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Computational electrode potential of a coumestan derivative: Theoretical and experimental studies

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Abstract

Electrode potential of a coumestan derivative, an important biological molecule, in aqueous solution is computed theoretically using Self-Consistent Field (SCF) theory at the level of Hartree–Fock and employing 6-31G(d) basis set and also obtained experimentally by employing electrochemical technique of cyclic voltammetry (CV). Frequency calculations have been carried out and thermal corrections and entropies have been taken into account. Polarizable continuum model is used to describe the solvent. The theoretical and experimental values for the standard electrode potential of the studied coumestan are in excellent agreement with each other and there is only 0.001 V discrepancy between experiment and theory. The agreement mutually verifies the accuracy of experimental method and the validity of mathematical model.

Keywords: Coumestan derivative; Standard electrode potential; Cyclic voltammetry; Electrochemical oxidation; Ab initio calculations

1. Introduction

Theoretical calculation of electrode potential of organic compounds has been in great interest to many chemists [1–10]. We, among others, have recently shown that the electrode potentials of some quinone derivatives in aqueous and non-aqueous solutions can be calculated with a low uncertainty [11–13]. The computational electrode potentials were obtained with different quantum mechanical methods, such as density functional theory [11,13] and Hartree–Fock ab initio calculations [12]. The average error for the calculation of electrode potentials depends on the level of employed theories and the kind of solvent in which quinones are dissolved. This error can be as small as 0.03 V for studied quinones in aqueous solution [13].

Flavonoids with the general structure of a 15-carbon skeleton, which consists of two phenyl rings and a heterocyclic ring, are a large group of phytochemicals found in fruits and vegetables [14,15]. Flavonoids are well known for their antioxidant abilities and hold promise for preventing age-related diseases including heart disease and cancer [16]. One of the main active ingredients in plant products, such as soy beans, which are taken in by humans through foods in everyday life, is coumestans [16,17]. Coumestans have similar structure to isoflavonoids and compete with estradiol for cytoplasmic receptors in mammary tumor cells. Substantial amounts of coumestans are found in traditional soy-based foods, as well as soy protein isolate, soy concentrate, or soy flour added to foods. Coumestan comes also from bean sprouts and fodder crops such as alfalfa and clover [18]. Dietary intake of these compounds is significantly higher in countries where the incidence of breast and prostate cancers is low, suggesting that they may act as chemopreventive agents [19]. The metabolism of coumestans has not been exactly characterized [18]. The electrochemical characteristic of coumestan might play an important role. Because of the importance of electron-transfer reactions in the biological systems and the role of electrode potential in this regard, we have studied the redox potential of a derivative of coumestan (3, 4-dihyroxy-

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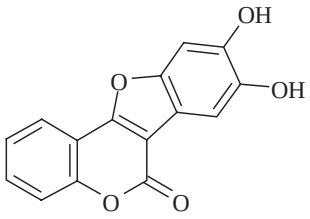


Fig. 1. Structure of the studied derivative of coumestan.

6H-benofuro [3, 2, c] [1] benzopyran-6-one), whose structure has been shown in Fig. 1. In this work, we present the theoretical calculations of electrode potential of the studied coumestan (Cou) which is compared with the experimental value. According to the literature and to the best of our knowledge, this is the first study on the studied coumestan of this kind and can extend to other biological molecules.

2. Theoretical consideration

The studied coumestan (Cou) can be oxidised by a two-electron oxidation reaction as shown in Scheme 1. The oxidised form of Cou (Cou_{ox}) can also be converted to its reduced form (Cou_{red}) using pyrocatechol (Q_{red}) as a reference molecule according to the following isodesmic reaction [11]:

$$Q_{red} + Cou_{ox} \rightarrow Q_{ox} + Cou_{red} \quad (1)$$

where Q_{ox} is *o*-benzoquinone, the oxidised form of pyrocatechol. The difference between the electrode potential of two species can be obtained from the change in Gibbs free energy of reaction (1):

$$\Delta G^0 = -nF\left(E^0_{Cou} - E^0_Q\right) \quad (2)$$

where n is number of electrons transferred ($n=2$ in this case) and F is the Faraday constant [12]. In order to obtain standard electrode potential of coumestan, the change of Gibbs free energy of reaction (1), ΔG^0, is required along with the experimental value of electrode potential of the reference molecule, pyrocatechol [13].

