

Experimental and Theoretical Studies of Oxalic Acid Dissociation in Water-Ethanol Solvents

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Abstract: *The first and second dissociation constants of oxalic acid were determined using potentiometric and spectrophotometric methods. Measurements were made in water-ethanol solvents of chemical composition in percentage weight of 0, 16.3, and 80. The temperatures ranged from 298K to 318K. The dissociation free enthalpy changes, enthalpy changes and entropy changes were determined and discussed. Furthermore, DFT was used at B3PW91/LanL2DZ level to compute molecular descriptors as E_{HOMO} , E_{LUMO} , energy gap ΔE and the charge δ on the oxygen of the hydroxyl group. Those parameters were then used to establish a QSPR model that furnishes pK_{a1} and pK_{a2} values. Experimental and theoretical results were in good agreement.*

Keywords: Oxalic acid, water-ethanol solvent, thermodynamic dissociation constant, molecular descriptor, QSPR model

1. Introduction

The acidity concept has been used in various areas of research and gives us some useful information about the molecular structure of organic molecules. Acid dissociation constants [1] also known as pK_a values play a fundamental role in analytical procedures such as acid-base titration, solvent extraction, complex formation and ion transport. It has been shown [2] that acid-base properties affect the toxicity, the chromatographic retention behaviour and the pharmaceutical properties [3] of organic compounds. Much of the theoretical foundation of modern organic chemistry [4] is based on the observation of the effects on acid-base equilibrium of changing molecular structure.

The determination of the dissociation constant of an acid in water- organic oxygen compounds mixtures provides useful data for the theoretical understanding of the ionization process in these media. Several methods are used for the determination of dissociation constants. Potentiometry [5] and UV-VIS absorption spectrometry [6] are useful techniques for the determination of pK_a values, due to their accuracy and reproducibility. Nowadays, some methods for dissociation constants determination, based on separation methods [7], [8] including high performance liquid chromatography (HPLC), capillary electrophoresis (CE) are used.

Recent progress in computational hardware and the development of efficient algorithms has assisted the routine development of molecular quantum mechanical calculations. New semiempirical methods supply realistic quantum chemical calculations in a relatively short computational time frame. Quantum chemical calculations are thus an attractive source of new molecular descriptors which can in principal express all the electronic and geometric properties of molecules and their interactions. Quantum chemistry [9] provides a more accurate and detailed description of electronic effects than empirical methods.

Methods other than thermodynamic cycles are often used to calculate acid dissociation constants. Many publications

[10]-[13] have shown a theoretical relationship between pK_a and the structural property, bond valences methods and bond lengths, pK_a correlations with highest occupied molecular orbital (HOMO) energies and frontier molecular orbitals, and artificial neural networks. The gas-phase free energy calculation [14] is the lowest source of error in pK_a calculations. The problem however, is producing accurate results without using a computationally expensive level of theory. Quantitative structure-activity/property relationship [15] constitute at present the most popular theoretical method for modeling the manner in which biological activity and physical, chemical and technological properties depend on chemical structure of a compound. There are basically two possible ways to create a QSPR model of a feature to be predicted. The first is to create as general a model as possible, with the risk that the accuracy of such a model may not be high. The second approach is to develop more models, each of them being dedicated to a certain class of compounds.

In the work herein, we aim to determine experimentally and theoretically the first and second dissociation constants of oxalic acid which [16] is an important biochemical and industrial compound. The theoretical study is based on the QSPR approach which is used to construct a quantitative model based on a set of the molecular descriptors of the studied compound and the experimental pK_a values. The molecular descriptors parameters calculations were performed in gas phase using Gaussian 03W at B3PW91/LanL2DZ level.

