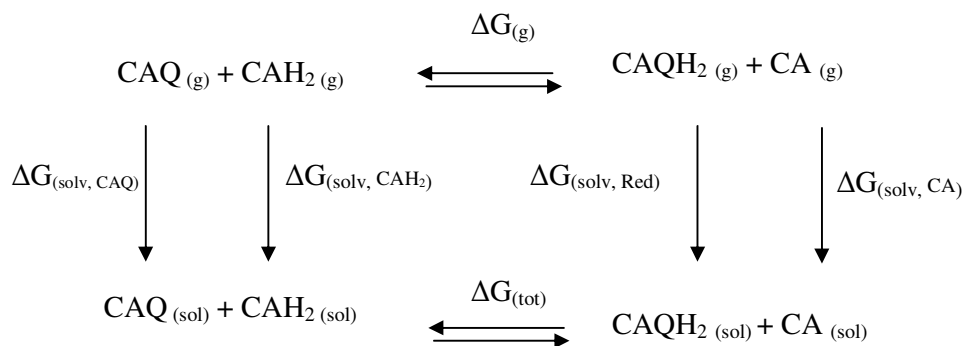


Figure 1. The thermodynamic cycle, proposed to convert the standard Gibbs energy of the isodesmic redox reaction in the gas phase to the standard Gibbs energy of the reaction in solution

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

$$\Delta G^\circ = \sum \nu_i \Delta G_i^\circ \quad (3)$$

where ΔG_i° 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:

$$\Delta G_i^\circ = \Delta G_{i,\text{gas}}^\circ + \Delta G_{i,\text{solv}}^\circ \quad (4)$$

where $\Delta G_{i,\text{gas}}^\circ$ is the gas-phase energy of each component and $\Delta G_{i,\text{solv}}^\circ$ is the solvation energy of the component. In the present work, the gas-phase contribution to the Gibbs energy, $\Delta G_{i,\text{gas}}^\circ$, was determined from ab initio calculation. This calculation has been performed at the Møller–Plesset

perturbation theory 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, $\Delta G_{i,solv}^{\circ}$, have been calculated using Polarizable Continuum Model (PCM) [36].

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 AND GAMESS has been employed [38].

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 in water (Figures 2a and 2b). Table 1 shows the significant changes of bond length and bond angle for CAQ and CAQH₂ from gas to solvent.

Table 1. The structural characteristics of CAQ and CAQH₂ in gas and solvent*

	CAQ			CAQH ₂	
	Gas	Solvent		Gas	Solvent
Bond lengths (Å)			Bond lengths (Å)		
C–C	1.4754	1.4758	C–C	1.474	1.517
C≡C	1.4025	1.4021	C≡C	1.413	1.429
C–H	1.0841	1.0843	C–H	1.085	1.084
C=O	1.238	1.244	C–O	1.391	1.391
O–H	0.981	1.006	C=O	1.240	1.222
17C–18O	1.378	1.363	O–H	0.978	0.995
17C=19O	1.238	1.244			
Bond angles(°)			Bond angles(°)		
C–C–C	117.83	118.216	C≡C≡C	119.838	119.795
C≡C≡C	120.107	120.208	C≡C–H	120.231	120.719
C≡C–H	119.884	118.998	C–C=O	126.102	125.172
C–C=O	120.893	120.652	C–C–O	113.054	112.972
C–C–O	113.080	113.360	C–O–H	109.229	104.775
C–O–H	110.027	111.581	O–C=O	120.844	121.857
O–C=O	121.813	122.434			

* The mean of bond lengths and bond angles are presented

Water is a protic solvent which makes strong hydrogen bonding with -OH groups in the structure of the studied molecules. Formation of hydrogen bonding cause displacement in the

electronic density from C-O and O-H bonds toward water molecule and makes these bonds weak and therefore increases the bond lengths. For example in CAQ, R(18,27) from 0.981 to 1.006, R(17,19) from 1.238 to 1.244 and in CAQH₂, R(16,18) from 1.240 to 1.222 and R(27,29) from 0.973 to 0.988 are changed. The other bond length their changed are not significant, and so, the entire bond angels changed are not significant except the bonds that formed hydrogen bonding.