In order to calculate the standard Gibbs energy of reaction (1), ΔG^0, one should calculate the standard Gibbs energy of each component, ΔG^0_i, in reaction (1):

$$\Delta G^0 = \sum v_i G^0_i \quad (3)$$

where G^0_i is the standard Gibbs energy of each component and v_i is the stoichiometric coefficient. The standard Gibbs energy of each component is obtained using the following expression [13]:

$$G^0_i = G^0_{i,gas} + G^0_{i,solv} \quad (4)$$

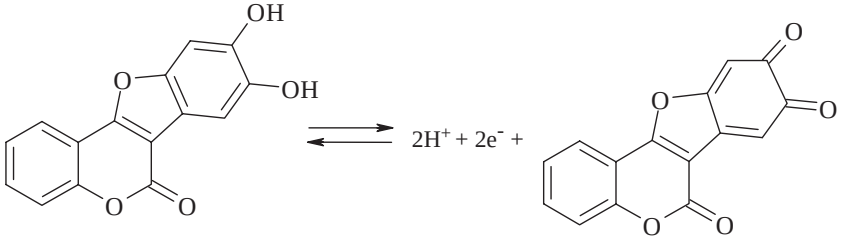
where $G^0_{i,gas}$ is the gas-phase energy of each component and $G^0_{i,solv}$ is the solvation energy of the component. In the present work, the gas-phase contribution to the Gibbs energy, $G^0_{i,gas}$, was determined from ab initio calculations. These calculations have been performed at the Hartree–Fock (HF) level using 6-31G(d,p) basis set [20,21]. 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, $\Delta G^0_{i,solv}$, have been calculated using Polarisable Continuum Model (PCM) [22]. Gaussian98 [23] have been employed for all ab initio calculations.

3. Experimental

3.1. Chemicals and apparatus

The studied derivative of coumestan was synthesized with electrooxidation of catechol in the presence of 4-hydroxycoumarine as nucleophile according to procedure described by Golabi and Nematollahi [24,25]. Doubly distilled water was used throughout the experiments. The buffer solution (0.1 M) was made up from H_3PO_4+ NaH_2PO_4, and then adjusting the pH with 0.1 M H_3PO_4 and 2.0 M NaOH.

All electrochemical experiments were carried out using a Autolab potentiostat PGSTAT 30 (Eco Chemie Utrecht, Netherlands) equipped with GPES 4.9 software. The used cell was equipped with a coumestan modified carbon paste disk as the working electrode, a graphite electrode as an auxiliary electrode and with saturated calomel electrode



(Cou_{red}) (Cou_{ox})

Scheme 1. Mechanism of oxidation of the studied coumestan. The Cou_{red} and Cou_{ox} are reduced and oxidised form of the studied coumestan, respectively.

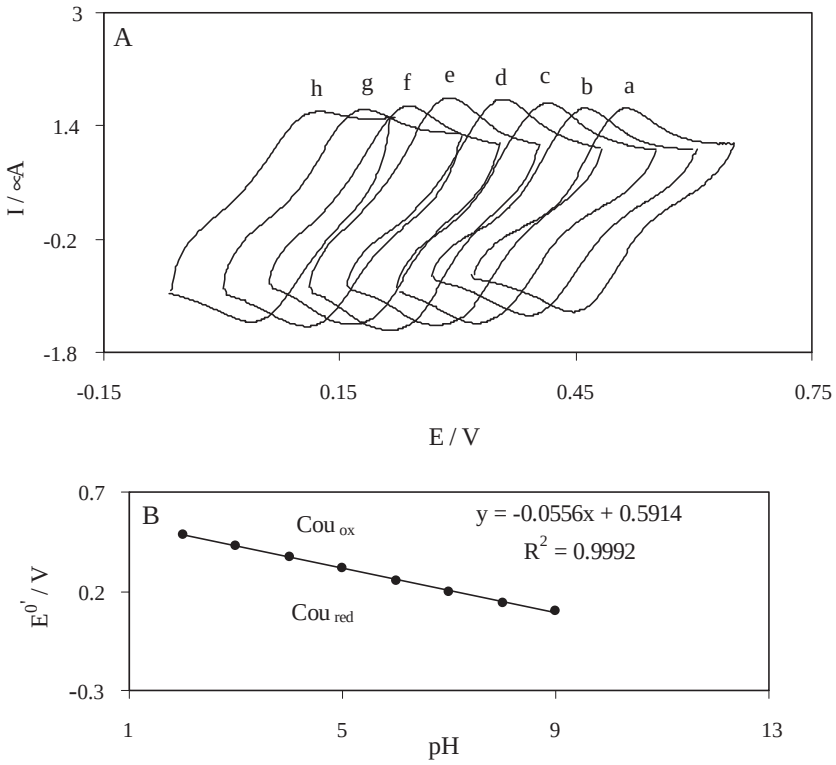


Fig. 2. (A) Cyclic voltammograms (at 20 mV s^{-1}) for the coumestan derivative modified carbon paste electrode in buffered pHs of (a) 2, (b) 3, (c) 4, (d) 5, (e) 6, (f) 7, (g) 8 and (h) 9. (B) Plot of $E^{0\prime}$ versus pH.

(SCE) as a reference electrode. The pH was measured with a Metrohm model 691 pH/mV meter.

