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Multiwavelength spectrophotometric determination of protolytic constants of 4-(2-pyridylazo) resorcinol (PAR) in binary DMF–water mixtures

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Abstract

A multiwavelength spectrophotometric titration method was applied to study the protolytic constants of 4-(2-pyridylazo) resorcinol(PAR), in binary DMF + water mixtures. UV–vis absorption spectra of PAR solution were recorded in the course of pH-metric titration of acidic solutions of PAR with standard base solution. The protolytic equilibrium constants, spectral profiles, concentration diagrams and also the number of components have been calculated from the fitting of the pH-spectral titration data with appropriate mass balance equations by a home written program according to an established target factor analysis. To precise determination of number of absorptive components a recently developed statistical indicator function (IND function) was used. A glass electrode calibration procedure based on a four-parameter equation $\mathrm{pH} = \alpha + S\mathrm{p_cH} + J_{\mathrm{H}^+}[\mathrm{H}^+] + J_{\mathrm{OH}^-}K_\mathrm{w}/[\mathrm{H}^+]$ based on the Gran's plots was used to obtain pH readings in the concentration scale ($\mathrm{p_cH}$). It has been observed that there is an inverse relationship between second and third protolytic constants and mole fraction of DMF. The effect of the solvent on the protolytic constants was discussed.

Keywords: 4-(2-Pyridylazo)resorcinol; PAR; Acidity constants; Multiwavelength spectrophotometry; DMF + water mixture; Target factor analysis; IND function

1. Introduction

Acid dissociation constants are useful physico-chemical properties describing the extent of ionization of functional groups with respect to pH. These parameters are important in research areas such as acid–base titration, solvent extraction, complex formation, and ion transport. It has been shown that the acid–base properties affect the toxicity [1], chromatographic retention behavior, and pharmaceutical properties of organic acids and bases. Much of the theoretical foundation of modern organic chemistry is based on the observation of the effects on acid–base equilibrium of changing molecular structure [2,3].

It has been shown that the spectrophotometric methods are suitable for determining protolytic constants of compounds which are contains chromophore(s) and ionizable center(s) such that the protonated and deprotonated forms [4].

The spectroscopic instrumentation used today, however, almost invariably has the capacity to collect data in a full spectral range. Using a single or a few wavelengths discards most of the information in the collected spectra and requires both the presence of and knowledge of such suitable wavelengths. However, in many cases, the spectral responses of components overlap and analysis is no longer straightforward [5,6]. The predefined model, known as hard-modeling analysis, cannot be applied if crucial information is missing. Soft modeling or model free approaches are based on much more general prerequisites, such as positive molar absorbance, positive concentration of all species, unimodality of concentration profiles, and closure (concentration of all species are the same for all solutions). Naturally, if the strengths of hard- and soft-modeling methodologies are combined, a much more powerful method of data analysis can be expected [7–9]. The

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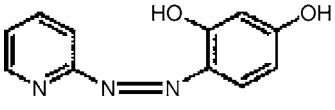
principle component analysis along with different curve resolution method [10–20] have been applied to spectral data to extract information utilizing a large number of absorbances measured at different wavelengths. In continuation of previously reported works [21,8], in this paper, we want to present a hard and soft combining model to determine the protolytic constants of PAR in DMF + water binary mixtures by spectophotometric titration. As DMF–water mixtures can be used in several research works especially as carrier phases in liquid chromatography these types of data may be very helpful and as good criteria to choose and apply appropriate solvents mixtures.

2. Theory

The spectra of 4-(2-pyridylazo)resorcinol [CAS RN 1141-59-9] (PAR, I) at different pH values are digitized and arranged in a data matrix X with size of $n_s \times n_w$, where n_s denotes the number of spectra and n_w the number of wavelengths for which absorbances were recorded.