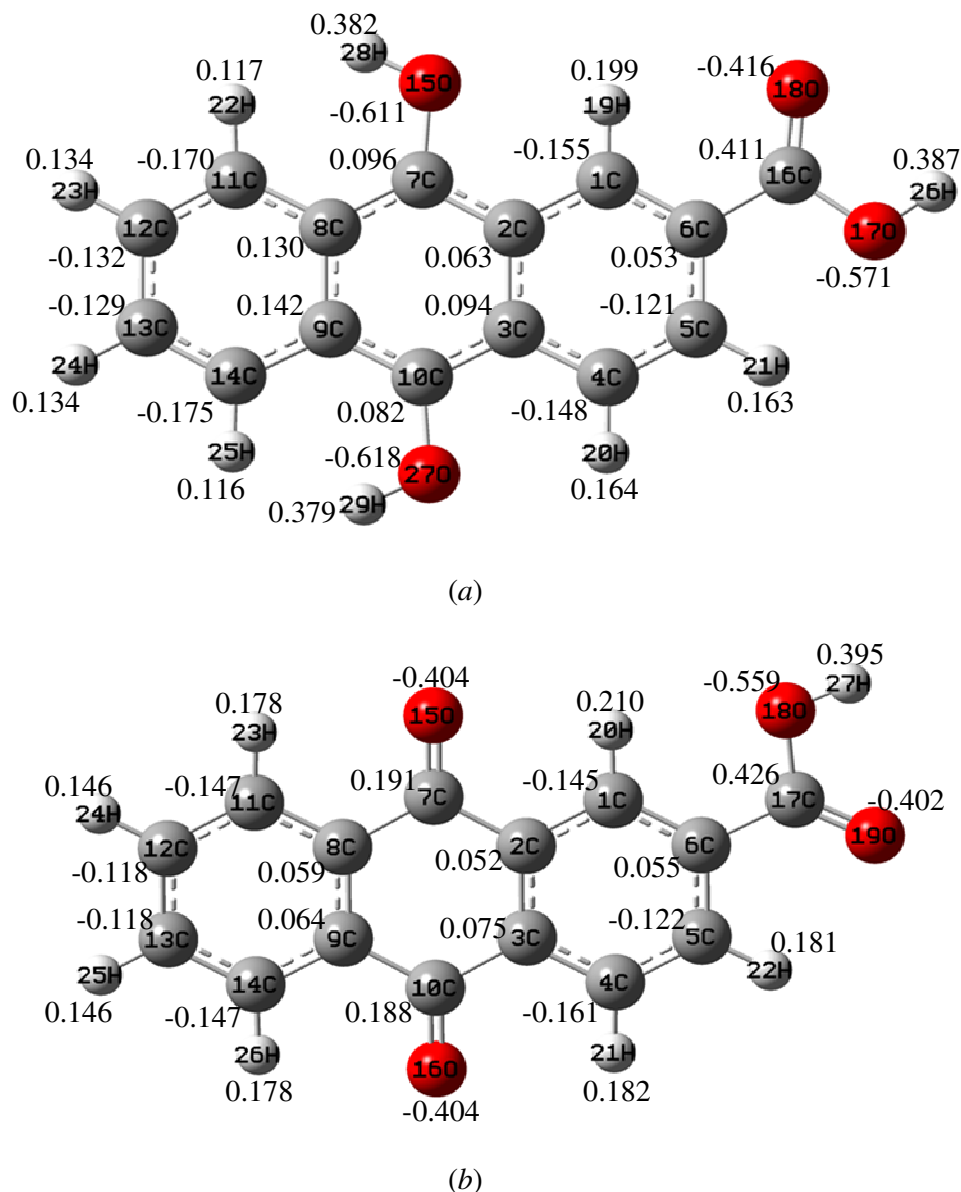


Figure 2. Optimized structures and atomic charges of (a) CAQH₂ and (b) CAQ in water.