3.2. pH dependence studies of the coumestan modified carbon paste electrode

The effect of pH on the response of carbon paste electrode, modified by the studied coumestan, was investigated by cyclic voltammetry using 0.1 M phosphate buffer solutions with various pH values, ranging from 2.0 to 9.0 (Fig. 2A). In all cases, the ionic strength was adjusted to 0.1 M phosphate buffer. As can be seen in Fig. 2B, the formal potential, $E^{0\prime}$, of the Cou_{ox}/Cou_{red} redox couple was pH dependent with a slope of −55.6 mV per unit of pH which is close to the anticipated Nernstian value of −59 mV for a two-electron, two-proton process [26]. The formal potential of the redox couple was obtained as the average of anodic and cathodic peak potentials [26]. Fig. 2B shows a linear relationship between formal potential of the redox couple and pH with the intercept of 0.5914 V. Based on the relation between formal potential of the redox couple, $E^{0\prime}$, and pH, Eq. (5) [26], the standard formal potential of Cou was obtained from the intercept of Fig. 2B and was equal to 591.4 mV.

$$E^{0\prime} = E^{0} - 2.303(m\mathrm{RT}/nF)\mathrm{pH} \quad (5)$$

where m and n are the number of H^+ and electrons in the redox reaction, respectively, and all other symbols have their conventional meanings. In the studied range of pH, both m and n are two [27,28].

Table 1
Gas-phase energies of the studied coumestan, Cou_{red}, and pyrocatechol, Q_{red}, and their oxidised forms, Cou_{ox} and Q_{ox},: internal energy, U (gas), zero-point energy, ZPE, total corrections to Gibbs free energy including thermal correction, entropy and pressure–volume contributions, TC, together with the gas-phase Gibbs free energies, G (gas)

	U (gas)[a]	ZPE[a,b]	TC[a,c]	G (gas)[a]	G (solv)[d]	G (gas)[a]
Cou_{ox}	−945.817404	0.190454	0.149635	−945.667769	−0.021259	−945.689028
Cou_{red}	−947.011498	0.215295	0.174683	−946.836815	−0.022773	−946.859588
Q_{ox}	−379.221355	0.092383	0.061905	−379.159450	−0.015075	−379.174525
Q_{red}	−380.412960	0.116881	0.086483	−380.326476	−0.015585	−380.342061

The Gibbs free energy of solvations are also presented.
[a] All energies are in atomic units, Hartree (1Hartree=2623.61722 kJ mol [20]).
[b] Zero-point energy.
[c] Total correction to Gibbs free energy including thermal correction, entropy and pressure–volume contributions.
[d] Gibbs free energies of solvation are in atomic units, Hartree.

4. Theoretical computation of electrode potential

As described earlier, Gibbs energy of each molecule in the gas phase is necessary for the calculation of electrode potentials. Table 1 shows the calculated Gibbs energy of molecules for both reduced and oxidised forms in the gas phase using frequency calculations at the Hartree–Fock level of theory. The basis set of 6-31G(d) was chosen considering the size of studied molecules. Solvation energies are also computed in order to convert gas-phase energies to energies in solution phase. These solute–solvent interactions, which are calculated using PCM model of solvation [22], are added to the gas-phase energies to give the change of Gibbs energy of each component in solution phase. The total Gibbs free energy of each component in the presence of solvent is also included in Table 1. The internal energy for the oxidised form of Cou (Cou_{ox}) is −945.817404 Hartree/Particle. The thermal correction to Gibbs free energy, including the zero-point energy, is 0.149635 Hartree/Particle. Therefore, the standard Gibbs free energy at 298.15 is −945.667769 Hartree/Particle for the oxidised form, Cou_{ox}. For the reduced form, Cou_{red}, these energies are −947.011498, 0.174683 and −946.836815 Hartree/Particle, respectively. The solvation energies for both oxidised and reduced forms of the studied coumestan are −13.34 and −14.29 kcal/mol, respectively. Therefore, the standard Gibbs free energy of Cou_{ox} in the presence of solvent is −945.689028 Hartree/Particle and for Cou_{red} in the presence of solvent is −946.859588 Hartree/Particle. Therefore, the standard Gibbs free energy of reaction (1) is 108.021 kJ mol^{-1}. Using this value together with the standard Gibbs free energy of pyrocatechol which are presented in Table 1, the standard electrode potential of Cou is obtained to be 0.592 V. The standard electrode potential of *o*-benzoquinone and Cou we obtained experimentally in the present work are 0.551 V and 0.591 V, respectively. The theoretical value for Cou is in an excellent agreement with the experimental electrode potential with a discrepancy of 0.001 V. This discrepancy is less than the values we previously reported for other quinone derivatives [12,13]. This consistency shows that the level of calculations is adequate for the studied biological molecule and is consistent with the previous studies which carried out for the ordinary quinone derivatives.

5. Conclusions

Electrode potential of the studied derivative of coumestan, in aqueous solution can be theoretically computed using Self-Consistent Field (SCF) theory at the level of Hartree–Fock and employing 6-31G(d) basis set. It is also obtained experimentally by employing electrochemical technique of cyclic voltammetry (CV). Polarizable continuum model of solvation is used to mimic the role of solvent. The theoretical and experimental values for the standard electrode potential of coumestan are in excellent agreement with each other and there is only 0.001 V discrepancy between experiment and theory.

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