2. Experimental

2.1 Materials and Solutions

All chemicals used were of analytical grade. Oxalic acid was purchased from Merck. It was dehydrated by heating to 100 °C and keeping in a vacuum for 18-20 h. Potassium chloride (KCl) from Merck was dried at 100 °C for 2h. Water, with conductivity lower than $10^{-6} \mu\text{S cm}^{-1}$ was obtained by double distillation. Ethanol from Prolabo was purified by double distillation in presence of sodium. Three kinds of

water-ethanol solvents of composition in percentage weight of ethanol 0, 16.3 and 80 were used. Disodium oxalate from Merck was dried at 125 °C for more than 4h. Monosodium oxalate salt was prepared by adding calculated quantities of sodium bicarbonate solution to known weights of pure oxalic acid, evaporating the solution to dryness on a steam bath, and recrystallizing the product from 95 % alcohol. The salt obtained was dried at 110-120 °C for at least 2 h. These salts were kept in vacuum desiccators until required.

Sodium hydroxide, potassium hydroxide, hydrochloric acid, formic acid and dichloroacetic acid were purchased from Merck. Stocks solutions of NaOH and HCl at the same concentration 2×10^{-2} M were made. Two sets of buffer solutions were used: (a) dichloroacetic acid-potassium hydroxide 2×10^{-3} M, covering the pH range from 1 to 3 and (b) formic acid-potassium hydroxide 2×10^{-3} M, covering the pH range from 3 to 6. Five buffer solutions were prepared with different ionic strength, using water-ethanol mixtures of composition in percentage weight of 0, 16.3 and 80. A stock solution of 2×10^{-3} M of oxalic acid was prepared by dissolving an accurately weighed amount of the pure reagent in double distilled water.

2.2 Apparatus and Procedures

2.2.1 Potentiometric method

Potentiometric determination of pK_{a1} and pK_{a2} values of the oxalic acid were obtained with respective measurements of pH of the cells: cell 1: Hg, Hg₂Cl₂ / KCl saturated // AH₂ (m), AHNa(m) / glass electrode and cell 2: Hg, Hg₂Cl₂ / KCl saturated // AHNa(m), ANa₂ (m) / glass electrode; where AH₂, AHNa, ANa₂ are respectively oxalic acid, mono- and disodium salts of the oxalic acid. *m* is the molal concentration of these reagents. These pHs were measured with a pH-meter Tacussel-Research which is combined with a glass and calomel-saturated electrodes. The accuracy of the instrument was ± 0.01 pH unit. The combined electrode system was stored in water when it is not used and soaked for 15-20 min in water-ethanol mixture before pH measurements. The measurements of the pH were carried out at the desired temperatures (298, 303, 308, 313, and 318 K). The temperature was controlled by water circulation through the jacket, from thermostat and maintained within ± 0.1 K.

For each of the three kinds of solvents, five equimolar solutions in acid and in alkaline salt of this acid of different concentrations ranging from 3×10^{-3} to 16×10^{-3} M were prepared in order to obtain buffer mixtures. The concentrations of these solutions were expressed in molality by weighing of chemicals at 10^{-4} unit of weight. The calibration of the electrodes was made with the buffers of Bates [17] at the desired temperatures (298, 303, 308, 313 and 318 K) and then the pH of these buffer solutions were measured with cell 1 and cell 2 and with a pH-meter Tacussel Research.

Triplicate pH measurements of each system was performed. In all instances, the pH-meter gave stable and reproducible pH values within 5 min. The pH values obtained allow calculation of pK_{a1} and pK_{a2} values. The pK_{a1} value of oxalic acid was determined with buffer solutions made with

oxalic acid and monosodium oxalate salt. As for pK_{a2} values, they were determined by realising buffer solutions formed with mono- and disodium salts of the oxalic acid.

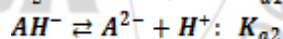
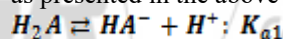
2.2.2 Spectrophotometric method

For pK_{a1} value's determination, five standards solutions were prepared adding 1 mL of stock solution of oxalic acid 2×10^{-3} M to 100 mL of five dichloroacetic acid-potassium hydroxide buffers (pH between 1 and 3) with water as solvent. The same procedure was used to prepare two standards solutions with stocks solutions of NaOH and HCl. The analytic concentration of these seven standard solutions was 2×10^{-5} M. Series of similar standard solutions were prepared using dichloroacetic acid-potassium hydroxide buffers at the same pH interval and stocks solutions of NaOH and HCl with the five others water-ethanol mixtures of composition in weight of 16.3 and 80. All these series of standard solutions were placed in UV cells, hermetically closed and the temperature was maintained at 298 K for 15 min. After that, the UV-Visible spectra were recorded on a Jasco V 530 UV-Visible double beam spectrophotometer, between 250 and 310 nm. The corresponding absorbance values were determined at 278 nm. For pK_{a2} value's determination, the procedure described for pK_{a1} was followed. In this case, formic acid-potassium hydroxide buffers (pH between 3 and 6) were used. UV-Visible spectra were recorded between 200 and 320 nm. The absorbance values were determined at 248 nm.

