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Spectrophotometric determination of acidity constants of 1-(2-pyridylazo)-2-naphthol in water and mixed water-organic solvents

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ABSTRACT

The acidity constants of 1-(2-pyridylazo)-2-naphthol(o-PAN) in water-organic solvents mixtures solutions at 25^0C and an ionic strength of 0.1 M have been determined by spectrophotometrically. The organic solvents used were the acetonitrile (AN), dimethyl sulfoxide (DMSO) and dimethyl formamid (DMF).To evaluate the pH–absorbance data, a resolution method based on the combination of soft- and hard-modeling is applied. The acidity constants of all related equilibria are estimated using the whole spectral fitting of the collected data to an established factor analysis model. DATAN program was used for determination of acidity constants. Generally, the pKa_1 values decreases and pK_2 increase with an increase in the content of the organic solvent. There are linear relationships between acidity constants and the mole fraction of different solvents in the mixtures. The effect of solvent properties on acid-base behavior is discussed.

KEYWORDS

1-(2-pyridylazo)-2-naphthol(o-PAN);
DATAN;
Acidity constants;
Organic solvents;
DMF;
AN;
DMSO.

INTRODUCTION

The acidity constants of organic reagents play a very fundamental role in many analytical procedures such as acid–base titration, solvent extraction and complex formation. But in determining of acidity constants of these molecules we are faced with several drawbacks, such as low solubility in aqueous solutions and the low values of acidity constants. Therefore, in order to enhance the acidity constants on one hand and to increase the solubility on the other, we forced to choose mixed solvents. Mixed solvents are interesting, because two solvents mixed together produce a solvent with quite different properties, both, physically (dielectric, density and viscosity) and chemically (acid–base and donor–acceptor properties). As far as the acid–base properties are concerned, an important feature is that the nature of the solvent is crucial for the strength of acids and bases. In particular, important is the proton affinity, in other words, the proton-donating and proton-accepting properties of solvent, as well as its polarity. In addition, the ionization degree of solute depends on the dielectric constant of solvent. Media of high dielectric constants are strongly ionizing, whereas those of low dielectric constants ionize to a lesser extent[1,2]. By mixing solvents of different polarity in proper ratios, dielectric constant of the medium can be varied and, at the same time, the strength of dissolved acids and bases[3].

Acid dissociation constants (i.e. pKa values) can be a key parameter for understanding and quantifying chemical phenomena such as reaction rates, biological activity, biological uptake, biological transport and environmental fate[4]. There have been several methods of the determination of acidity constants, including potentiometric titration, spectrophotometry, capillary electrophoresis, and so on. Spectroscopic methods are, in general, highly sensitive and are as such suitable for studying chemical equilibria solution. If the components involved can be obtained in pure form, or if their spectral responses do not overlap, such analysis is, in general, trivial[5]. For many systems, particularly those with similar components, this is not the case, and these have been difficult to analyze. Therefore, to overcome this problem we have to employ the graphical and computational methods. Up to the middle of the 1960s, the evaluation of equilibrium measurements was based on the different graphical methods. These methods were reviewed in considerable details by Rossotti[6]. Starting from middle of the 1960s, computers acquired ever-greater importance in the evaluation of equilibrium measurement data using multiple wavelengths or full spectrum to determining the stability and acidity constants. The most relevant reports are on LETAGROP-SPEFO[7], SPECFIT[8], SQUAD[9] and HYPER QUAD[10]. All these computational approaches are based on an initial proposal of a chemical equilibrium model defining species stoichiometrics and based on mass-action law and mass balance equations (hard modeling methods) and also involve least-squares curve-fitting procedures. The starting point of using soft modeling was in 1971 that Lawton and Sylvestre[11] introduced chemometrics-based method for spectral analysis. These approaches are free from the restriction of the mass-action law and do not require an initial model of species to be set up. Data analysis, carried out by the DATAN package that was developed by Kubista group[12,13] and is called a physical constraints approach, provides a unique solution by requiring that the calculating concentrations obey an assumed equilibrium expression. It has been demonstrated by application to the determination of the acidity constants of two and four protolytic forms of fluorescein. A possible advantage of the Kubista et al.[13] method is that it mixes a soft-modeling approach with a hard-modeling approach. This might be a better and more general strategy, since it can handle different situations, with only a partial knowledge of the chemistry of the system. The physical constraints method calculates spectral profiles, concentrations, and equilibrium constants by utilizing equilibrium expressions that are related to the components. The theory and application of the physical constraints method has been discussed by Kubista et al. in several papers[13-23].