The longest bond lengths in both gas and solvent are all of the C-C bonds and after that, the longest that are C=C bond in the molecule. The most negative charge is (18O) because this electronegative atom connected to (27H and 17C). The most positive charge is (17C) because of connected to two electronegative atoms (18O and 19O).

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. 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° , in both gas and solution phases^a

Mol.	$\Delta G_{i,gas}^\circ$ ^b		$\Delta G_{i,solv}^\circ$ ^b		ΔG_i°	
	Red.	Ox.	Red.	Ox.	Gas	Solution
DFT/ CAQ	-878.11509	-876.95047	-878.19358	-876.96237	0.06395	-0.00254
6-31G CA	-380.95453	-379.77474	-380.98108	-379.78978	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)

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 3 presents the electrode potentials of the molecules, studied in water at the DFT/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 3. Electrode potentials of the studied molecules, compared with the experimental values^a. The differences (in mV) between the experimental and the calculated

Mol. ^b	Exp.(E ^{o'} (mV)) ^c	E ^{o'} (mV) ^d (DFT/6-31G)
CAQ	-479	-460
CAH ₂	375	375

^a Calculated by Equation 2 ($E^{o'} = E_{CA}^{o'} - \frac{\Delta G^\circ}{2F}$)

^b Studied Molecules

^c Experimental values.

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

Table 4 summarizes the highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO) and HOMO and LUMO energy gaps for CAQH₂ calculated at DFT level in the 6-31G basis set. 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 4, it is obvious that the LUMO energies of CAQH₂ are lower than those of CAH₂ and the energy gap of CAQH₂ is smaller than that of CAH₂. Consequently, the electrons transfer from HOMO to LUMO in CAQH₂ is relatively easier than that in CAH₂. With the decrease of the LUMO energies, LUMO in CAQH₂ accepts electrons easily. The same methods were employed to study CAQH₂, 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 4.

Table 4. 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

	CAQ	CAQH ₂	CA	CAH ₂
E _{HOMO} (eV)	-7.32 (-7.38) [*]	-5.08 (-5.10)	-6.36	-7.62
E _{LUMO} (eV)	-3.32 (-3.30)	-2.02 (-1.85)	7.19	3.96
E _{LUMO} - E _{HOMO} (eV)	4.00 (4.08)	3.06 (9.47)	13.55	11.58
μ	2.34 (3.10)	4.92 (6.67)	1.49	4.00
I	7.32 (7.38)	5.08 (5.10)	6.36	7.62
A	3.32 (3.30)	2.02 (1.85)	-7.19	-3.96
χ	5.32 (5.34)	3.55 (1.48)	-0.40	1.83
η	2.00 (2.04)	1.53 (1.63)	6.775	5.79

^{*} The calculated parameters in water are presented in parenthesis

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



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:

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

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

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

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

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.

The electron affinity is calculated directly as $EA = E(N+1) - E(N)$ where $E(N)$ and $E(N+1)$ are the total ground-state energies in the neutral (N) and singly charged (N+1) configurations. In a similar way, the ionization potential is defined as $IP = E(N-1) - E(N)$ [30,31].

For almost all of the commonly used exchange-correlation functional, the HOMO and LUMO energy are not close to the exact IP and EA respectively but, excellent linear correlation relationship exists between HOMO energies and calculated IP and also between the negative of the LUMO energies and calculated EA. Therefore based on these linear correlation relationships, the calculated HOMO and LUMO energies can be used to semi quantitatively estimate the ionization potential and electron affinity [39].

4. CONCLUSIONS

For CAQH₂ the formal electrode potentials were predicted with the help of DFT with the 6-31G basis set. It was revealed that the data from the experiments coincided with the predicted formal electrode potentials for the CAQH₂ half reactions. The average discrepancy between the theoretical and the experimental values was less than 20 mV. This theoretical method is very effective for the prediction of an unknown formal electrode potential of any compound involved in biochemistry. Since water make strong hydrogen bonding, it affects bonds contain oxygen atom.

In this paper we have showed some of 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) have changed in water.

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