3. Results and Discussion

3.1 Thermodynamic functions

As a diacid, the dissociation of oxalic acid can be considered as presented in the above scheme:



The dissociation constants are given by:

$$pK_{a1} = pH - \log \frac{m_{HA^-}}{m_{H_2A}} - \log \gamma_{HA^-} \quad (1)$$

$$pK_{a2} = pH - \log \frac{m_{A^{2-}}}{m_{HA^-}} - \log \frac{\gamma_{A^{2-}}}{\gamma_{HA^-}} \quad (2)$$

$$pH = -\log a_{H^+} \quad (3)$$

Where:

a_{H^+} , m_{H_2A} , m_{HA^-} and $m_{A^{2-}}$ are respectively hydrogen cation activity and molal concentration of H₂A, HA⁻ and A²⁻. γ_{HA^-} and $\gamma_{A^{2-}}$ are the activity coefficients of ionized species calculated from Debye-Hückel's theory according to equation:

$$-\log \gamma_i = \frac{S' z_i^2 \sqrt{I}}{1 + A' a_i \sqrt{I}} \quad (4)$$

With:

$$I = \frac{1}{2} \sum_i m_i Z_i^2 \quad (5)$$

$$S' = \frac{1.8245 \times 10^6}{(\epsilon T)^{3/2}} \quad (6)$$

$$A' = \frac{50.29}{(\epsilon T)^{1/2}} \quad (7)$$

In relations (4) and (5), *I* is the ionization strength, *Z_i* is the charge of the ion *i*, *S'* and *A'* are coefficients depending on the values of dielectric constant ϵ and temperature; *a_i* is the

so called ionic parameter [18], [19] which characterizes the average of approach distant of the solvated ions supposed to be 5\AA . S' and A' were computed using equations (6) and (7). In aqueous solution at $T = 298\text{ K}$, $S' = 0.51$ and $A' = 0.329$

Combining the above equations one can compute the first and second dissociation constant of oxalic acid using the following equations:

$$pK_{a1} = pH + \frac{S' z_1^2 \sqrt{I}}{1 + A' a_1 \sqrt{I}} \quad (8)$$

$$pK_{a2} = pH + \frac{2S' z_2^2 \sqrt{I}}{1 + A' a_2 \sqrt{I}} \quad (9)$$

The plots of pK_{a1} and pK_{a2} versus \sqrt{I} for different temperature in aqueous solutions at $T = 298\text{ K}$ are giving by Figure 1.

The plots yield straight lines. This is in full agreement with the Debye Hückel equation. First and second dissociation constants (at $I = 0$) were determining using linear regression analysis.

The values of pK_{a1} and pK_{a2} at different temperatures and different ionic strengths are included in Table 1.

Mean constants values of the hydroorganic solvents are listed in table 2.

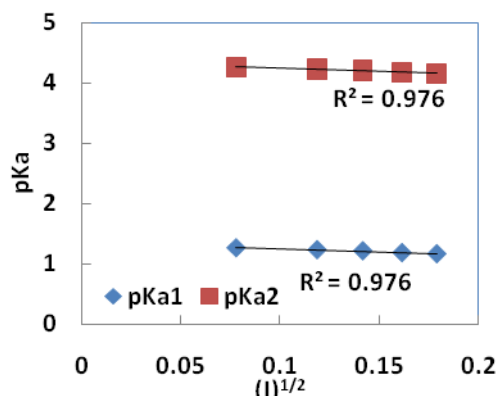


Figure 1: Plots of pK_{a1} and pK_{a2} values of oxalic acid versus \sqrt{I} in water at $T = 298\text{ K}$.

