

THEORETICAL STUDY (AB INITIO AND DFT METHODS) ON ACIDIC DISSOCIATION CONSTANT OF XYLENOL ORANGE IN AQUEOUS SOLUTION

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ABSTRACT. Analytical measurement of materials requires exact knowledge of their acid dissociation constant (pK_a) values. In recent years, quantum mechanical calculations have been extensively used to study of acidities in the aqueous solutions and the results were compared with the experimental values. In this study, a theoretical study was carried out on xylenol orange (in water solution) by ab initio method. We calculated the pK_a values of xylenol orange in water, using high-level ab initio (PM3), DFT (HF, B3LYP/6-31+G(d)) and SCRf methods. The experimental determination of these values ($pK_{a,s}$) is a challenge because xylenol orange has a low solubility in water. We considered several ionization reactions and equilibriums in water that constitute the indispensable theoretical basis to calculate the pK_a values of xylenol orange. The results show that the calculated pK_a values have a comparable agreement with the experimentally determined pK_a values. Therefore, this method can be used to predict such properties for indicators, drugs and other important molecules.

KEY WORDS: Ab initio, DFT method, Ionization constant, Xylenol orange, Atomic charge

INTRODUCTION

The pM indicator is a visual one which can act as a chelating agent to give a dye-metal complex for end point detection in the complexometric analyses. It is different from its dye, in color, and also has a low stability constant than the chelate-metal complex. Over 200 organic compounds form colored chelates with ions in a pM range that is unique to the cation and the dye selected. To be useful, the dye-metal chelates will usually be visible at 10^{-6} to 10^{-7} M concentration. Many of these indicators also have the typical properties of acid-base indicators and the color changes are the result of the displacement of the H^+ by a metal ion [1]. The xylenol orange (3,3'-bis[N,N-bis(carboxymethyl)aminomethyl]-ocresolsulfonephthalein) is a weak polybasic acid which belongs to triphenylmethane dyes (Figure 1). It is an excellent complexometric indicator and potentiometric reagent for determination of many metal ions which is used in analytical chemistry with bind to metal cations at both their amino and acidic groups [2, 3]. It can be represented by the symbolic formula H_6L . It shows the presence of six ionizable hydrogens in the aqueous solutions. The six possible forms of xylenol orange (XO) are distributed in the pH range from 2 to 12 [2]. Due to the existence of more than one chelating system and the various acidic and basic properties of the XO molecule, which can form various complexes, the investigation on this system can be difficult. XO is used as an indicator, with color change from lemon to yellow, for determination of Bi and Th at pH range 1 to 3, Pb and Zn at pH range 4 to 5 and also Cd and Hg at pH range 5 to 6 [1]. It is also introduced (in form of Al-XO complex) as a colored reagent for determining trace amount of fluoride. This method is based on the

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decolorization of a complex of Al(III) with xylenol orange as an ultra-sensitive colored reagent [4].

It must be pointed out that the acid equilibrium constants (K_a , $pK_a = -\log K_a$) is one of the most important molecular properties and has received considerable attention for understanding many chemical and biochemical processes. It depends on proton transfer and interprets the functional mechanism of ionizable groups in a protein at a molecular level. Accurate pK_a data are also important for understanding reaction mechanisms that do not involve proton transfer. For example, thermodynamic cycles that use pK_a data, are used to determine the hydricities and bond dissociation energies of metal hydrides and other compounds. These critical data can be used for elucidating reaction mechanisms that involve hydrogen atom transfer/proton-coupled electron transfer [5]. For these reasons, there is a strong interest for the development of reliable methods for pK_a prediction.

There are several experimental methods, like capillary electrophoresis [6] potentiometric titration [7], bromatographic [8] and IR, NMR or UV-Visible spectrometric [9-11], for studying on components acidities. In addition to these experimental methods, both ab initio and semi-empirical levels of theory have been extensively employed to the study of acidities and the results have been compared with the experimental values. Therefore, there are some studies dealing with the acid-base properties of compounds in aqueous solutions and gas phases [12, 13]. Computational chemistry can be valuable tool for evaluating the right sequence of deprotonation. This explains the many attempts to develop reliable methods for the calculation of accurate absolute or relative $pK_{a,s}$ [14-17].