I

Under the assumption of bilinearity, X can be described by the concentration profiles (c_i, $n_s \times 1$) and the pure analyte spectra (a_i, $1 \times n_w$) according to:

$$X = \sum_{i=1}^{n_c} a_i c_i = CA + E_1 \tag{1}$$

where n_c is the number of chemical components. E_1 is the residual matrix and should contain only noise. Principal component analysis decomposes the spectral data matrix into a score T and a loading matrix P (P^T is the transpose of P):

$$X = TP^T + E_2 \tag{2}$$

With the correct number of principal components, that is, equal to n_c [22–24] E_2 is a residual matrix and contains insignificant information. Since the concentration and spectral profiles are a linear combination of the T and P matrixes, thus,

$$C = TR^{-1} \tag{3}$$

$$A = RP^T \tag{4}$$

in which R ($n_c \times n_c$) is a square transformation matrix. From a known (or tested) system of equilibrium equations describing the system and the trial values of equilibrium constants, concentration profiles $C_{\text{sim},i}$ ($n_s \times 1$) for all species and pH values can be calculated. The concentration vectors for all species are gathered in a matrix C_{sim}, and a least-squares fit is performed (cf. Eq. (3)):

$$R^{-1} = (T^T T)^{-1} T^T C_{\text{sim}} \tag{5}$$

Target testing has been applied to a variety of problems and proved to be a useful technique [25–30]. So, according to a standard target testing procedure, [25] if Eq. (5) is inserted in Eq. (3), we obtain a matrix C_{calc} and then the residual matrixes C_{res} and T_{res}, calculated as:

$$C_{\text{res}} = C_{\text{sim}} - C_{\text{calc}} = C_{\text{sim}} - TR^{-1} \tag{6}$$

$$TR^{-1} = C_{\text{sim}} - T(T^T T)^{-1} T^T C_{\text{sim}} \tag{7}$$

$$T_{\text{res}} = T - T_{\text{calc}} = T - C_{\text{sim}} R \tag{8}$$

The C_{res} and T_{res} can be used in different ways in an objective function that has a minimum for C_{sim}, that is, for C_{sim} calculated using the correct equilibrium constants. A computer program based upon the Levenberg–Marquardt algorithm [31] was written in MATLAB (Mathworks, version 6.5) and used to refine the acidity constants.

3. Experimental

The pure reagent PAR, acetic acid, boric acid, phosphoric acid, sodium hydroxide, hydrochloric acid and potassium nitrate were all from Merck Company and extra pure DMF Fluka Company was used as received. The absorption spectra were recorded using a Camspec M330 spectrophotometer. The pH measurements were made using a Metrohm 692 pH meter equipped with a glass calomel combined electrode. The solutions of 0.01 M oxalate and succinate buffers were employed to precalibrate the pH meter in the various binary DMF + water mixtures. A stock solution ($\sim 2.0 \times 10^{-5}$ M) of PAR was prepared. All titrations were performed under argon atmosphere at 25 °C using standardized HCl and NaOH titrants. In all experiments, the ionic strengths of the solutions used were kept constant at 0.1 M using potassium nitrate as the supporting electrolyte.

The pH values in DMF + water solvent mixtures were corrected using the Four-Plus^{TM} procedure for glass electrode calibrations in both aqueous and semi-aqueous media. Nine titrations of known concentration of PAR were performed in 0–80% of DMF, using NaOH solution. The operational pH scale was established by calibrating the pH measuring circuit with a mentioned buffers and assuming the Nernst slope. All data reported in this study are based on the concentration scale with respect to an ionic strength 0.1 M and 25 °C. As the proton concentrations generated from strong acid–base titrations can be readily calculated, the concentration pH value (p_cH = $-\log[H^+]$) is related to the operational pH reading by the equation as given below [4].

$$\text{pH} = \alpha + S\text{p}_c\text{H} + J_{H^+}[H^+] + J_{OH^-}\frac{K_w}{[H^+]} \tag{9}$$