In this work, we applied the physical constraints approach to determine the acidity constants of o-PAN in different binary water-organic solvents (MDF, AN, DMSO) mixtures at 25°C and an ionic strength of 0.1 M spectrophotometrically. The analysis is readily performed with the computer program DATAN[13].

Theory

The theory and application of the physical constraints method was discussed by Kubista et al., in several papers[13-27]. However, the general principal will be outlined briefly.

Spectra of o-PANat different pH values are digitized and arranged in a data matrix A, which is decomposed into an orthonormal basis set by NIPALS or any equivalent method[13]:

$$\mathbf{A} = \mathbf{TP^T} + \mathbf{E} \approx \sum_{i=1}^{r} \mathbf{t_i p_i^T} \qquad (1)$$

where the orthogonal target vectors t_i and orthonormal projection vectors p_i^T are mathematical constructs that cannot be directly related to component spectra and concentrations, r is the number of independent spectroscopic components, which corresponds to the number of light-absorbing chemical species. It is determined by visual inspection of the t and P^T vectors or by performing statistical methods, such as, χ^2-test[28-30]. E is an error matrix.

By assuming linear responses, the spectra in matrix

A are linear combinations of the concentrations, C, and spectral responses, V, of the chemical components.

$$A= CV+E\approx CV \qquad (2)$$

If the spectral profiles of the components are known, the concentration of each component can easily be calculated, for example, by least squares minimization. If standards are not available the common belief has been that the components' spectral responses can not be separated, which precludes their identification. This is due to ambiguity in determining the rotation matrix, R, in the following equations; from Eqs. (1) and (2) follows that there is a square matrix R (r × r) that satisfies.

$$T=CR \qquad (3a)$$

$$P=R^{-1}V \qquad (3b)$$

since $A=CV=C(RR^{-1})V=(CR)(R^{-1}V)=TP^{T}$

If R can be determined, the spectral responses V and concentrations C of the components can be calculated from the target T and projection P^{T} matrices:

$$C=TR^{-1} \qquad (4a)$$

$$V= RP^{T} \qquad (4b)$$

The thermodynamic expression that describes the components' concentration is the main constraint used to determine R, from which thermodynamic parameters and components' spectral responses and concentration are calculated. Therefore, the strategy for determining the rotation matrix R is as follows. Concentrations of the chemical species are calculated from the equilibrium expressions for various trial values of the equilibrium constants, and are fitted to the calculated target vectors according to Eq. (3a).

The accuracy of this fit depends crucially on the trial values of the equilibrium constants, and best fit determines their values and the elements of matrix R.

EXPERIMENTAL

Materials

1-(2-pyridylazo)-2-naphthol (o-PAN), DMF, AN, DMSO, hydrochloric acid, sodium hydroxide and potassium nitrate were analytical grade commercial products from Merck. These reagents were used without further purification. Standard stock solution of 4.0×10^{-5} M of o-PAN was prepared by dissolving appropriate amounts of o-PAN in AN, DMF, DMSO.

Instrumentation

A Scinco (S-2100) spectrophotometer controlled by a computer and equipped with a 1-cm path length quartz cell was used for UV-vis spectra acquisition. Spectra were acquired between 320 and 650nm (1nm resolution). The pH values were measured by a Metrohm CH-9101 pH meter furnished with combined calomel Ag/AgCl electrode. To precalibrate the pH meter in the various binary organic + water mixtures used, 0.01M solutions of oxalate and succinate buffers were employed. Then to calibrate the pH meter according to the concentration of H^{+} some strong acid-base titrations were performed. As the proton concentrations driving strong acid-strong base titrations can be readily calculated, the concentration pH value (pH) = -log $[H^{+}]$) is related to the operational pH. The details of the electrode calibration in partially aqueous solutions media are presented elsewhere[31]. The data were treated in an AMD 2000 XP (256 MB RAM) microcomputer using the DATAN package.

Spectrophotometric titrations

For the o-PAN (8.65×10^{-6}M) in water- organic solvents mixtures titrations, absorption spectra were measured with a titration set-up consisting of a computer interfaced to a spectrophotometer. After each pH adjustment, solution is transferred into the cuvette and the absorption spectra are recorded. Ionic strength was maintained at 0.1M by adding appropriate amounts of KNO_3. All measurements were carried out at the temperature (25 ± 0.5^{0}C).