In this paper, a theoretical study carried out on the pK_a of xylenol orange, in water, by ab initio and density functional theory (DFT) methods. Hartree-Fock (HF), ab initio and density functional geometry optimizations were performed with the Gaussian 09 program. The results were reoptimized at the B3LYP (the Becke's three-parameter exchange functional and the Lee-Yang-Parr correlation functional) type of DFT by using the basis set 6-31+G(d). The ab initio geometries were employed for calculating the solvation free energies at the self-consistent reaction field (SCRF) level [18]. ΔG^0 was calculated and employed for determination of pK_a by $pK_a = \Delta G^0/2.303RT$ formula.

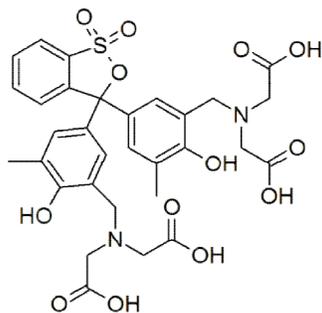


Figure 1. The structure of xylenol orange

EXPERIMENTAL

Ab initio calculations were performed with the Gaussian 09 system in the framework of density functional theory utilizing different combinations of functional and basis sets. By the semiempirical PM3 method includes in the program Hyper Chem version 7.0, the initial geometries of the different conformers of neutral xylenol orange, its anions and cations were

modeled. Hartree-Fock ab initio and density functional geometry optimizations were performed with the Gaussian 09 program. The optimizations were done using HF/6-31+G(d) method. The results were reoptimized at the B3LYP type of Density Functional Theory by using the basis set 6-31+G(d). The ab initio geometries were employed in calculating the solvation free energies at the mentioned basis set (Table 1).

RESULTS AND DISCUSSION

Xylenol orange is a triphenylmethane dye. It is well-known that the xylenol orange, in water, loses three protons and generates H_9L^{3+} . The H_9L^{3+} form has tendency to lose nine acidic hydrogens. For H_9L^{3+} , a proton can be lost from four different groups to give different ionized species. These groups are including the carboxyl group, ammonium group, hydroxyl group and sulfonate (SO_3H) group. The proton losing from the sulfonate group is more probable than the other groups.

The chemical interpretation of the changes is not straightforward. It is predicted that the proton of sulfonyl has the most acidic property. The calculations of microscopic constants indicate that the first and second $pK_{a,s}$ correspond to remove the proton of sulfonyl and hydroxyl groups, respectively. The third, fourth, fifth and sixth $pK_{a,s}$ correspond to remove the protons of the four carboxyl groups. The seventh pK_a belongs to remove of the next hydroxyl group and finally the eighth and ninth $pK_{a,s}$ correspond to remove the protons of the two ammonium groups. It can be exactly approved by NMR spectroscopy [3].

The different models of molecules (zwitterions and unizwitterions) were investigated by the G09 program and different reactions including cationic, neutral, and anionic species were tested. But some of these reactions were not further considered because the estimated error in its acidic dissociation constants was unacceptable. Suitable models finally were chosen for the studied systems and the calculated values of the acidic dissociation constants for species are listed in Table 2.

Table 1. Calculated total energy at the B3LYP/6-31+G(d) level of theory for cationic, neutral, and anionic species of xylenol orange at 298.15 K.

Solvated species	G_{sol}^0 (Hartree)	G_{sol}^0 /molecule (kcal·mol ⁻¹)	Solvated species	G_{sol}^0 (Hartree)	G_{sol}^0 /molecule (kcal·mol ⁻¹)
H_9L^{3+}	-269	-1.67×10 ⁹	H_4L^{2-}	-269	-1.69×10 ⁹
H_8L^{2+}	-269	-1.69×10 ⁹	H_3L^{3-}	-268	-1.68×10 ⁹
H_7L^+	-269	-1.69×10 ⁹	H_2L^{4-}	-268	-1.68×10 ⁹
H_6L	-269	-1.69×10 ⁹	HL^{3-}	-268	1.68×10 ⁹
H_5L^-	-269	-1.69×10 ⁹	L^{6-}	-268	1.68×10 ⁹

G_{sol}^0 : total free energy in solution.