Table 1: Potentiometric determination of pK_{a1} and pK_{a2} at different temperatures and ionic strengths for oxalic acid in mixed solvents of different weights in percentage of ethanol

Wt(%)	I (mol.dm ⁻³)		T (K)									
			298		303		308		313		318	
			pKa ₁	pKa ₂	pKa ₁	pKa ₂	pKa ₁	pKa ₂	pKa ₁	pKa ₂	pKa ₁	pKa ₂
0	0.032	0.064	1.16	4.16	1.15	4.20	1.14	4.24	1.13	4.28	1.12	4.32
	0.026	0.052	1.18	4.18	1.17	4.22	1.16	4.26	1.15	4.30	1.14	4.34
	0.020	0.040	1.21	4.21	1.20	4.25	1.19	4.29	1.18	4.33	1.17	4.37
	0.014	0.028	1.23	4.23	1.22	4.27	1.21	4.31	1.20	4.35	1.19	4.39
	0.006	0.012	1.26	4.26	1.25	4.30	1.24	4.34	1.23	4.38	1.22	4.42
16.3	0.032	0.064	1.50	4.74	1.49	4.78	1.47	4.83	1.46	4.88	1.44	4.92
	0.026	0.052	1.53	4.76	1.52	4.80	1.50	4.85	1.49	4.90	1.47	4.94
	0.020	0.040	1.56	4.79	1.55	4.83	1.53	4.88	1.52	4.93	1.50	4.97
	0.014	0.028	1.59	4.81	1.58	4.85	1.56	4.90	1.55	4.95	1.53	4.99
	0.006	0.012	1.63	4.84	1.62	4.88	1.60	4.93	1.59	4.98	1.57	5.02
80	0.032	0.064	2.87	7.04	2.84	7.12	2.81	7.18	2.78	7.24	2.76	7.30
	0.026	0.052	2.89	7.06	2.86	7.14	2.83	7.20	2.80	7.26	2.78	7.32
	0.020	0.040	2.92	7.09	2.89	7.17	2.86	7.23	2.83	7.29	2.81	7.35
	0.014	0.028	2.94	7.11	2.91	7.19	2.88	7.25	2.85	7.31	2.83	7.37
	0.006	0.012	2.97	7.14	2.94	7.22	2.91	7.28	2.88	7.34	2.86	7.40

Table 2: Mean values of dielectric constant ϵ and that of coefficients S' and A' .

	Percentage weight of ethanol		
	0	16.3	80
ϵ	78.5	69.70	35.30
S'	0.5099	0.6095	1.6911
A'	0.3288	0.3489	0.4903

In the case of the spectrophotometric measurements the relations that give pK_{a1} and pK_{a2} are:

$$pK_{a1} = pH - \log \frac{A_{H_2A} - A}{A - A_{HA^-}} - \log \gamma_{HA^-} \quad (10)$$

$$pK_{a2} = pH - \log \frac{A_{HA^-} - A}{A - A_{A^{2-}}} - \log \frac{\gamma_{A^{2-}}}{\gamma_{HA^-}} \quad (11)$$

Where:

A is the absorbance of various acid species in buffer solutions at the given pH values, A_{H_2A} is the absorbance of the acid in the neutral form, A_{HA^-} et $A_{A^{2-}}$ are the absorbance of the mono-anion and the di-anion species (of the acid HA^- and A^{2-}). The observed absorbance and the computed pK_{a1} and pK_{a2} of oxalic acid at 298K are listed in table 3.

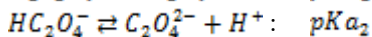
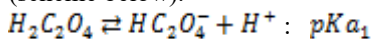
Table 3: Absorbance and pKa_1 and pKa_2 values of oxalic acid at 298K

A^a	$-\log \frac{A_{H_2A} - A}{A - A_{HA^-}}$	pH^a	pKa_1	A^b	$-\log \frac{A_{HA^-} - A}{A - A_{A^{2-}}}$	pH^b	pKa_2
0.2748	0.2003	1.04	1.28	0.0948	0.5723	3.57	4.27
0.2651	0.1421	1.11	1.29	0.0909	0.5368	3.61	4.27
0.2519	0.0647	1.17	1.27	0.0900	0.5027	3.65	4.28
0.2449	0.0242	1.22	1.28	0.0885	0.4489	3.69	4.26
0.2353	-0.0311	1.27	1.28	0.0873	0.4079	3.75	4.28