RESULTS AND DISCUSSION

The absorption spectra of o-PAN in binary solvent mixtures at various pH values and in the interval (320 to 650) nm were recorded. Sample spectra of o-PAN at different pH values in 50 vol % of the organic solvents (AN, DMSO, DMF with the pH ranging from 1.5 to 14) to water at constant. Ionic strength 0.1 M is shown in figure 1. The principal component analysis of all absorption data matrices obtained at various pH values shows at least three significant factors that also supported by the statistical indicators of Elbergali et al.[23] These factors could be attributed to the two dissociation equilibria of a diprotic acid such o-PAN. The

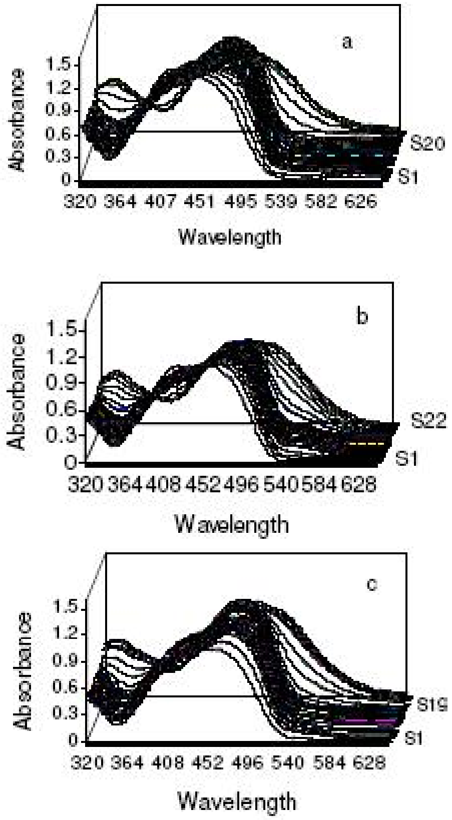


Figure 1 : Absorption spectra of o-PAN in (a) 50wt % acethonitrile to water, (b) 50wt % dimethylsulfoxide to water, and (c) 50wt % dimethylformamid to water at constant ionic strength of 0.1M.at different pH values

TABLE 1. Acidity constants of o-PAN in different organic solvents + water mixtures at 25°C and constant ionic strength of 0.1M

	Previous report		Dimethyl formamid		Dimethyl sulfoxide		Acetonitrile	
Wt%	Pk_{a1}	pK_{a2}	Pk_{a1}	pK_{a2}	Pk_{a1}	pK_{a2}	Pk_{a1}	pK_{a2}
	2.0^a	12.3^a						
	1.9^b	12.2^b						
	1.6^c	12.2^c						
	2.9^d	11.2^d						
	1.9^e	12.2^e						
25			2.12	11.74	2.7	11.65	2.19	12.16
50			2.05	11.93	2.3	11.81	1.84	12.74
75			1.95	12.25	1.9	11.99	1.62	12.91

^{a}Reference[32]; ^{b}Reference[32]; ^{c}Reference[34]; ^{d}Reference[35]; ^{e}Reference[36]

p*K*a values of o-PAN were investigated in three different water-AN, water-DMSO and water-DMF mixtures spectrophotometrically at 25^0C and an ionic strength of 0.1 M.

Acidity constants of o-PAN in several mixtures were evaluated using the DATAN program using the corresponding spectral absorption-pH data. From inspection of the experimental spectra, it is hard to guess even the number of protolytic species involved. The three calculated most significant projection vectors with clear spectral features (as compared to noise) evidence the presence of three spectroscopically distinguishable components. Their shapes, however, are clearly unphysical and cannot be directly related to the spectral response of the three protolytic forms. The output of the program are pKa values and their standard deviation, the number of principal components, projection vectors (loadings), concentration distribution diagrams, and the pure spectrum of each assumed species. The obtained pKa values are listed in TABLE 1. The pKa values correspond to the pH dependent variation of absorption spectra in all solvent mixtures. There is a good agreement between the obtained results for

