Spectral Study of 1,4-bis(3-(2-pyridyl)pyrazol-1-ylmethyl)benzene (PPB): UV-VIS Absorption Spectra Investigation in Single and Binary Solvents and Spectrophotometric Determination of the Dissociation Constant (pKₐ)

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ABSTRACT
The effect of solvents of different polarity and hydrogen bonding ability on electronic absorption spectra of PPB was investigated. UV absorption spectra (200-400 nm) were recorded in five single solvents and one binary solvent (DCM-EtOH). PPB has two absorption maxima (250 and 280 nm) due to pyridyl pyrazole and benzene systems. The spectral shifts and absorption maxima in various solvents were correlated with the Kamlet and Taft parameters (α, β and π*) using linear solvation energy relationships. The multiparametric analysis indicates that hydrogen bond donor ability of the solvent (for band I) and non-specific dipolar interactions of the solvents (for band II) play an important role in absorption maxima of PPB in pure solvents. Index of preferential solvation was calculated as a function of solvent composition. Preferential solvation by ethanol (band I) and by dichloromethane (band II) was detected in DCM-EtOH solvent mixture. The pKₐ of PPB in two solvent mixtures; EtOH – H₂O & THF – H₂O, were determined using UV-Vis spectrophotometry. Two graphical methods were used to estimate the base dissociation constant (pKₐ) using absorbance measurements. The resulting average of pKₐ values in the two solvent mixtures using the two methods were 10.77 and 11.14 with a standard deviation of 0.03 & 0.33, respectively.

Keywords: spectral study, solvatochromism, spectrophotometric determination of pKₐ

INTRODUCTION
Chemistry of flexible ligands, which consist of a –CH₂- spacer connected with a pyrazolylpyridine and aromatic spacer, has attracted a lot of inorganic chemistry researchers due to its ability to form different structures when combining with labile metal cations under same
ration of 1.5 ligand per metal ion [1]. Pyrazoles [2] have been used as versatile ligands for a variety of coordination compounds ranging from bioinorganic models [3] and antitumor agents [4] to materials with efficient luminescent properties [5].

The effects of a solvent on the absorption spectrum of a solute is an essential study for the development of solution chemistry [6-11]. When absorption spectra are measured in solvents of different properties, it is found that the positions, intensities, and shape of absorption bands are usually influenced by the solvent. These changes are a result of intermolecular solute-solvent interactions, such as dipole-dipole, dipole-induced dipole, hydrogen bonding, which may change the energy difference between the ground and excited state of the absorption species containing chromophore. These solute-solvent interactions are referred to as solvatochromism [12] and can be studied using the absorption spectra in different solvents. Most used tools, which can provide information about these types of interactions are: UV-Vis, IR, $^1$H and $^{13}$C NMR spectra [13].

The separation of specific (hydrogen bonding ability) from non-specific (solvent polarity) interactions in the interpretation of experimental measurements of absorption spectra is a difficult task. Quantitative measurements for polarity are necessary in order to differentiate between these two effects [14]. Among all the existing solvent polarity scales, in this work we use the empirical solvatochromic scale of Kamlet and Taft [15, 16]. One of the most successful quantitative treatments of solvent effects is linear solvation energy relationships (LSER). This treatment uses a multiparameter equation of the form:

$$v_{\text{max}} = v_0 + s\pi^* + a\alpha + b\beta$$

(1)

where: $v_{\text{max}}$ is solute-dependent values, i.e., absorption frequencies, $v_0$ is the value of this property for the same solute in the absence of any solvent effect (gas phase) for which $\pi^* = \alpha = \beta = 0$, $\pi^*$ is an index of the solvent dipolarity/polarizability; $\alpha$ is a measure of the solvent hydrogen-bond donor (HBD) capacity; and $\beta$ is a measure of the solvent hydrogen-bond acceptor (HBA) capacity. The regression coefficients $s$, $a$ and $b$ in Eq. (1) are constants characteristic of the solute, and their magnitudes and sign reflect the relative influence of the corresponding solvent-solute interactions on the electronic transition energy. The linear solvation energy relationship (LSER) concept developed by Kamlet and Taft [15, 16] is one of the most ambitious and successful quantitative treatments of solvation effects. This treatment assumes attractive interactions between a solute and its environment and enables an estimation of the ability of the investigated compounds to form hydrogen bonds.