The α term corresponds to the negative logarithm of the activity coefficient of H$^+$ at working temperature and ionic strength. The S term denotes the ratio between the actual slope and the Nernst slope. The J_H term corrects pH readings for the non-linear pH response due to liquid junction and asymmetry potentials in moderately acidic solution (pH 1.5–2.5), while the J_{OH} term corrects for any high-pH (pH ≥ 11) nonlinear effects. These parameters are determined by a weighted non-linear least squares procedure and the results showed a good agreement with the result of such fitting with solver tool pack of Excel. For aqueous titrations, the ionization constants of water (K_w) as a function of temperature and ionic strength, were taken from Sweeton et al. [32]. For semi-aqueous titrations, literature values of K's (the ionization constants of water in the solvent–water mixtures) were utilized from references [33,34]. In processing the titration data, contribution from carbonate was incorporated into the calculations. The acid dissociation constants of carbonic acid in solvent–water mixtures were determined iteratively in parallel with the parameters as defined in Eq. (9). Gran's plots were used to find the end point of the calibration titrations [35].

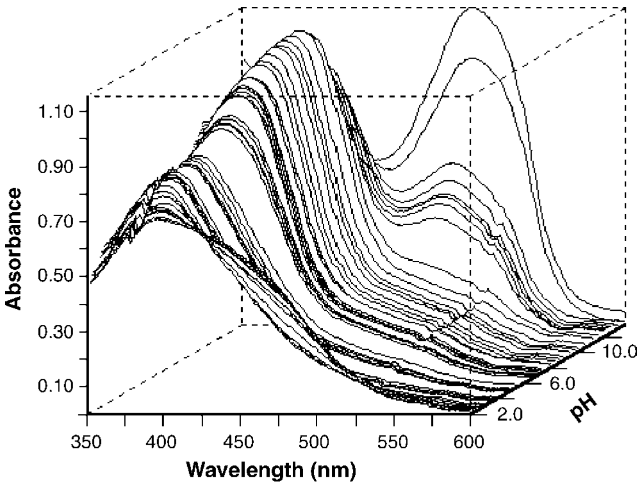


Fig. 2. Absorption spectra of PAR in 60 vol.% DMF at different pH.

4. Results and discussion

The electronic absorption spectra of PAR in binary solvent mixtures at various pH values at 350–600 nm interval were recorded. Sample spectra of PAR at different pH values in pure water and 60 vol.% DMF to water are shown in Figs. 1 and 2, respectively. The principal component analysis of all absorption data matrices obtained at various pH values shows at least four significant actors that also supported by the statistical indicators of Elbergali et al. [36]. These factors could be attributed to the three dissociation equilibria of a triprotic acid such as PAR. The pK_a values of PAR were investigated in nine different DMF + water binary mixtures spectrophotometrically at 25 °C. Protolytic constants of PAR in several mixtures were evaluated using the above algorithm 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 four calculated most significant projection vectors with clear spectral features (as compared to noise) is an evidence of the presence of four spectroscopically distinguishable components. Their shapes, however, are clearly unphysical and cannot be directly related to the spectral response of the four protolytic forms. Outputs of the program are pK_a 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 pK_a values are listed in Table 1. The pK_a values correspond to the pH dependent variation of absorption spectra in all solvent mixtures. The previous reported values of acidity constants are mainly in definite mixtures of DMF, methanol, and ethanol with water. The obtained values in pure water are in good agreement with previous values, [8,21,37,38] which are listed in Table 1 for comparison. Since chemometrics based methods, by using the whole spectral domain, reduce consid-