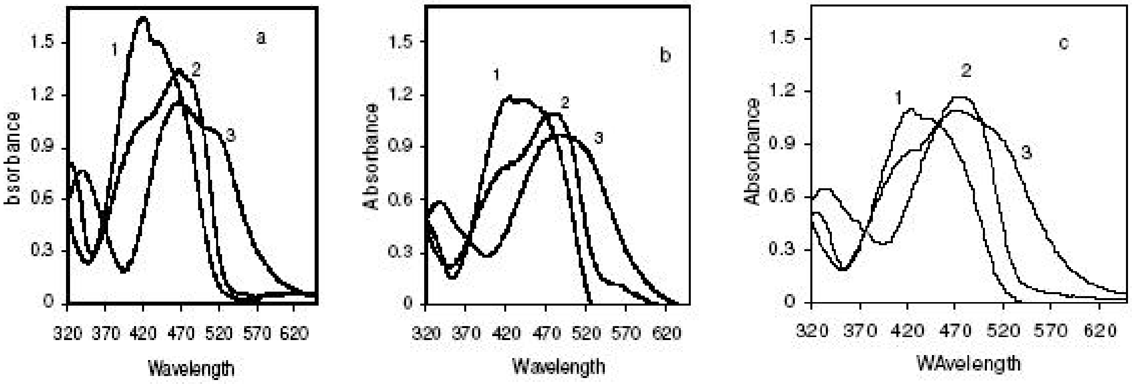


Figure 2 : The pure spectra of different form of o-PAN (a) 50 wt % acethonitrile to water, (b) 50wt % dimethylsulfoxide to water, (c) 50 wt % dimethylformamid to water at constant ionic strength of 0.1M.at different pH values, H_2L^+(1), HL^- (2), L^{2-} (3)

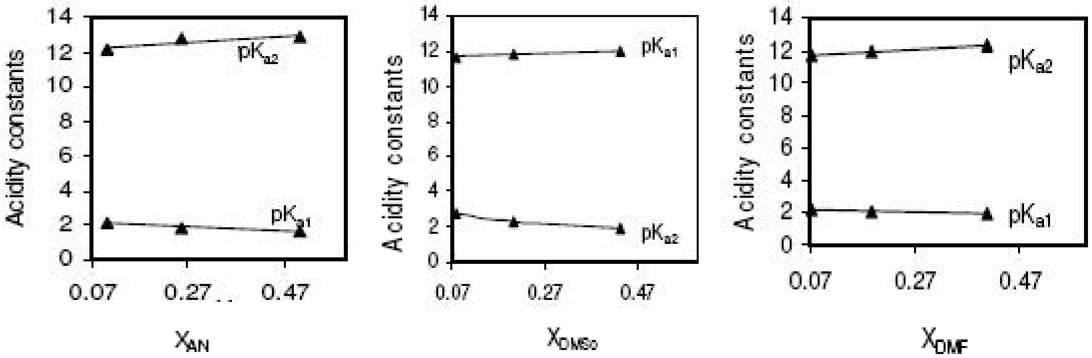
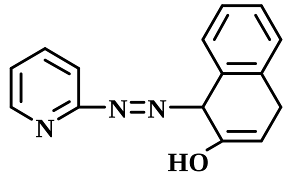


Figure 3 : Variation of acidity constants values of o-PAN with mole of different organic solvents

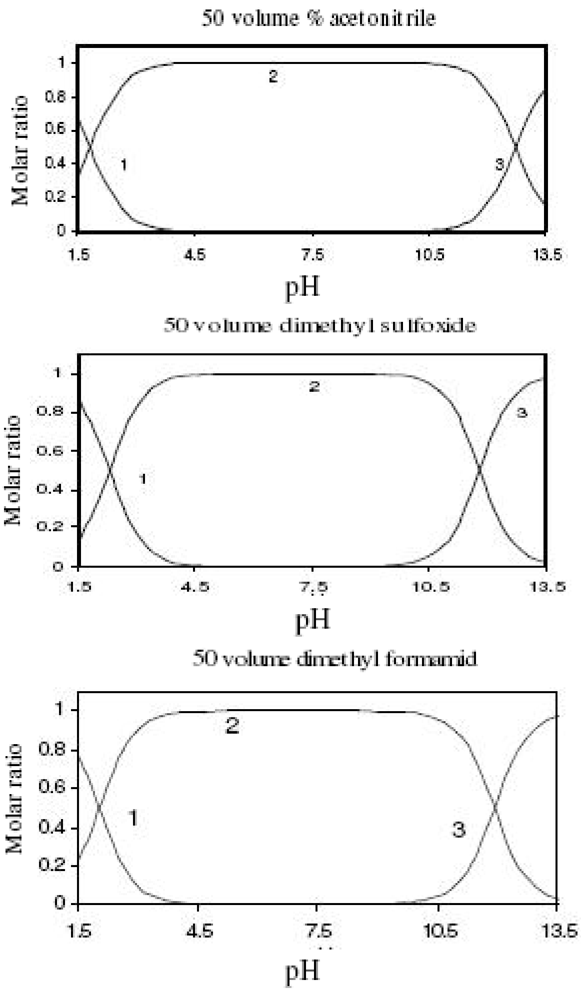
pKa values in this work and previously reported values[31-35]. The differences observed between the pKa values are due to probable experimental errors of old methods, against chemometrics based methods, by using the whole spectral domain, reduce considerably the level of noise. So the obtained acidity constants are more reliable and precise than previous methods. One of the very important outputs of DATAN is calculated spectrum of different forms of o-PAN at each solvent mixture. Sample spectra of the calculated pure spectral profiles of all species in different organic solvents/water mixtures are shown in figure 2. As the mole fraction of organic solvents increased, the absorption intensity changes differently for each species of o-PAN. It is interesting to note that the nature and the composition of the solvent have a fundamental effect on each pure spectrum. As is clear from figure 2, this effect is more for H_2L^+ and L^- than HL. The spectrum of the H_2L^+ species has a λ_{max} at 425nm. The solvent effect on this spectrum is very interesting. As the various solvent, the changed absorption intensity. This can be described using the nonelectrostatic (H-bonding) property of the stabilization and/or destabilization of the ground and excited states of the $n\rightarrow\pi^*$and $\rightarrow\pi^*$ transitions. The appearance and disappearance of some shoulder and absorption peaks of each species is related to the type and mass percent of the organic solvent.