The dissociation constant (pK$_a$) is an important parameter that indicates the degree of ionization of molecules in solution at different pH values. Many chemical, physical and biological properties of natural and synthetic compounds are governed by the basic and acidic properties. In such compounds, the pK$_a$ controls many aspects of metabolism and even transport across membranes; therefore, the study of this parameter is a significant interest in biology, pharmaceutics, medicine, and numerous other scientific fields [17-19]. There are two methods for determining the pK$_a$ of a compound: potentiometric titration and spectrophotometric titration [20-23].
In the present work, an experimental study on the solvatochromic effects of PPB is carried out in pure solvents as well as in binary mixture solvents using UV-vis spectroscopy method in order to describe the solute-solvent interactions that this compound present. Also, the dissociation constants of PPB in various solvent mixtures (EtOH : H₂O and THF : H₂O) have been determined spectrophotometrically.

**EXPERIMENTAL**

All obtained solvents were HPLC or spectroscopic grade and used without further purification. The solvents employed were ethanol (99.9%), 2-propanol (99.9%), tetrahydrofuran (99.9%), dichloromethane (99.9%), and ethyl acetate (99.5%).

The ligands were prepared by reaction of 3-(2-pyridyl)pyrazol-1-ylmethyl)benzene under basic conditions by the procedure described elsewhere [24, 25].

The UV absorption spectra were recorded in the range from 200 to 400 nm in five solvents of different polarity using the Agilent Cary 60 UV-Vis Spectrophotometer. Spectra were recorded at 25°C. The stock solution of PPB was prepared in each solvent by dissolving 0.0300 – 0.0400 g in 25 ml of a solvent. A series of diluted solutions, in concentrations range (10⁻⁸ – 10⁻⁶ M) were used in the calculation of molar absorptivity.

The pH measurements were performed using an Jenway pH 3505 pH meter.
Figure 1. UV-visible absorption spectra of PPB in different solvents

Figure 2. (continues on the next page)
RESULTS AND DISCUSSION

Spectra of PPB in Single Solvents

Scheme 1 shows the structure of PPB. The UV-vis absorption spectra of PPB exhibit two absorbance maxima (band I and band II). Band I can be found in the range from 252 to 255 nm and band II from 280 to 282 nm depending on the used solvent. The compound has two
chromophores; pyridyl-pyrazole and benzene (Scheme 2). The peak around 250 nm can be attributed to the benzene and the peak around 280 nm is attributed to the pyridyl-pyrazole system. The solvent exerts an influence on the electronic absorption, changing their shape, and spectral maxima positions. Figure 1 shows the electronic absorption spectra of PPB in different solvents.

A bathochromic shift on band I is observed upon going from EtOH to EtAoc. Also, A bathochromic shift on band II is observed upon going from EtAoc to DCM. It is important to notice that the \( \lambda_{\text{max}} \) in THF is closer to the values obtained in polar protic solvents (EtOH and Pro-2-OI). In Table 1 the maximum absorption wavenumbers (\( \nu_{\text{max}} \) in cm\(^{-1}\)) and molar absorptivities of the band I and II of PPB in single solvents along with relevant solvents parameters [26] are summarized. Figure 2 shows the electronic absorption spectra of different concentrations of PPB in each solvent along with the calibration curves. The \( \varepsilon \) values of band I are higher than those of band II. This is attributed to the contribution of \( n \rightarrow \pi^* \) transitions in band II. While band I is mainly due to \( \pi \rightarrow \pi^* \) transitions.