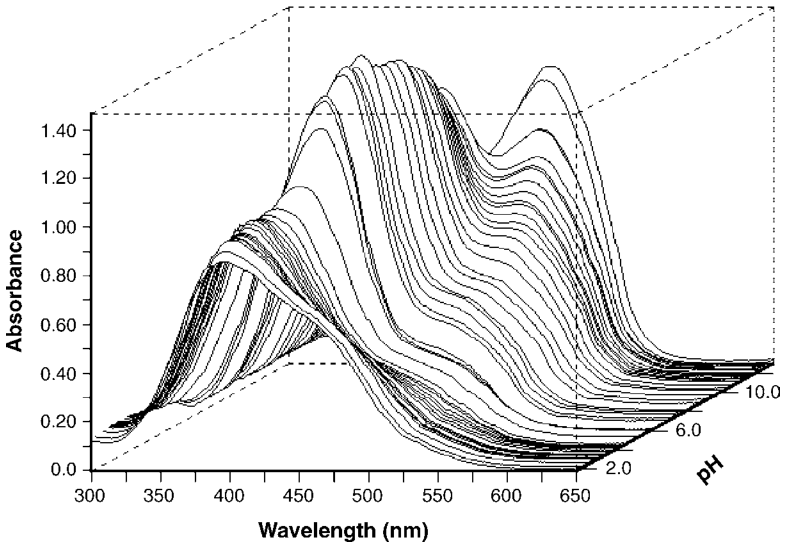


Fig. 1. Absorption spectra of PAR in pure water at different pH.

Table 1
Protolytic constants of PAR at different percentage of DMF at 25 °C and constant ionic strength (0.1 M KNO_3)

pK_3	pK_2	pK_1	Mole fraction of DMF	vol.%
11.99 ± 0.05	5.50 ± 0.07	3.03 ± 0.17		0
12.04[a]	5.50[a]	3.07[a]		
12.30 ± 0.10[b]	5.46 ± 0.02[b]	3.09 ± 0.02[b]		
11.95[c]	5.50[c]	3.03[c]		
11.98[d]	5.56[d]	3.02[d]	0.00	
12.14 ± 0.04	5.91 ± 0.05	2.82 ± 0.09	0.025	10
12.39 ± 0.04	5.78 ± 0.03	2.79 ± 0.05	0.055	20
12.32 ± 0.08	5.72 ± 0.05	2.71 ± 0.09	0.091	30
12.62 ± 0.03	6.38 ± 0.04	2.70 ± 0.06	0.135	40
12.60 ± 0.05	6.35 ± 0.06	2.66 ± 0.10	0.189	50
13.01 ± 0.03	6.81 ± 0.04	2.61 ± 0.11	0.260	60
13.05 ± 0.06	6.94 ± 0.06	2.40 ± 0.16	0.353	70
12.90 ± 0.10	7.11 ± 0.21	2.29 ± 0.28	0.484	80

[a] Ref [8].
[b] Ref [21].
[c] Ref. [37].
[d] Ref. [38].

erably the level of noise so the obtained protolytic constants could be more reliable and precise than those have been calculated using the previous classical methods. One of the very important outputs of the algorithm is the calculated spectrum of different forms of PAR in each solvent mixture. The calculated spectra of all species in 10 and 60% solvent mixtures are shown in Fig. 3. It is interesting to note that the nature of the solvent composition has a fundamental effect on each pure spectrum. There is a λ_{max} at 490 nm and a shoulder at about 410 nm in the spectrum of L^{2-}.

The solvent effect on this spectrum is very interesting. There are characterized hydrogen bonds between the oxygen site of DMF and hydrogen of water [39]. This hydration affects on the stabilization of the DMF molecule in aqueous solution. As the mass factor of DMF increased, the absorption intensity at 490 nm decreased and that at 410 nm increased. 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 $\pi \rightarrow \pi^*$ transitions. The most important features of the distribution diagrams are the pH limits of the evolving and disappearing of components. The distribution diagrams of PAR species at 10 and 60% are shown in Fig. 4.