^a $A_{H_2A} = 0.5569$, $A_{HA^-} = 0.1399$, $\lambda = 278 \text{ nm}$, $-\log(\gamma_{HA^-}) = 0.0428$

^b $A_{HA^-} = 0.1054$, $A_{A^{2-}} = 0.0410$, $\lambda = 248 \text{ nm}$, $-\log(\gamma_{A^{2-}}/\gamma_{HA^-}) = 0.1287$

Examining tables 1 and 2, one can see that pKa_1 decreases with increasing temperature whereas we note an increasing trend for pKa_2 . These behaviors could be explained by a strong acid character of oxalic acid and a weak acid character for its conjugated ion, hydrogenooxalate ion (scheme below).



On the whole, the pKa values depend on that of the dielectric constant: pKa increases with decreasing value of the dielectric constant, meaning that the dissociation of the acid depends on the extent of the quantity of modifier (ethanol) in the mixture. This statement [20], [21] has been reported in the literature. The mean values of $pKa_1(1.28 \pm 0.02)$ and $pKa_2(4.27 \pm 0.02)$ obtained for spectrophotometric measurements at 298K (table 3) are more or less identical to those obtained using the potentiometric method. The thermodynamic quantities ($\Delta G^\circ, \Delta H^\circ, \Delta S^\circ$) associated with the dissociation of oxalic acid at different values of dielectric constants have been determined using the following equation:

$$\Delta G^\circ = -RT \ln K \quad (12)$$

This equation can be written as follows:

$$\Delta G^\circ = 2.303RT pK \quad (13)$$

R is the perfect gas constant and T is the temperature in Kelvin. Both the standard enthalpy (ΔH°) and entropy (ΔS°) changes are correlated with the Gibb's free energy change by the relation:

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (14)$$

Figures 2 and 3 give the plots of ΔG° versus the temperature. The values of free standard enthalpy changes (ΔG°), standard enthalpy changes (ΔH°) and standard entropy changes (ΔS°) for the first and second dissociation at different percentage in weight of ethanol and different temperatures are listed in table 4.

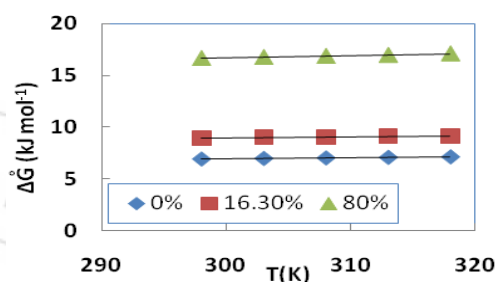


Figure 2: Free standard enthalpy changes versus temperature for the first dissociation.

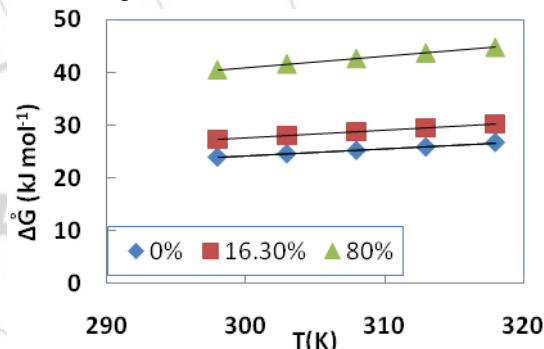


Figure 3: Free standard enthalpy changes versus temperature for the second dissociation.