In order to obtain a better description on the solvatochromism of PPB, the empirical solvation parameters of Kamlet and Taft were analyzed. Table 1 summarizes the corresponding parameters \( \alpha \), \( \beta \) and \( \pi^* \) of the used solvents. The maximum absorption wavenumber (\( \nu_{\text{max}} \)) can be related to these parameters separately. However, the use of a multiparametric equation provides a better quantitative description of the solvatochromic shifts and takes into account specific (\( \alpha \) and \( \beta \)) and non-specific (\( \pi^* \)) interactions. The following multiparametric relationship was obtained for PPB, applying Eq. (1) and using the \( \nu_{\text{max}} \) values (for the two bands) listed in Table 1.

For band I:

\[
\nu_{\text{max}} = 39192 + 2.347\pi^* + 564.5\alpha + 48.41\beta \\
(\eta = 5, R^2 = 0.9973, SD = 17.24, \text{Significance F} = 0.003) \tag{2}
\]

The effects of each parameter are: \( \pi^* = 0.38 \% \), \( \alpha = 91.8 \% \) and \( \beta = 7.9 \% \). It can be seen that specific interactions have the most contribution to the solvatochromism of PPB. For this reason, Eq. (2) can be rewritten as,
\[ \nu_{\text{max}} = 39194 + 564.8\alpha + 47.33\beta \]

\[ (n = 5, R^2 = 0.9973, \text{SD} = 24.38, \text{Significance F} = 0.66) \]  

(3)

The effects of each parameter are: \( \alpha = 92.3\% \) and \( \beta = 7.7\% \). Different types of intermolecular hydrogen bonding (IHGs) may affect the electronic transitions of this compound. However, the results obtained suggest that the HBA ability of the solvent is the most important factor. The positive sign of \( \alpha \) is consistent with the blue shift observed in solvents with higher \( \alpha \) values, indicating that the hydrogen bonds formed by PPB with the solvent may stabilize the ground state more than the excited state.

When Equation (1) is used to analyze the solvatochromism of band II, the following result is obtained:

\[ \nu_{\text{max}} = 36357 - 1066\pi^* - 42.55\alpha - 268.6\beta \]

\[ (n = 5, R^2 = 0.9750, \text{SD} = 22.8, \text{Significance F} = 0.2) \]  

(4)

The effects of each parameter are: \( \pi^* = -77.4\% \), \( \alpha = -3.1\% \) and \( \beta = -19.5\% \). It can be seen that the standard error of the parameter \( \alpha \) (62.2) which indicates that there is not a statistically significant variable in the regression equation and this parameter may be neglected. Equation (4) shows that the solvation of PPB is mainly affected by dipolar interactions (\( \pi^* \)) and the acceptance of hydrogen bonds (\( \beta \)) by the solvent molecules. Therefore, the multiparametric equation can be rewritten as a biparametric equation,

\[ \nu_{\text{max}} = 39194 - 1300.2\pi^* - 386.4\beta \]

\[ (n = 5, R^2 = 0.9633, \text{SD} = 19.53, \text{Significance F} = 0.04) \]  

(5)

The effects of each parameters are: \( \pi^* = -77.1\% \) and \( \beta = -22.9\% \). Moreover, the negative signs of the \( \pi^* \) and \( \beta \) coefficients indicate that the specific and non-specific interactions in solvents may stabilize the excited state more than the ground state, resulting in a red shift.

From previous results, the solvatochromic shifts of PPB can be explained by the polarization effects of the solvents. These interactions stabilize the excited state more than the ground state (for band II), and a red shift is observed in solvents with higher \( \pi^* \) parameter. However, the solvatochromic shifts of band I are mainly due to the formation of IHGs between the H in the pyridyl-pyrazole of PPB and the solvents. This interaction stabilizes the ground state more than the excited state, and a blue shift is observed in solvents with a higher \( \alpha \) parameter.

**Solvatochromism of PPB in Binary Solvent Mixtures**

The solvent effects on the electronic absorption spectra of PPB in binary mixtures were also analyzed. The maximum absorption wavenumber of PPB was measured in DCM-EtOH mixture using different solvent ratios. The spectra of PPB at different solvent ratios are shown in Figure 3.

