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# AMPHOTERIC BEHAVIOR OF DI-2-PYRIDYL KETONE BENZOYLHYDRAZONE IN ETHANOL-WATER MIXTURES\*

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**ABSTRACT:** The ligand di-2-pyridyl ketone benzoylhydrazone (DPKBH) is widely used for the determination of transition metal ions in environmental samples. Due to its low solubility in water it is used in aqueous-ethanol (1:1) solvent and for higher sensitivity the pH must be properly adjusted. The properties of DPKBH solutions must be known at different ethanol-water percentages in order to achieve higher sensitivity and/or selectivity for metal analysis. The acid-base behavior of this reagent in aqueous-ethanol solvent and the dissociation/ionization constants ( $pK_1$  and  $pK_2$ ) of DPKBH have been determined in different aqueous-ethanol solvent mixtures (10, 20, 30 and 50 % V/V of ethanol) from potentiometric titrations at  $25.0 \pm 0.1^\circ$  C. As the amount of ethanol increases from 10 to 30% the  $pK_1$  and  $pK_2$  values increased, but they decreased in 50% of the organic solvent. The results are correlated with the medium composition and its effects.

**KEYWORDS:** di-2-pyridyl ketone benzoylhydrazone; aqueous-ethanol solvent mixtures; dissociation/ionization constants; potentiometry.

## Introduction

Hydrazones are azomethines characterized by the triatomic grouping  $C=N-N$  and they are interesting substances because of their physiological activities like in the treatment of several diseases such as tuberculosis. This activity is attributed to the formation of stable chelates with transition metals which catalyse the physiological processes<sup>25,30,42</sup>. They also act as herbicides, insecticides, nematocides,

rodenticides, plant growth regulators, sterilants for houseflies, among other applications<sup>25,30,32</sup>.

In analytical chemistry hydrazones find application by acting as multidentate ligands<sup>3,9-13,19,20,22,27,29,38,43,45</sup> with metals (usually from the transition group). Some methods and several techniques are reported and among them the colorimetric or fluorimetric methods are more frequently used as selective and sensitive for the determination by the formation of colored metal-complexes<sup>11,45</sup>.

Di-2-pyridyl ketone benzoylhydrazone (DPKBH) was first synthesized by Garcia-Vargas *et al.*,<sup>18</sup> it is a soluble reagent in different organic solvents but slightly soluble in water. It is widely used for metal determinations like as Fe(II)<sup>34</sup> in natural waters, Fe(II) and Fe(III) simultaneously<sup>17,37,50</sup> in cloud water samples<sup>37</sup>, Co(II)<sup>3,49</sup> in different metal alloys, Pd(II) in dental alloys<sup>33</sup> and Ni(II) in various natural samples<sup>46,47</sup>.

Owing to the great importance of this reagent in the determinations of transition metals, more accurate studies were developed by Suárez-Iba *et al.*<sup>44</sup> on the stoichiometry, structure and thermodynamics of Fe(II) and Fe(III) complexes of DPKBH as well as by Rossi *et al.*<sup>39</sup> on Co(II).

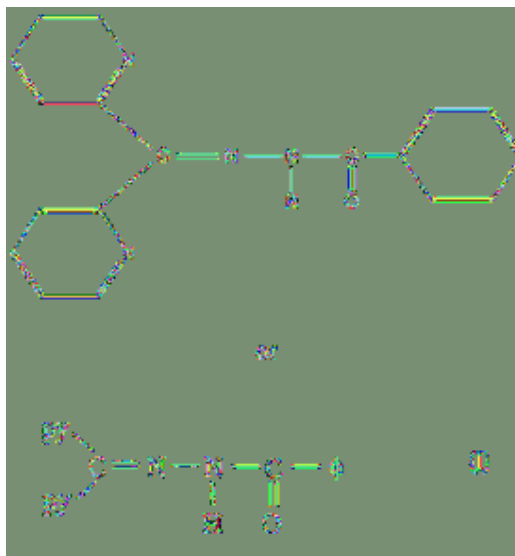
The behavior of DPKBH in different ethanol-aqueous mixtures must be known in order to achieve, in different conditions, higher sensitivity and/or selectivity for the metal determinations. These different behaviors are here presented from the determination of the dissociation/ionization constants of DPKBH in several percentages of ethanol (10, 20, 30 and 50%).

