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Medium Effect on the Acid Dissociation Constants of 2,2′,6′,2″-Terpyridine

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The acid dissociation constants of 2,2′,6′,2″-terpyridine were determined in aqueous + organic solvents mixtures. The organic solvents were methanol, ethanol, acetone, dimethyl formamide (DMF), and dimethyl sulfoxide (DMSO). The ionization constants of terpyridine depend largely on both the proportion and nature of the organic cosolvent. Solvent properties play a major, but not exclusive, role in the ionization of the protonated terpyridine molecule. Basicity and stabilization of the different species existing in equilibrium through hydrogen bonding together with ion−solvent interaction play an important role in the acid dissociation in the presence of organic solvent. The overall dissociation constant (pK_{a1}+ pK_{a2}) of the protonated terpyridine increase in the various solvents according to the following order: methanol < ethanol < acetone < dimethyl formamide < dimethyl sulfoxide

Introduction

Although terpyridine (Figure 1) represents a very interesting compound from both the analytical and structural points of view[1,2] little attention has been focused on its acid−base properties.

Two pK_a values have been determined for terpyridine in aqueous-dioxane solutions,[3] but no study of the medium effect on the acid dissociation constants of this compound is reported. In the present article, the aim is to investigate the effect of both the nature and the concentration of organic cosolvent on the ionization of the protonated form of terpyridine.

For this purpose, the acid dissociation constant values of terpyridine have been determined in aqueous solutions containing varying proportions of organic solvents making use of the Irving and Rossotti[4,5] as well as Rossotti[6] techniques. The organic solvents used were methanol, ethanol, acetone, dimethyl formamide, and dimethyl sulfoxide.

The procedure used was the pH-titration at a constant ionic strength (0.1 M KNO_3).

Experimental Section

All of the organic solvents used were of spectro-grade and were used without further purification. Terpyridine was purchased from Sigma Chemical Co. and was used as supplied. Other chemicals such as KNO_3, KOH, and HNO_3 were of analytical grades. A 0.5 mol dm^{-3} solution of terpyridine was prepared by dissolving the requisite quantity of the solid in the required volume of the solvent. Dilute solutions were prepared by accurate dilution of the stock solution. A stock solution (1.0 mol dm^{-3}) of KNO_3 was prepared by dissolving the exact mass of KNO_3 in the required volume of bidistilled water. KNO_3 was used to adjust the ionic strength of solution (at $I = 0.1$ mol dm^{-3}). A nitric acid solution, 1.0 mol dm^{-3}, was prepared and used after standardization by titration with standard KOH solution. Carbonate-free[7] KOH solution was prepared using bidistilled water. The solution was standardized against 0.1 mol dm^{-3} potassium hydrogen phthalate solution.

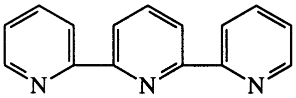

Figure 1. Structure of terpyridine.

Generally dilute solutions were prepared by appropriate dilutions of the stock. The proton-ligand formation constants of terpyridine were determined by titrating 50 mL of an aqueous solution containing different mass fractions of the organic solvents with standard carbonate-free KOH solution at 25 °C.

The titrated 50 cm^3 solution contains HNO_3 (5 cm^3 of 1.0 mol dm^{-3}), KNO_3 (5 cm^3 of 1.0 mol dm^{-3}), and terpyridine (10 cm^3 of 0.5 mol dm^{-3}). The required mass fractions of the organic solvents were attained by making the total volume 50 cm^3 with the accurate amounts of both the organic solvent and bi-distilled water. Potentiometric pH measurements were made on solutions in a double-walled glass vessel at (25 ± 0.1) °C with a commercial Orion electrode using an Orion 510 pH meter accurate to ±0.01 in pH. The temperature was controlled by circulation of water through the jacket from an ultrathermostat bath. Purified nitrogen was bubbled through the solution in order to maintain an inert atmosphere. Efficient stirring of the solution was achieved with a magnetic stirrer. For each solvent mixture, at least 4 titrations were performed.