For the ideal binary mixture, a linear additive equation can be written for \( \nu_{\text{max}} \) of the solute [26].
\[ \nu_{12_{\text{ideal}}} = \nu_1 X_1 + \nu_2 X_2 \]  

In this equation \( X_1 \) and \( X_2 \) are the mole fraction of solvents 1 and 2, and \( \nu_1, \nu_2, \nu_{12_{\text{ideal}}} \) are the values of \( \nu_{\text{max}} \) of PPB in solvent 1, solvent 2 and in the binary mixture, respectively.

The \( \nu_{12_{\text{ideal}}} \) values for the binary mixtures (DCM-EtOH) are calculated by using Equation (6) over the entire range of solvent composition and compared with the experimental values of band I and band II (Figure 4).

From previous figures, there is a deviation from linearity for the experimental values indicating a preferential solvation by one solvent. To explain this interaction, the preferential solvation equation [27] is used. This approach considers the solvent to be distributed between two phases, the bulk and the solvation shell of the solute. It is assumed that the solvation shell is made up of independent sites that are always occupied. In a non-ideal mixture, the \( \nu_{12} \) can be expressed by Equation (7)
\[ \nu_{12} \text{ideal} = \nu_1 X_1^L + \nu_2 X_2^L \]  

(7)

where \( X_1^L \) and \( X_2^L \) represent the mole fraction of the solvents 1 and 2 in the solvation shell of the solute, respectively. \( X_2^L \) can be calculated from experimental measurements through the following expression:

\[ X_2^L = \frac{\nu_{12} - \nu_1}{\nu_2 - \nu_1} \]  

(8)

In order to quantify the extent of preferential solvation, a parameter \( \delta_{S2} \) may be used. This parameter can be defined as the difference between \( X_2^L \) and \( X_2 \) [28]:

\[ \delta_{S2} = X_2^L - X_2 \]  

(9)

A positive value of \( \delta_{S2} \) indicates a preference for solvent 2 over solvent 1, while a negative value of \( \delta_{S2} \) signifies the opposite. In Table 2 the values of \( \delta_{S2} \) for PPB in both analyzed bands are listed.

An increase in the \( \nu_{12} \) values as the mole fraction of EtOH increases in the mixtures can be seen. In the case of band I, the preferential solvation for EtOH is observed and the index \( \delta_{S2} \) is maximum at \( X_2 = 0.108 \). This indicates that at low concentrations of EtOH in the bulk phase, there are more EtOH than DCM molecules surrounding the solvation shell of PPB. To explain this effect, it must be noticed from our results for pure solvents that the solvatochromism of PPB (Band I) is mainly affected by the HBD ability of the solvent (\( \alpha \)). Then, the IHB formation between PPB and EtOH may be responsible for the preferential solvation of this solute in DCM-EtOH mixture.

Different observations can be seen for band II in the mixture. In Figure 4 the variation of \( \nu_{12} \) with \( X_2 \) in DCM-EtOH mixtures is seen. An increase in the \( \nu_{12} \) values as EtOH is added to the mixture is observed, but preferential solvation for DCM is detected (because of a negative value of \( \delta_{S2} \)) and the index \( \delta_{S2} \) value for DCM is maximum at \( X_2 = 0.108 \). This result may be explained using the \( \pi^* \) parameter of the solvents. In pure solvents, the solvatochromism of PPB (Band II) is mainly affected by the dipolarity interactions of the solvent (\( \pi^* \)). The higher

<table>
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<th>( X_2 )</th>
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<th>( \lambda_2 )</th>
<th>( \delta_{S2} )</th>
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</table>

Table 2. Indexes of preferential solvation (\( \delta_{S2} \)) of PPB in DCM-EtOH mixture for two bands. \( X_2 \) is the ethanol mole fraction in the mixture, \( \nu_{12} \) is the experimental absorption wavenumber measured in the mixture and \( \nu_{12} \text{ideal} \) are calculated by using Equation (6). \( \nu_{12} \) and \( \nu_{12} \text{ideal} \) are expressed in cm\(^{-1}\).
value of $\pi^*$ for DCM (0.82) may be responsible for the preferential solvation of this solute in DCM-EtOH mixture. Then, DCM may show non-specific interactions with this solute.