## **Materials and Methods**

### ***Synthesis of DPKBH (I)***

The synthesis was performed according the procedure outlined by Garcia-Vargas *et al.*<sup>18</sup>. Equimolar quantities of di-2-pyridyl ketone and benzoylhydrazide were mixed in ethanol, and a few drops of concentrated hydrochloric acid were added. The mixture was refluxed for one hour, and after cooling, distilled water was added to a 1:3 volume ratio (volume of ethanol to volume of water). Sodium hydroxide was added to the refluxed solutions to increase the pH up to  $\cong 5$ . The resulting precipitate was collected on a Buchner funnel and recrystallized

twice from ethanol-water solutions. The melting point of the product (I) was determined (134° C) and it is very closed to that (130-132°C) obtained by Garcia-Vargas *et al.*<sup>18</sup>. The IR spectrum for DPKBH was checked and it is also similar with the spectrum previously reported<sup>44</sup>.



### ***Reagents and Solutions***

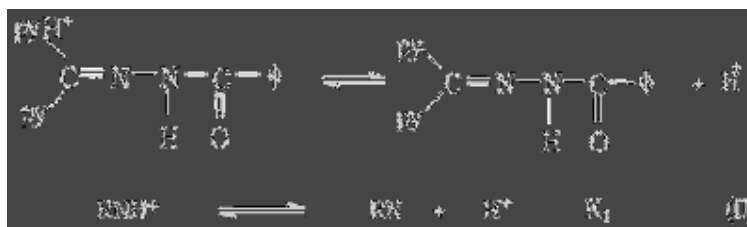
Perchloric acid, hydrochloric acid and sodium hydroxide solutions were prepared with deionized water. The perchloric and hydrochloric acids were standardized against potassium hydrogenphthalate and the sodium hydroxide against potassium tetraborate by using potentiometric methods. Solutions were diluted to 10, 20, 30 and 50 % (V/V) of ethanol by using 95% ethanol. All reagents were of AR grade.

### ***Potentiometric Titrations***

The potentiometric measurements were carried out in a 5 mL Metrohm 6.1418.150 thermostated jacketed cell at  $(25.0 \pm 0.1)^\circ \text{C}$ . Small volumes were added from a 5 mL Metrohm E 274 piston burette. A Metrohm 654 pHmeter adapted to a Metrohm glass electrode, combined with an Ag/AgCl reference electrode filled with  $3 \text{ mol.L}^{-1} \text{ NaCl}$  was used for the pH measurements.

Solutions *ca.*  $1.00 \times 10^{-3} \text{ mol.L}^{-1}$  of DPKBH were titrated with *ca.*  $3.00 \times 10^{-3} \text{ mol.L}^{-1} \text{ HClO}_4$  and NaOH solutions in order to obtain  $\text{pK}_1$  and  $\text{pK}_2$ , respectively.

The  $pK_1$  value is obtained when the following equilibrium (II) involving the protonation of pyridine nitrogen is considered:



The  $pK_1$  represents the relationship between the pH and the ratio of the RN and  $\text{RNH}^+$  species concentrations :

$$\text{pH} = \text{p}K_1 + \log \frac{[\text{RN}]}{[\text{RNH}^+]} \quad (I)$$

To obtain  $pK_2$ , the second protonation equilibrium must be considered from the DPKBH's tautomeric balance (III), involving the enol and ketone groups, as follows:



The enolic form (equilibrium (III)) presents a second balance resulting in ionic species:



The  $pK_2$  represents the relationship between the pH and the ratio of the ROH and  $\text{RO}^-$  species concentrations:

$$\text{pH} = \text{p}K_2 + \log \frac{[\text{RO}^-]}{[\text{ROH}]} \quad (II)$$

As the response of the glass electrode is not known in ethanol-aqueous solution, its behavior was determined in a previous step for each ethanol percentage from a potentiometric titration process where a certain volume of  $1.00 \times 10^{-2} \text{ mol.L}^{-1}$  HCl standard solution was titrated against

$3.00 \times 10^{-2} \text{ mol.L}^{-1}$  NaOH solution, both of them prepared in ethanol (10, 20, 30 and 50 %). The emf data were plotted as a function of the pH calculated from each mass balance and a linear relationship was obtained. From this curve the slope is obtained and used as a correction factor for all of the next measurements carried out with this electrode<sup>8,28,35</sup>. Before each measurement of the pH ( $-\log a_H$ ) for the DPKBH solutions, in different ethanol percentage, the glass electrode was calibrated at  $(25.0 \pm 0.1)^\circ \text{C}$  with  $0.0500 \text{ mol.L}^{-1}$  potassium hydrogenphthalate solution prepared in each ethanol percentage. The pH of these solutions considered as  $-\log [H^+]$  were determined by the direct emf reading after calibration of the glass electrode with HCl (strong acid) solution. The values 4.262; 4.681; 5.116 and 5.296 were found for the hydrogenphthalate solution, respectively, for 10, 20, 30 and 50% of ethanol.