Table 2. Values of pK_a for the protonation of xylenol orange obtained at the B3LYP/6-31G(d) level of theory, at 298.15 K.

Selected equations	pK_a (calculated) this work	pK_a (experimental)	Ref
$H_9L^{3+} + OH^-(H_2O) \rightleftharpoons H_8L^{2+} + 2H_2O$	-1.78	-1.74	[3]
$H_8L^{2+} + OH^- \rightleftharpoons H_7L^+ + H_2O$	-1.05	-1.09	[3]
$H_7L^+ + OH^- \rightleftharpoons H_6L + H_2O$	0.872	0.76	[3]
$H_6L + OH^- \rightleftharpoons H_5L^- + H_2O$	1.12	1.15	[3]
$H_5L^- + OH^-(H_2O) \rightleftharpoons H_4L^{2-} + 2H_2O$	2.53	2.58	[3]
$H_4L^{2-} + OH^- \rightleftharpoons H_3L^{3-} + H_2O$	3.30	3.23	[3]
$H_3L^{3-} + OH^-(H_2O) \rightleftharpoons H_2L^{4-} + 2H_2O$	6.33	6.40	[3]
$H_2L^{4-} + OH^-(H_2O) \rightleftharpoons HL^{3-} + 2H_2O$	10.7	10.5	[3]
$HL^{3-} + OH^-(H_2O) \rightleftharpoons L^{6-} + 2H_2O$	12.8	12.6	[3]

The acidic dissociation constants of xylenol orange have been determined using the potentiometric technique. The method of determining acidic dissociation constants was previously described, and its values were used in this work. These values are listed in Table 2 together with the calculated values using B3LYP type of Density Functional Theory by using the basis set 6-31+G(d) [3].

Solvent- solute interactions

Ionic product of water. It is well-known that all aqueous solutions contain hydrogen (H^+) and hydroxyl (OH^-) ions. In pure water, these ions are derived completely from the ionization of the water molecules as shown in the following equation:



The H^+ ion is hydrated by water molecules and appears as H_3O^+ . Therefore, the autoprotolysis of water molecules is better represented by the bellow reaction:



Taking into account that water is only slightly dissociated, and also to simplify the discussion, we shall make the approximations of replacing the activities in acidity constants by the numerical values of the molar concentrations. Consequently:

$$K_w = [H_3O^+][OH^-] \quad (3)$$

At $T = 298.15$ K, $K_w = 1.008 \times 10^{-14}$. It shows that only a few of the water molecules are ionized [19]. Equations 2 and 3 are more used in studies of acid-base equilibria in aqueous media. On the other hand, the solvation of anions is effective in protic solvents where hydrogen bonds may be formed between the proton of the solvent and the lone pairs of electrons of the anion [20, 21]. The total energies of the single and solvated OH^- ions have been calculated in water at the B3LYP/6-31+ G(d) level of theory, using Tomasi's model.

Considering these facts and to provide a more satisfactory representation of the protolysis of water, the reaction has been shown as follows:



The above reaction shows that both H^+ and OH^- ions are hydrated with one water molecule. Moreover, indicating with K_N the equilibrium constant of the reaction of equation 5 and taking into account equations 2 and 3, it is inferred that [11]:

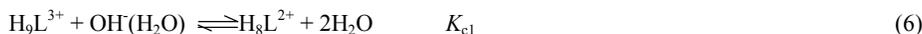
$$K_N = K_w/[H_2O] = 1.831 \times 10^{-16} \quad (5)$$

Where, $[H_2O]$ is the molar concentration of water at 298.15K.

The total energies of xylenol orange species (cationic, neutral, and anionic) were calculated in water at the B3LYP/6-31+G(d) level of the theory. Table 1 summarizes the variations of the total energy ($\text{kJ} \cdot \text{mol}^{-1}$) of the species.