Figure 5. The spectra of PPB at different solvent ratios. (a) Ethanol : H$_2$O (b) Tetrahydrofuran : H$_2$O

Figure 6. Absorption Spectra at different concentrations of PPB in two solvent mixtures along with their calibration curves (a) in Ethanol : H$_2$O (b) in Tetrahydrofuran : H$_2$O
Spectrophotometric determination of dissociation constant of PPB in Binary Solvent Mixtures

Spectrophotometric measurements were performed to determine the pK_b of PPB in two binary solvent mixtures (EtOH-H_2O and THF-H_2O) and two graphical methods were applied. The results obtained using the different methods were compared. The spectra of PPB at different solvent ratios for the two mixtures are shown in Figure 5. In the case of ethanol : H_2O mixture, hypsochromic shift is observed with increasing of H_2O ratio for both bands. However, no significant changes in the absorption intensity; till the 1:1 ratio, are observed, after that the intensity starts to decrease dramatically. This is because of PPB is slight soluble in H_2O. Therefore, the 1:1 ratio has been chosen for further study. In the case of THF : H_2O mixture, both bands are red shifted as the ratio of H_2O is increased; till the 1:1 ratio is reached, then they are blue shifted. However, the absorption intensities for both bands are decreased as the ratio of H_2O increased. Also, the 1:1 ratio has been chosen for further study.

Figure 7. Absorption Spectra of PPB At different pH levels in: (a) EtOH : H_2O mixture (b) THF : H_2O
The 1:1 ratio was used to determine the pKₐ of PPB in both mixtures. Figure 6 shows the electronic absorption spectra of different concentrations of PPB in both solvent mixtures (1:1) along with their calibration curves. The values of molar absorptivities are shown in Table 3.

Plots of absorbance against λ for PPB at different pH levels and in both solvent mixtures are illustrated in Figure 7.

### Theoretical Foundations

When an acid HA is dissolved in water, equilibrium is established:

\[
HA + H_2O \leftrightarrow A^- + H_3O^+ \tag{10}
\]

The acid HA donates a proton to water, and it converts to the anion A⁻ (conjugate base). HA and A⁻ are referred to as a “conjugate pair” [29]. The acid dissociation constant, Kₐ, for HA can be expressed as follows:

\[
K_a = \frac{[A^-][H_3O^+]}{[HA]} \tag{11}
\]

Kₐ is a constant and can be defined in terms of the concentration ratio [A⁻]/[HA], which can be determined spectrophotometrically [30]. If a solution with a total concentration Cₜ becomes very acidic, all acid exists as HA. The absorbance of the solution at a given wavelength λ is given by:

\[
A_{HA} = \epsilon_{HA} \cdot b \cdot C_T \tag{12}
\]

where \(\epsilon_{HA}\) is the molar absorptivity of HA at wavelength λ and b is the width of the cell containing the solution. If the solution is too basic, the same concentration of acid is converted into A⁻ and the absorbance at the same wavelength is given by:

\[
A_{A^-} = \epsilon_{A^-} \cdot b \cdot C_T \tag{13}
\]

where \(\epsilon_{A^-}\) is the molar absorptivity of A⁻. At an intermediate pH, the absorbance is given by:

\[
A_{HA} = \epsilon_{HA} \cdot b \cdot C_T + \epsilon_{A^-} \cdot b \cdot C_T \tag{14}
\]

where the total concentration of the acid is defined as:

\[
C_T = C_{HA} + C_{A^-} \tag{15}
\]