Table 4: Standard thermodynamic functions for the first and second dissociation processes of oxalic acid

W _t (%)	T(K)	First dissociation			Second dissociation		
		ΔG° (kJ.mol ⁻¹)	ΔH° (kJ.mol ⁻¹)	ΔS° (J.mol ⁻¹ K ⁻¹)	ΔG° (kJ.mol ⁻¹)	ΔH° (kJ.mol ⁻¹)	ΔS° (J.mol ⁻¹ K ⁻¹)
0	298	6.904	3.63	-11.00	24.022	-16.70	-136.6
	303	6.962			24.657		
	308	7.018			25.299		
	313	7.072			25.950		
	318	7.124			26.791		
16.3	298	8.912	5.45	-11.70	27.331	-16.73	-147.7
	303	9.004			28.022		
	308	9.035			28.779		
	313	9.121			29.546		
	318	9.145			30.261		
80.0	298	16.650	10.16	-21.70	40.454	-23.22	-213.8
	303	16.755			41.597		
	308	16.854			42.638		
	313	16.948			43.689		
	318	17.097			44.753		

The positive sign of standard free enthalpy changes for both first and second dissociations denotes that these processes are not spontaneous. It can be seen

in table 4 that the enthalpy changes for the first dissociation are positive showing an endothermic process while that of the second dissociation are negative implying an exothermic process. The negative values of entropy changes point to increased ordering due to an association. It is obvious that as the composition of organic solvent increases, the pKa values also increase. The dielectric constant of a solvent is the measure of a solvent's efficiency to separate oppositely charged ions. According to Coulomb's law the attraction forces (F , in Newton) between two ions charged with q^- and q^+ (in coulombs) separated by distance r (in meter) is:

$$F = 8.988 \times 10^9 \frac{q^2}{\epsilon r^2} \quad (15)$$

Where ϵ is the dielectric constant of the solvent. The attractive force [21] is inversely proportional to the dielectric constant. The larger the value of the dielectric constant, the smaller the attraction forces between the two ions (H^+ and $HC_2O_4^-$ for the first dissociation) and thus the larger acidity constant Ka values and lower pKa values. The dielectric constant of water and ethanol are 78.5 and 24.5 respectively. With an increase of ethanol concentration, the dielectric constant value of the solvent [21] will decrease resulting in a decrease of acidity constant or increase in pKa values. When the ionization of an acid gives a net increase of ions, a decrease in the dielectric constant of the solvent should be accompanied by a decrease in the protonation constant (increase of pKa) of a weak acid dissolved in it. A solvent of low dielectric constant increases the electrostatic forces between the ions and facilitates the formation of molecular species, and should increase pKa.

For the second dissociation process one can observed that the values of the standard enthalpy changes ΔH° decrease with increasing organic content of the solvent mixtures, suggesting that the second dissociation process becomes increasingly exothermic. The standard entropy changes are large and negative showing an ordering trend.

3.2 Computational Details

Molecular descriptors have been computed using density functional theory DFT at B3PW91 (Becke 3 parameters Perdew/Wang 91) level with LanL2DZ basis set. The calculations have been performed using Gaussian 03 W package. The descriptors were computed after a geometry optimization of the molecule. The descriptors in concern are the HOMO energy E_{HOMO} , the LUMO energy E_{LUMO} , the energy gap ΔE , the dipole moment μ and the charge δ on the oxygen of the hydroxyl group. Table 5 gives the quantum parameters of the oxalic acid.

Table 5: Computed molecular descriptor of oxalic acid using B3PW91/LanL2DZ

E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE (eV)	μ (D)	δ (e)
-8.1962	-2.9310	5.265	0	-0.4272

3.3 QSPR Models

QSPR models with three descriptors were constructed using five sets of descriptors. The general equation of the model is given by the multiple linear regression equation below:

C and E). The solutions of these systems were computed using Excel 2007 program. The selection of appropriate descriptors that are significantly related to the property of interest is very important.

$$pK_a = AD_1 + BD_2 + CD_3 + E \quad (16)$$

Where:

D_i is the descriptor i (i ranges from 1 to 3). A, B, C and E are linear regression coefficients. So using four experimental pKa values, we obtained a system of four equations with four unknowns (A, B, C, E). The descriptors [22] can be chosen using domain knowledge about the examined property (literature considerations), or the mathematical methods for the selection of descriptors can be applied. The reasons for the choice of the above quantum descriptors are mentioned below:

- The HOMO energy is related to ionization energy and characterized the susceptibility of the molecule towards electrophiles attacks;
- The LUMO energy is related to electron affinity and indicates the susceptibility of the molecule to nucleophiles attacks;
- The energy gap ΔE is an important reactivity index. Large value of energy gap implies lower reactivity in chemical reactions.
- The dipole moment μ is the most often used quantity to describe the polarity of a molecule which is important for various physicochemical properties,
- Partial atomic charge δ which allows the prediction of relative acidity or reactivity by estimating the extent of charge delocalization based on molecular structure information.