The pK_a values of PAR obtained in DMF–water mixtures increase with percentage of DMF. These variations could be explained by the fact that there is preferential solvation in these media that is related to the structural features of these mixtures. The composition of the immediate surroundings of a solute may differ from the composition of the bulk mixture. Preferential solvation is attributable to an excess or deficiency of molecules of one of the solvents in these surroundings [40]. If the solute displays no preference for the solvent molecules, the solvent composition in the primary coordination shell, in the immediate neighborhood of the solute, is the same as that in the bulk. The deviation from the ideal dependence on the composition of the mixtures indicates that the solvent composition in the neighborhood of the solute may be different from that in the bulk. As discussed above, the data shown in Table 1 clearly illustrate the important influence of the nature of the solvent on the dissociation reactions. It has been shown that the solvating ability [41] (as expressed by the Guttmann 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 = 33.0) and dielectric constant ($\varepsilon = 78$) which can dissociate the acid and stabilize the produced anion and hydrogen ion. Thus, it is expected that addition of DMF with lower donor number (DN = 26.0) and dielectric constant ($\varepsilon = 44.0$) to water decreases the extent of interaction of the acid anion and the proton with solvent, and this decreases the first protolytic constant and increasing the second and third steps. The change in the acidity constants versus the percentages of DMF in the binary mixed solvents are shown in Fig. 5. The same trend has already been reported for various organic molecules in the numbers of organic solvents [42,43]. It has been reasonably assumed that preferential solvation of the charged particles by water is mainly responsible for such a monotonic dependence of the acidity constants of PAR on

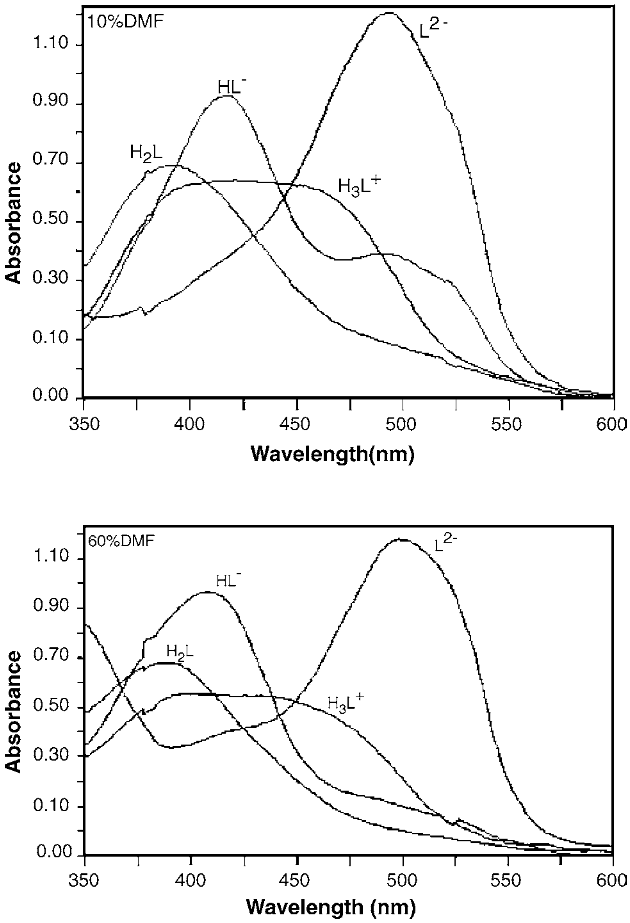


Fig. 3. Pure spectra of PAR species in the various mixtures of DMF + water: H_3L^+, H_2L, HL^-, L^{2-}.