For a given \(C_T\), Equations (12)-(15) can be combined to obtain:

\[
\frac{[A^-]}{[HA]} = \frac{C_{A^-}}{C_{HA}} = \frac{A - A_{HA}}{A_{A^-} - A} \tag{16}
\]
This relationship must be studied at multiple wavelengths, including one where HA absorbs appreciably but A\(^-\) does not, other where A\(^-\) is much more absorbent than HA. The pH (−\(\log[H_3O^+]\)) of the solutions must be in the transition range of the acid so that both HA and A\(^-\) are present in appreciable concentrations. \(K_a\) can be evaluated graphically by converting Equation (11) to logarithmic form:

\[
\log K_a = \log[H_3O^+] + \log\left(\frac{[A^-]}{[HA]}\right)
\]

(17)

In addition, the combination of Equation (16) and the definition of \(pK_a = −\log K_a\) results in:

\[
\log\left(\frac{[A^-] - [HA]}{[A^-] - [A]}\right) = pH - pK_a
\]

(18)

Figure 8. Plot of absorbance vs. pH at wavelengths of 281 and 308 nm in (a) EtOH : H\(_2\)O (b) THF : H\(_2\)O

Figure 9. Linear regression of \(\log([A - A_{HA})/(A_{A^-} - A)]\) vs. pH in (a) EtOH : H\(_2\)O (b) THF : H\(_2\)O
Therefore, a graph of \( \log\left(\frac{A - A_{HA}}{A_{A} - A}\right) \) vs. pH has a slope of one. If this condition holds, the y-axis intercept gives the negative \( pK_a \). In our study, the PPB is considered to be a weak base. Therefore, the dissociation constant of it is referred to as \( K_b \) and can be calculated from the equation (19):

\[
pK_b = 14 - pK_a
\]  

(19)

Spectrophotometric measurements were performed for PPB to determine its \( pK_b \), and two graphical methods were applied. The results obtained using the different methods were compared, and the \( pK_b \) value was determined. The first method was to take the spectra of the species with extreme pH levels (pH = 1.5 and pH = 10.0 in this case) and determine the wavelengths of maximum absorbance. As illustrated in Figure 7, the absorbance spectrum of the solution of pH = 1.5 exhibited a peak at 308 nm; the peak of the basic solution occurred at 281 nm. The plot of the absorbance vs. pH at these wavelengths is presented in Figure 8. The \( pK_a \) was obtained by determining the pH of the point of intersection of the two linear curves as shown in Figure 8. The \( pK_b \) can be then calculated from Equation (19).

The second method was to plot \( \log\left(\frac{A - A_{HA}}{A_{A} - A}\right) \) vs. pH (Equation (18)), where \( A_{HA} \) is the absorbance of the acid solution, \( A \) is each of the intermediate absorbances and \( A_{A} \) is the absorbance of the basic solution. A graph of the data and the linear regression are shown in Figure 9. The \( pK_b \) is obtained from the intercept of the line with the y-axis according to the equation (18) and then the \( pK_b \) value from equation (19).

Table 4 shows a summary of the results obtained using the two methods.

**CONCLUSION**

The solvent effect on the electronic absorption spectra of two bands of PPB was analyzed in single and binary solvent mixtures of diverse nature using UV-vis spectroscopy. The solvatochromic shifts observed in pure solvent were evaluated using linear solvation energy relationships (LSER) with the Kamlet and Taft parameters. The spectroscopic behavior in binary solvent mixtures was analyzed using the preferential solvation approach.

The solvatochromism of PPB (band I) in pure solvent is affected mainly by the HBA ability of the solvent. On the other hand, the solvatochromic shifts of PPB (band II) are affected mainly by dipolar interactions and the acceptance of hydrogen bonds by the solvent molecules.
In DCM-EtOH solvent mixtures, PPB (band I) exhibits preferential solvation by EtOH in the whole concentration range. However, band II appears to be solvated preferentially by DCM (because of a negative value of $\delta_{S2}$).

The application of spectrophotometric titration allowed the acid dissociation constant of PPB be determined. Two methods of analysis were used and produced results with good similarity.

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