First ionization constant of xylenol orange (XO)

As it has been mentioned, the first proton has lost from the sulphonyl group in XO and it suffers a reaction of partial neutralization as follows:



In this reaction, H_9L^{3+} and H_8L^{2+} are the cation forms of xylenol orange. This reaction is characterized by an equilibrium constant, K_{c1} , which theoretically were determined. By combining equations 6 and 4, we obtained the reaction of equation 7 which defines the first ionization constant of xylenol orange (K_{a1}) and which considers the solvation of the H_9L^{3+} :



It is evident that:

$$K_{a1} = K_{c1} \times K_N \quad (8)$$

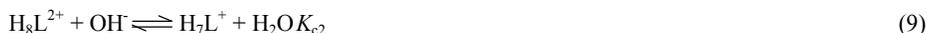
The above equations were used to theoretically determine the value of the first ionization constant of xylenol orange in water.

The formation of H_8L^{2+} implies that the electronic density of the O_{72} atom ($q = -0.673$) decreases, in absolute value, compared with the O_{72} atom of the H_9L^{3+} ($q = -0.780$). It shows the first deprotonation of XO.

On the other hand, the $\text{p}K_{a1}$ value of xylenol orange was theoretically obtained ($\text{p}K_{a1} = -1.78$) (Table 2). It is relatively comparable with the experimental $\text{p}K_{a1}$ value ($\text{p}K_{a1} = -1.74$) [3].

Second ionization constant of xylenol orange

In second stage of ionization of xylenol orange, the H_8L^{2+} losses proton from the hydroxyl agent and changes to H_7L^+ by a total neutralization as follows:



In the above equation, H_8L^{2+} and H_7L^+ represent the xylenol orange cations with two and one positive charges, respectively. The reaction of eq. 9 is characterized by another equilibrium constant, K_{c2} , which was also theoretically determined. By combining equations 2 and 9, the second ionization constant of xylenol orange were obtained as the bellow:



The equilibrium constant K_{a2} that characterizes the above reaction, are:

$$K_{a2} = K_{c2} \times K_W \quad (11)$$

Equation 11 was used to obtain the value of the second ionization constant of xylenol orange in water.

The formation of the H_7L^+ implies that the electronic density of the O_{32} atom ($q = -0.583$) decreases, in absolute value, compared with the O_{32} atom of the H_8L^{2+} ($q = -0.614$). It is evidence for the second deprotonation of XO.

Also, as seen in Table 2, the theoretically calculated $\text{p}K_{a2}$ value of xylenol orange ($\text{p}K_{a2} = -1.05$) is relatively comparable with the experimentally determined $\text{p}K_{a2}$ ($\text{p}K_{a2} = -1.09$) [3].

Third ionization constant of xylenol orange

Equation 12 shows the total neutralization for H_7L^+ :



In the above reaction, H_7L^+ represents the xylenol orange with one positive charge and H_6L represents the natural xylenol orange molecule. The reaction of equation 12 is characterized by another equilibrium constant, K_{C3} , which was also theoretically determined. By combining equations 2 and 12, the third ionization constant of xylenol orange were obtained as the bellow:



The equilibrium constant, K_{a3} , that characterizes the above reaction, are:

$$K_{\text{a3}} = K_{\text{C3}} \times K_{\text{w}} \quad (14)$$

Equation 14 was used to obtain the value of the third ionization constant of xylenol orange in water.

At this step, the proton is lost from O_{60} of carboxyl group. The formation of the H_6L implies that the electronic density of the O_{60} atom ($q = -0.557$) increases notably (in absolute value) compared with the O_{60} atom of the H_7L^+ ($q = -0.0177$). It shows the third deprotonation of XO.

Also the $\text{p}K_{\text{a3}}$ value of xylenol orange was theoretically calculated ($\text{p}K_{\text{a3}} = 0.872$) (Table 2). It is relatively comparable with the experimentally determined $\text{p}K_{\text{a3}}$ ($\text{p}K_{\text{a3}} = 0.76$) [3].