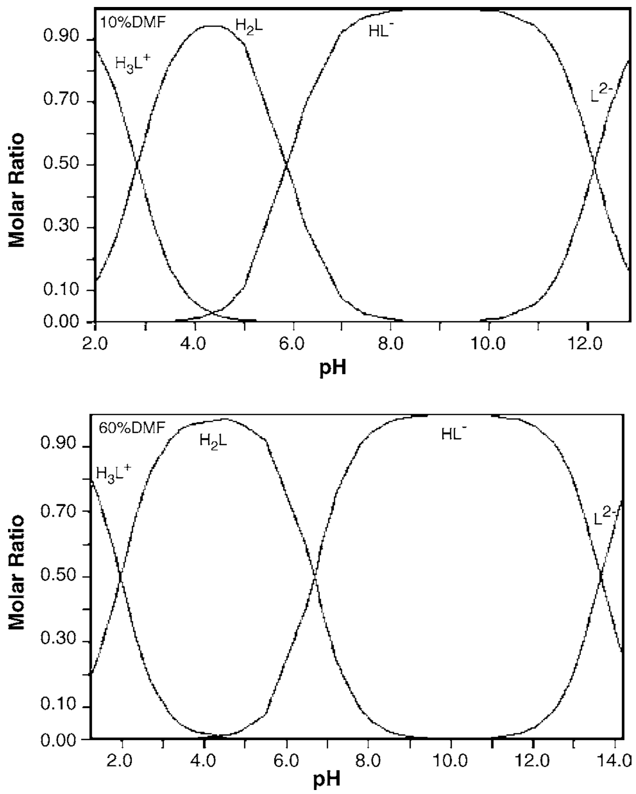


Fig. 4. Distribution diagram of different species of PAR in different DMF + water mixtures: H_3L^+, H_2L, HL^-, L^{2-}.

the solvent composition. 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 the acid will be lowered. Therefore, the decrease in the K_a of the first step and the decrease in those of the second and third steps are due to increasing the mole fraction of DMF in the binary mixed solvent.

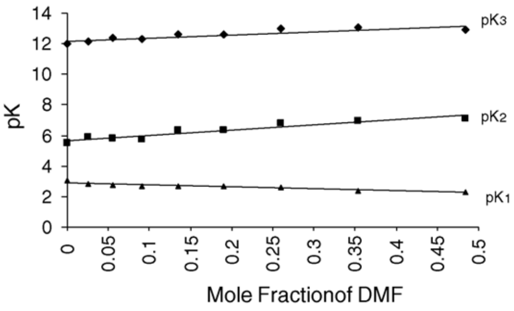


Fig. 5. Plot of pK_a values against mole fraction of DMF in the binary mixtures.

Table 2
Acidity constants of PAR in two selected mole fraction of acetonitrile (AN), DMF and methanol (MeOH) in water

Solvent	Mole fraction	Donor number (DN)	Dielectric constant (ε)	pK_{a1}	pK_{a2}	pK_{a3}
AN[a]	0.158	14.0	36.0	2.47	6.27	13.00
	0.396			2.43	9.94	14.50
MeOH[b]	0.124	19.0	32.6	2.90	5.86	12.21
	0.458			2.65	6.35	12.45
DMF	0.135	26.0	38.3	2.70	6.38	12.62
	0.353			2.40	6.94	13.05

[a] Ref. [21].
[b] Ref. [8].

The same trends are obtained from the determination of acidity constants of PAR in methanol–water [8] and acetonitrile–water [21] binary mixtures. Table 2 lists the acidity constants of PAR for comparison at two selected mole fractions for three of organic solvents and also the physical properties such as dielectric constants and donor numbers. The variations of the acidity constants, at selected mole fractions, (the mole fraction are chose close as much as possible to each other for better comparing, of the all mentioned organic-water solvent systems) are according to variation in the donor number and also dielectric solvents. As it is clear by addition of all organic solvents to water the second and third ionization steps decreased and also the first step increased. The amounts of the variations are fully depending on the extent of the differences of physical parameters (donor number and dielectric constant) of the added organic solvents with water. Of course, as described above, the changing to solvation ability which controls the equilibrium constants are influenced by the changing to the bulk properties as such dielectric constant and donor number which these in turn has drastic effect on the solvation shell or coordination shell compositions.

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