Results and Discussion

The measured pH values of the different water + organic solvent mixtures under investigation were corrected making use of the equation $pH^* = pH\,[R] - \delta$, where pH* is the corrected value and pH[R] is the pH-meter reading obtained in water + organic solvent mixtures.

According to this equation, the values of δ corresponding to each of the different organic solvent + water mixtures under investigation were obtained from the results of Douheret.[8] It should be noted, however, that the constant δ, according to Bates,[9] is written for $E_j - \log {}_m\gamma_H{}^+$ where E_j is the liquid junction potential and ${}_m\gamma_H{}^+$ refers to the hydrogen ion activity coefficient on transfer from water to the organic solvent + water mixture. This quantity is substantially constant for a medium of given composition.

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Table 1. Values of pK_{a1} and pK_{a2} of Terpyridine in Various Organic Solvent Mass Fractions, w_2 in Water (1) + Organic Solvent (2), at (25 ± 0.1) °C and Ionic Strength $I = 0.1$ mol dm^{-3}

w_2	pK_{a1}	pK_{a2}	$pK_{a1} + pK_{a2}$
Water (1) + Methanol (2)			
0.1653	3.16	4.60	7.76
0.2535	2.90	4.44	7.34
0.3456	2.60	4.30	6.90
0.4421	2.70	3.90	6.60
Water (1) + Ethanol (2)			
0.1659	2.90	4.90	7.80
0.2542	2.82	4.30	7.12
0.3465	2.50	4.20	6.70
0.4430	2.44	3.92	6.36
Water (1) + Acetone (2)			
0.1654	3.08	5.10	8.18
0.2535	2.80	4.44	7.26
0.3456	2.75	3.88	6.63
0.4421	2.62	3.62	6.24
Water (1) + DMF(2)			
0.1921	3.98	5.30	9.28
0.2896	2.70	4.94	7.64
0.3881	2.65	4.68	7.33
0.4875	2.82	3.28	6.10
Water (1) + DMSO (2)			
0.2160	3.88	5.46	9.34
0.3179	3.42	4.44	7.86
0.4230	2.90	3.94	6.84
0.5245	2.86	3.94	6.80

It was found that δ is small up to a high mass fraction of the organic solvent (about 0.8 in both methanol and ethanol).[9] This is apparently because E_j and log ${}_{m}\gamma_{H^+}$ compensates to a considerable extent in this region of solvent composition (below 0.8 mass fraction organic solvent). Therefore, pH* is considered as a useful quantity that plays a simple and unequivocal role in chemical equilibria in nonaqueous media, where it meets many of the requirements for a useful acidity scale in such cases.

The mean pK_a values of the protonated forms of the terpyridine in different aqueous + organic solvent mixtures are listed in Table 1. These results reveal that the pK_a values, in all the ratios studied, are largely dependent upon both the proportion and the nature of the organic cosolvent used.

Generally, the acid dissociation constant (K_a) of the protonated form of terpyridine increases as the amount of the amphiprotic solvent (methanol or ethanol) or the aprotic solvent [acetone, dimethyl formamide, or dimethyl sulfoxide] in the aqueous media is increased. Accordingly, increasing the organic cosolvent content in the medium results in a decrease in the pK_a value, and the acidity constant in pure aqueous medium $K_a^{\,w}$ is related to that in water + organic solvent mixture $K_a^{\,s}$ by the relation:[9,10]

$$pK_a^{\,s} - pK_a^{\,w} = \log \frac{{}_{m}\gamma_{H^+} \cdot {}_{m}\gamma_{B}}{{}_{m}\gamma_{HB^+}}$$

where ${}_{m}\gamma$ is the activity coefficient of the subscripted species in partially aqueous medium relative to that in pure aqueous one.

Because it is known that the electrostatic effects operate only on the activity coefficients of charged species, one can expect that the increase in the amount of the organic cosolvent in the medium will increase the activity coefficient of both H^+ and HB^+ ions.

Because the magnitude of the electrostatic effect resulting from the relative permittivity of the medium is inversely proportional to the radius of the ionic species considered, the magnitude of this effect on the proton exceeds that on the acid forms HB^+ or H_2B^{2+}; thus, the acid dissociation constant value of the protonated form of the compound is expected to decrease with the increase in the proportion of the organic solvent in the medium. This is not the case as evident from the results reported in Table 1.