Fourth ionization constant of xylenol orange

There is selected that the H_6L suffers total neutralization as the bellow:



In the above reaction, H_6L represents the natural xylenol orange molecule and H_5L^- represents xylenol orange anion with one negative charge. The reaction of equation 15 is characterized by another equilibrium constant, K_{C4} , which was also theoretically determined. By combining equations 2 and 15, the forth ionization constant of xylenol orange, in water, was obtained:



The equilibrium constant, K_{a4} , that characterizes the above reaction, are:

$$K_{\text{a4}} = K_{\text{C4}} \times K_{\text{w}} \quad (17)$$

Equation 17 were used to obtain the value of the forth ionization constant of xylenol orange in water.

O_{40} atom of other carboxyl group losses another proton. The formation of the H_5L^- implies that the electronic density of the O_{40} atom ($q = -0.719$) increases notably (in absolute value) compared with the O_{40} atom of the H_6L ($q = -0.616$). It is evidence for the fourth deprotonation of XO.

Also the $\text{p}K_{\text{a4}}$ value of xylenol orange was theoretically calculated ($\text{p}K_{\text{a4}} = 1.12$) (Table 2). It can be seen that the theoretical $\text{p}K_{\text{a4}}$ value is relatively comparable with the experimentally determined $\text{p}K_{\text{a4}}$ ($\text{p}K_{\text{a4}} = 1.15$) [3].

Fifth ionization constant of xylenol orange

The fifth pK_a value of XO in aqueous solution can be calculated using the following proton-transfer reaction:



In this reaction, H_5L^- and H_4L^{2-} are the xylenol orange anions with one and two negative charges, respectively. This reaction is characterized by an equilibrium constant, K_{c5} , which were theoretically determined. By combining equations 18 and 5, we obtained the reaction of equation 19 which defines the fifth ionization constant of xylenol orange, K_{a5} :



It is evident that:

$$K_{a5} = K_{c5} \times K_N \quad (20)$$

The above equations were used to theoretically determine the value of the fifth ionization constant of xylenol orange in water.

At this step, proton is lost from O_{43} atom of another carboxyl group, obviously. The formation of the H_4L^{2-} implies that the electronic density of the O_{43} atom ($q = -0.665$) increases notably (in absolute value) compared with the O_{43} atom of the H_5L^- ($q = -0.0450$). It shows the fifth deprotonation of XO.

The pK_{a5} value of xylenol orange was theoretically obtained ($pK_{a5} = 2.53$). Table 2 shows that the theoretically obtained pK_{a5} value of xylenol orange is relatively comparable with the experimental pK_{a5} value ($pK_{a5} = 2.58$) [3].

Sixth ionization constant of xylenol orange

There is selected that the H_4L^{2-} suffers total neutralization as the bellow:



In the above reaction, H_4L^{2-} and H_3L^{3-} represent the xylenol orange anions with two and three negative charges, respectively. The reaction which was described in equation 21 is characterized by another equilibrium constant, K_{c6} , which was also theoretically determined. Combining equations 2 and 21 results the sixth ionization constant of xylenol orange, in water:



The equilibrium constant, K_{a6} , that characterizes the above reaction, are:

$$K_{a6} = K_{c6} \times K_w \quad (23)$$

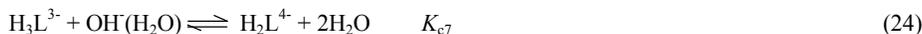
Equation 23 was used to obtain the value of the sixth ionization constant of xylenol orange in water.

At this step proton is lost from O_{58} atom of the latest carboxyl group. The formation of the H_3L^{3-} implies that the electronic density of the O_{58} atom ($q = -0.706$) increases notably (in absolute value) compared with the O_{58} atom of the H_4L^{2-} ($q = -0.615$). It is evidence for sixth deprotonation of XO.

The pK_{a6} value of xylenol orange was theoretically calculated ($pK_{a6} = 3.29$). It is relatively comparable with the experimentally determined pK_{a6} ($pK_{a6} = 3.23$) (Table 2) [3].