As discussed above, this indicates that the acid ionization constants of o-PAN obtained in various aqueous mixture media of acetonitrile, dimethyl sulfoxide, dimethyl formamid and are governed by electrostatic effects. Acidity constants of two steps of dissociation o-PAN at first step decrease and second step increases with increasing mole fraction of the solvents in the mixed binary solvents. It has been shown that the solvating ability[37] (as expressed by the Gutmann donicity scale) and dielectric constant of the solvent play a fundamental role in dissociation reactions. Water is a solvent of high solvating ability (i.e., donor number DN = 33, dielectric constant ε = 87.3), which can dissociate the acid and stabilize the produced anion and hydrogen ion. Thus, it is expected that addition of acetonitrile (DN = 14, ε=36), dimethyl sulfoxide (DN = 26.5, ε= 46.6) and dimethyl formamid (DN = 26, ε=44), with lower donor numbers and dielectric constants relative to water decrease the extent of interaction between the acid anion and proton with solvent, and this decreases the acidity constants of o-PAN.



SCHEME 1: Chemical structure of o-PAN

It is interesting to note that there is actually a linear relationship between the pKa of two dissociation steps and the mole fraction of different solvents ($X_{Solvents}$) in the binary mixed solvents used in figure 3. The same trend has already been reported for various organic molecules in different solvent mixtures[38-40]. It has been reasonably assumed that preferential solvation of the charged particles by water is mainly responsible for such a monotonic dependence of acidity constants of the o-PAN on the solvent composition. So according to distribution diagrams it is may conclude that the spectra at smaller pH than 1.5 assigned to H_2L^+ form because this form is dominated at this range. At pH 2.0-10.5 inter-


50 volume % acetonitrile

50 volume dimethyl sulfoxide

50 volume dimethyl formamid

Figure 4: Distribution of major species of o-PAN H_2L^+(1), HL^- (2), L^{2-} (3), as a function of pH for the spectral data of figures 1

vals the HL form is dominated and hence the spectra mostly attributed to this form. The L^{-2} form appeared at pH>11.5. Samples of obtained distribution diagrams are shown in figure 4.

It is clear that, the dissociation of an uncharged acid in a solvent requires the separation of two ions of opposite charges. The work required to separate these charges is inversely proportional to the dielectric constant of the solvent. The energy required for dissociation is supplied by solvation of the ions and also the proton transfer from acid to the solvent molecule supplies an additional energy. If the dielectric constant and the solvating ability of the solvent are decreased, more energy will be required to separate the anion and cation and consequently the extent of dissociation of acid will be lowered. Therefore, the decrease in first step and the increase in second step of dissociation constants is due to increasing the mole fraction of acetonitrile, dimethyl sulfoxide and dimethyl formamid, in the binary mixed solvent.

CONCLUSION

In this study we report, acidity constant of the 1-(2-pyridylazo)-2-naphthol (o-PAN) in different and mixed solvents at 25°C and an ionic strength 0.1M. We have used the DATaAnalysis (DATAN) program to analyze correlated spectroscopic data. The pK_a values of 1-(2-pyridylazo)-2-naphthol(o-PAN) obtained in dimethyl formamid, acetonitrile and dimethylsulfoxide-water mixtures. The effect of solvent properties on acid-base behavior is discussed. This indicates that the acid ionization constants of 1-(2-pyridylazo)-2-naphthol (o-PAN) obtained in various organic-water mixtures are governed by electrostatic effects. The pKa values correspond to the pH-dependent variation of absorption spectra in all solvents mixtures. The physical constrains method (DATAN) is a useful tool for the resolution of different species present in a multi-equilibria system.

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