With the experimental pH values from the titrations of DPKBH with NaOH and HCl, considering the mass balances and all corrections for dilution by tritrant addition, the  $pK_1$  and  $pK_2$  values can be determined<sup>2</sup>.

## Results and Discussion

The experimental behavior of glass electrode was determined in the acid region of the titration and considered constant in both of the ranges, acidic and alkaline. This assumption is based on the constant correlation between the measured E (potential) and the calculated pH for three different pH ranges, 2 - 3; 4 -5 and 7 - 10, observed by Hedwing & Powell<sup>24</sup>.

The  $pK_1$  and  $pK_2$ , values relative to the dissociation/ionization constants for every ethanol percentage are listed in [Table 1](#). These results reveal that  $pK_1$  and  $pK_2$  values increase when ethanol percentage changes from 10 to 30% but decrease in 50% of the solvent. This initial increase may be related to the decrease of the water percentage and the consequent change in the dielectric constant of the medium.

**Table 1 - Values of  $pK_1$  and  $pK_2$  for DPKBH in different percentages of ethanol/water and the respective standard deviations. Temperature:  $(25 \pm 0.1)^\circ\text{C}$**

% Ethanol	$pK_1^{(a)}$	$pK_2^{(a)}$
0%	$9.810 \pm 0.003$	$10.034 \pm 0.007$
10%	$9.741 \pm 0.006$	$11.019 \pm 0.004$
30%	$9.594 \pm 0.002$	$11.788 \pm 0.007$
50%	$9.392 \pm 0.007$	$11.392 \pm 0.010$

<sup>(a)</sup> These values represent the average from at least ten determinations.

The electrostatic effect resulting from the change in the dielectric constant of the medium affects the activity coefficient of any charged species ( $\text{RNH}^+$ ,  $\text{RO}^-$  and  $\text{H}^+$ ). The magnitude of this effect is inversely proportional to the ionic species radii. In this way it is more significant on the activity coefficient of the proton than on the other species ( $\text{RNH}^+$  and  $\text{RO}^-$ ), thus the expected (and actually observed) tendency of DPKBH dissociation/ionization constants is to decrease as the mole fraction of ethanol increases<sup>1,15,16,41</sup>.

In 50% of the last mentioned solvent a decrease of  $pK_1$  and  $pK_2$  values was observed, in connection with 30% of ethanol as shown in [Table 1](#). This opposite behavior may be attributed to other factors which act in the dissociation/ionization processes. Bates *et al.*<sup>4</sup> and other authors<sup>1,4-6,14,23,26,36</sup> have studied the effect of change in solvent composition on the dissociation constants and the free energy of Gibbs. They have suggested that the electrostatic effects resulting from the change of dielectric constants (D) with the molar fraction of the solvent present a lesser influence in the interpretation of solvent effects than the solute-solvent interactions.

At present, there is no known way to characterize all of the nonelectrostatic effects. Born have correlated<sup>7</sup> the change in standard free energy of transfer a single ionic species from water to another solvent with an electrostatic and a nonelectrostatic term. According to Born, assuming that only electrostatic effects are taking place and the radii of all ions are equal, the plot<sup>7</sup> of  $pK$  versus  $1/D$  can show some evidences. For a hypothetical monoprotic acid, HA, where A is negatively charged and HA has no charge, such a plot (e.g.: dissociation constants determined in solutions of varying ethanol percentages versus  $1/D$ ) should be a straight line with a positive slope. For a different acid where HA is positively charged and A has no charge, the same plot ( $pK$  versus  $1/D$ ) should be a straight line with zero slope. The first case is confirmed, at least in a specific range of solvent percentage, for some

examples and fails for other. However, the pK values for cationic acids (second case) do not stay constant as predicted<sup>7</sup> by Born.

Yasuda<sup>48</sup> and Shedlovsky<sup>40</sup>, by different ways, have studied the effect of the water in different molar fraction in mixed solvents and proposed a new dissociation constant for acids and bases which is dependent on the concentration (the activity is not known) of water. Considering the terms of the derivated equations, a plot of  $pK + \log [H_2O]$  versus  $1/D$  should be linear and the extrapolation of  $(pK + \log [H_2O])$  values should correspond to  $pK_a$  in water. This proposition was checked for different acids<sup>7,40,48</sup> and confirmed only for values of  $1/D$  lesser than 0.02 which correspond to water concentrations greater than 50%. The treatment was also applied for  $AgClO_4$ -pyridine (py) complexes by Molina *et al.*<sup>31</sup>. The simple relationship between the logarithm of the stability constants of  $Ag(I)/py$  complexes and the inverse of the dielectric constant of the ethanol-water medium was found to be linear<sup>31</sup> and the plots  $\log \beta_n \cdot [H_2O]$  versus  $1/D$  for  $n = 1$  and  $n = 2$  also showed a linear variation in the ethanol percentage range (9.9 to 93.8 %), confirming the Yasuda<sup>48</sup> and Shedlovsky<sup>40</sup> approach.