Seventh ionization constant of xylenol orange

Equation 24 shows the seventh ionization step of xylenol orange:



In this reaction, H_3L^{3-} and H_2L^{4-} are the xylenol orange anions with three and four negative charges, respectively. This reaction is characterized by equilibrium constant, K_{c7} , which was theoretically determined.

By combining equations 24 and 5, we reach to reaction of equation 25 which defines the seventh ionization constant of xylenol orange, K_{a7} , and which shows the solvation of the H_3L^{3-} :



It is evident that:

$$K_{a7} = K_{c7} \times K_N \quad (26)$$

The above equation was used to theoretically determine the value of the seventh ionization constant of xylenol orange in water.

At this step, proton is lost from O_{28} atom of the latest carbonyl group. The formation of the H_2L^{4-} implies that the electronic density of the O_{28} atom ($q = -0.705$) increases notably compared with the O_{28} atom of the H_3L^{3-} ($q = -0.774$). It shows the seventh deprotonation of XO.

The pK_{a7} value of xylenol orange theoretically was obtained ($pK_{a7} = 6.33$). It is relatively comparable with the experimental pK_{a7} value ($pK_{a7} = 6.40$) (Table 2) [3].

Eighth ionization constant of xylenol orange

Equation 27 shows the eighth stage of ionization of xylenol orange:



In this reaction, H_2L^{4-} and HL^{5-} are the xylenol orange anions with four and five negative charges, respectively. This reaction is characterized by equilibrium constants, K_{c8} , which was theoretically determined. By combining equations 27 and 5, we obtained the reaction of equation 28 which defines the seventh ionization constant of xylenol orange, K_{a8} . It shows the solvation of the H_2L^{4-} :



It is evident that:

$$K_{a8} = K_{c8} \times K_N \quad (29)$$

Equation 29 was used to theoretically determine the value of the eighth ionization constant of xylenol orange in water.

At this step, proton is lost from N₃₅ atom. The formation of the HL⁵⁻ implies that the electronic density of the N₃₅ atom (q = 0.146) increases, in absolute value, compared with the N₃₅ atom of the H₂L⁴⁻ (q = -0.391). It is evidence for eighth deprotonation of XO. The pK_{a8} value of xylenol orange was theoretically obtained (pK_{a8} = 10.7). Table 2 shows that the pK_{a8} value of xylenol orange is relatively comparable with the experimental pK_{a8} value (pK_{a8} = 10.5) [3].

Ninth ionization constant of xylenol orange

Finally the latest proton is transferred according to the equation 30:



In this reaction, HL⁵⁻ and L⁶⁻ are the xylenol orange anions with five and six negative charges, respectively. This reaction is characterized by equilibrium constants, K_{c9}, which was theoretically determined.

By combining equations 30 and 5, we obtained the reaction of equation 31 which defines the ninth ionization constant of xylenol orange, K_{a9}. It shows the solvation of the HL⁵⁻:



It is evident that:

$$K_{a9} = K_{c9} \times K_N \quad (32)$$

Equation 32 was used to theoretically determine the value of the ninth ionization constant of xylenol orange in water. At this step, proton is lost from N₅₃ atom. The formation of the L⁶⁻ implies that the electronic density of the N₅₃ (q = 0.152) atom increases notably (in absolute value) compared with the N₅₃ atom of the HL⁵⁻ (q = -0.318). It shows the ninth deprotonation of XO.

The pK_{a9} value of xylenol orange was theoretically obtained (pK_{a9} = 12.8). It is relatively comparable with the experimental pK_{a9} value (pK_{a9} = 12.6) (Table 2) [3].

CONCLUSION

In this study, the pK_a values of xylenol (XO), in water, have theoretically determined at 298.15 K using the ab initio and DFT methods. For XO, we compared the theoretical values of pK_a with the experimental ones and found that there is a good agreement between them. This agreement along with the electronic density (q) and structural properties are useful in nano calculation and nanotechnology for building nano sensors.

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