Set 1: $\Delta E, \mu, \delta$

Table 6: Computed values of coefficients relating pK_{a1} and pK_{a2} to the molecular descriptors at $T = 298K$.

Ethanol weight (%)	A_1	A_2	B_1	B_2	C_1	C_2	E_1	E_2
0	125.15	49.13	50.87	20.03	-46.79	-18.93	759.16	301.48
16.3	146.65	65.36	59.44	26.45	-54.98	-25.17	890.72	401.19
80	202.53	96.55	82.03	39.03	-75.95	-37.09	1231.13	592.99

Figure 4 gives the representations of experimental pK_a versus computed ones.

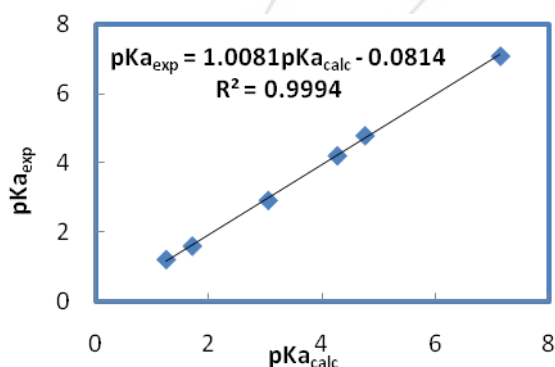


Figure 4: Experimental pK_a values versus computed ones.

The representation yields a straight line with a correlation coefficient very close to unity. To express the consistency between experimental and calculated pK_a values we have also calculated the root mean square errors using the relation below:

$$RMSE = \sqrt{\sum_{i=1}^N \frac{|pK a_{exp}^i - pK a_{calc}^i|^2}{N}}$$

Where $pK a_{exp}^i$ and $pK a_{calc}^i$ are respectively experimental and computed pK_a values with the model. N denotes the number of data points. $N = 6$ and $RMSE = 0.082$: this lower value indicates high correlation between experimental and theoretical values.

4. Conclusions

From the above results one can draw the following conclusions:

- 1) The first and second dissociation constant of oxalic acid are directly proportional to the square root of the ionic strength of the solution of water-ethanol solvent.

So we have constructed five sets:

Set 2: $E_{LUMO}, E_{HOMO}, \Delta E$

Set 3: E_{LUMO}, E_{HOMO}, μ

Set 4: $E_{LUMO}, \Delta E, \mu$

Set 5: $E_{HOMO}, \Delta E, \mu$

As it can be seen in our previous work [23], the best set is: $(E_{HOMO}, \Delta E, \mu)$. The mathematical relation for first and second dissociation constant is:

$$pK a_i = A_i E_{HOMO} + B_i \Delta E + C_i \mu + E_i \quad (17)$$

Using three other carboxylic acids: salicylic acid, benzoic acid and lactic acid in the same conditions (three other pK_a values) [23] we obtained the systems of four equations with four unknowns.

Table 6 gives the coefficients connecting pK_{a1} and pK_{a2} to the descriptors.

- 2) The first and the second dissociation constant pK_{a1} and pK_{a2} of the oxalic acid in water-ethanol solvent increases with increasing weight of ethanol.
- 3) The first dissociation constant pK_{a1} of oxalic acid decreases with increasing temperature, whereas we note the reverse behaviour with the second dissociation constant pK_{a2} .
- 4) The sign of the standard free changes of first and second dissociation constants indicates spontaneous processes.
- 5) The sign of the obtained enthalpy changes indicates an exothermic process for the first dissociation process and an endothermic one for the second.
- 6) For both, first and second dissociation processes, the negative sign of entropy changes shows a trend of increasing order.
- 7) Experimental and theoretical results are in good agreement.

References

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