In the present work, the amphoteric behavior of DPKBH permits the comparison with both of the hypothetical acids above mentioned. The equilibrium associated to  $pK_2$  can be correlated to the first example of HA where HA is ROH (DPKBH) and A is  $RO^-$  and the equilibrium associated to  $pK_1$  involves the species HA ( $RNH^+$ ) and A (RN).

The variation of  $pK_1$  and  $pK_2$  for DPKBH can be correlated to the inverse of dielectric constant<sup>21</sup> of the ethanol-water mixtures as represented in [Figure 1](#) that also includes the data found in the literature ([Table 2](#)). As can be observed in this figure, the correlation between  $pK_1$  and  $1/D$  cannot be considered as linear or almost constant; the pK values increase, pass through a maximum, and then decrease at 50% of ethanol. However, the plot  $pK_2$  versus  $1/D$  shows a straight line with a positive slope for values of  $1/D$  less than 0.016, corresponding to 30% of ethanol. It appears that at  $1/D$  values greater than 0.016 the nonelectrostatic terms in the free energy are no longer negligible. However, we must consider that the correlation coefficient of the line is not good (0.94) and in spite of the apparent good fitness of the data from the literature<sup>18,34</sup> they were obtained in very different conditions from the present work because the ionic strength was adjusted at 0.1 mol.L<sup>-1</sup> with NaCl.



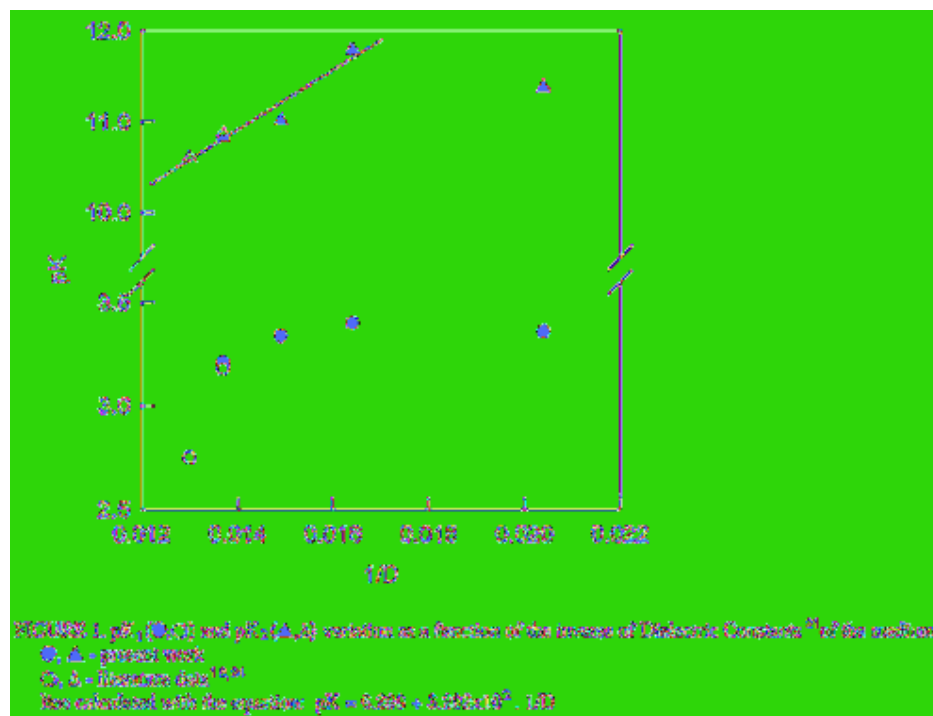


Table 2 - Some  $pK$  values from literature and present work. Ethanol/water mixtures, at  $(25 \pm 0.1)^\circ\text{C}$

% Ethanol	$pK_1$	$pK_2$	Reference
5	3.76	10.6	(48)
10	3.16	10.97	(49)
10	3.219	10.634	present work

The approach proposed by Yasuda<sup>48</sup> and Shedlovsky<sup>49</sup> was also checked with all data from [Table 1](#) and [2](#). Similar behavior was observed for the plot  $pK + \log[H_2O]$  versus  $1/D$  in comparison with the plot  $pK$  versus  $1/D$ , making not possible and different conclusions, as observed by Molina *et al*<sup>31</sup> for the Ag(I)/py complexes.

The solute-solvent interactions are probably the reason for the different behavior of DPKBH, when it forms the protonated ( $RNH^+$ ) or the anionic ( $RO^-$ ) species.

The  $pK_1$  values vary from 3.210 (10% of ethanol) to 3.398 (30% of ethanol), corresponding to 0.188 units of  $pK$ ; the  $pK_2$  vary from 10.834 (10%) to 11.793 (30%), corresponding to almost one  $pK$  unit and the pH of the hydrogenphthalate solution vary from 4.262 (10%) to 5.116 (30%), resulting in a variation of *ca.* 0.85 units.

The similar behavior for both DPKBH in basic ethanolic solution and hydrogenphthalate ethanolic solution, in the different ethanol percentages, gives strong evidence for the solute-solvent interactions between ethanol and the charged  $-CO^-$  moiety, found in both of them, and not found in the neutral and protonated form of DPKBH ( $RN$ ,  $RNH^+$ ,  $RC=O$ ).

The small extent of solute-solvent interaction is probably the main reason for the small difference among the values of  $pK_1$  when the ethanol percentage was changed from 10 to 50%.

Concerning to the complex formation, Suárez-Iba *et al.*<sup>44</sup> showed that DPKBH is coordinated to Fe(III) ions as an anionic species ( $RO^-$ ). Although the dissociation of a proton from the neutral DPKBH molecule is not favorable under the conditions ( $pH \cong 6$ ) for the determination<sup>37</sup> of Fe (II) and Fe(III), enhancement of the DPKBH acidity after metal complex formation may promote its dissociation. A very important conclusion from our results about the  $pK_2$  values is that the acidity of the DPKBH ligand drops to almost half when the ethanol percentage is changed from 10 to 50%, but it is still favorable for coordination of the metallic cations with DPKBH, and the different percentages of ethanol may probably be used to control the selectivity and/or the sensitivity of the metal ion determinations.

Another important factor in the determination of dissociation/ionization constants is the influence of the ionic strength, since it affects the activity coefficients of ionic species in equilibrium. An evaluation of this factor was carried out in this work by considering the species involved in the titrations. The ionic strength of the solutions at different ethanol percentages and during the titrations vary only by a tenth and the absolute values are in the  $10^{-4}$  to  $10^{-3}$  mol.L<sup>-1</sup> range, leading to activity coefficients very close to unity and, in this way, the concentration can be assumed as the activity. As a consequence of these considerations the constants presented here can be regarded as a good estimate of the thermodynamic constants.

## Conclusion

The literature shows only the pK values for 3<sup>18</sup> and 10 %<sup>34</sup> of ethanol. [Table 2](#) shows these values and those from the present work. The comparison is restricted to the 10% ethanol values, and a very good agreement is observed between the spectrophotometric values obtained by Nakanishi & Otomo<sup>34</sup> and the corresponding ones determined in the present work. This good agreement suggests that both the experimental design and the method adapted in this work are appropriate.

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GAUBEUR, I. et al. Comportamento anfótero da di-2-piridil cetona benzoilhidrazona em misturas etanol-água. *Ecl. Quím. (São Paulo)*, v.25, p. 2000.

**RESUMO:** O ligante di-2-piridil cetona benzoilhidrazona (DPKBH) é frequentemente usado para determinação de íons metálicos de transição em amostras ambientais. Devido a sua baixa solubilidade em água, é utilizado em solução aquo-etanólica (1:1) e com pH adequadamente ajustado para resultar na maior sensibilidade. As propriedades do DPKBH devem ser conhecidas em diferentes porcentagens de etanol, para que se estabeleçam as condições de maior sensibilidade e/ou seletividade para análise de metais. O comportamento ácido-base desse reagente em solvente aquo-etanólico, as constantes de dissociação/ionização (pK<sub>1</sub> e pK<sub>2</sub>) do DPKBH foram determinados em diferentes soluções do solvente aquo-etanólico (10, 20, 30 e 50% V/V de etanol, fazendo-se titulações potenciométricas em 25,0 ± 0,1°C. Os valores de pK<sub>1</sub> e pK<sub>2</sub> aumentaram em função do aumento da porcentagem de etanol, de 10 a 30%, mas diminuíram para 50% de solvente orgânico. Os resultados são correlacionados à composição do meio e seus efeitos.

**PALAVRAS-CHAVE:** di-2-piridil cetona benzoilhidrazona; mistura de solventes água-etanol; constantes de dissociação/ionização; potencimetria

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