The relative permittivity of water + organic solvent mixtures was obtained using the following equation:[11]

$$\epsilon = \epsilon_1 m_{f(w)} + \epsilon_2 m_{f(s)}$$

where ϵ is the relative permittivity of the water + organic solvent mixture, ϵ_1 and ϵ_2 is the relative permittivity of the water and organic solvent, respectively, and m_f is the mole fraction and the subscripts w and s refer to water and organic solvent, respectively.

On the other hand, ethanol and acetone have approximately similar relative permittivity (24.3 and 20.7, respectively, at 25 °C)[12] so that electrostatic effects in aqueous solutions containing the same mass fraction of these two solvents are expected to be virtually identical (i.e., pK_a values of the compound in such solutions should be the same). This is not the case also as the data of Table 1 imply. Moreover, though methanol and DMF have comparable relative permittivity (32.6 and 36.7, respectively, at 25 °C),[12] the pK_a values of terpyridine are, in general, higher in water + DMF mixtures than in methanol + DMF mixtures, where a similar mass fraction of each is used.

Accordingly, factors other than the electrostatic play a major role in determining the effect of the amphiprotic or dipolar aprotic solvent on the acid dissociation process of the terpyridine.

This suggestion is further substantiated by the obtained nonlinear relationships on plotting pK_a against $1/\epsilon$ of the medium. This is in accordance with the equation given by Denison and Ramsey,[13] as well as by Glikerson[14] which relates the variation of the pK_a of the acid with the relative permittivity of the medium (ϵ). However, the variation of pK_a with relative permittivity (ϵ) in solvent mixtures is given by the relation[15]

$$pK_a = pK_o + \frac{0.43Ne^2}{RT}\left[\frac{Z_1Z_2}{r_1 + r_2}\right]\frac{1}{\epsilon}$$

where pK_a = acid dissociation constant in the solvent mixture, pK_o = acid dissociation constant in pure water, Z_1 and Z_2 are charges carried on the ions involved in the equilibrium, and r_1 and r_2 are radii of the ions involved in the equilibrium.

The plot of pK_a against $1/\epsilon$ is not linear. This indicates that changes in the pK_a with the solvent concentration, though mainly governed by the relative permittivity, are strongly influenced by other solvent characteristics too. In general, it is recognized that properties of the solvent such as relative permittivity and acidic or basic strengths play a major but not exclusive role. Other factors, such as basicity and stabilization of the different species existing in equilibrium through hydrogen bonding together with ion−solvent interaction play an important role in the acid dissociation process in the presence of organic solvents.[16]

It is evident from Table 1 that the overall dissociation constant (pK_{a1} + pK_{a2}) of the protonated terpyridine increases in water + solvent mixture in the following order:

$$\text{methanol} < \text{ethanol} < \text{acetone} < \text{dimethyl formamide} < \text{dimethyl sulfoxide}$$

This order is consistent with the decrease in basicity of the solvents based on their autoprotolysis constant values (pK_s) which are as follows:[17]

$$\text{methanol} = 17.20,\ \text{ethanol} = 18.88,\ \text{dimethyl formamide} = 29.50,\ \text{acetone} = 32.5,\ \text{and dimethyl sulfoxide} = 33.30.$$

Therefore, one can deduce that the basicity of the organic cosolvent has a contribution in the ionization of the protonated terpyridine molecules.

On the other hand, for the same solvent, the value of ($pK_{a1} + pK_{a2}$) decreases, in general, as the proportion of the organic cosolvent is increased. This behavior is in agreement with the decrease in the basicity of the medium in the same direction, because water ($pK_w = 14$) is more basic than any of the organic solvents used. A decrease in the basicity of the medium will decrease the stabilization of the protonated base (H_2 terpyridine)$^{2+}$ and in turn promote the ionization, i.e., pK_a decreases.

Furthermore, it is expected that there should be an increase of the acid dissociation constant (pK_a decrease) of the protonated form with the increase in the amount of organic cosolvent in the medium because of the effect of the possible hydrogen bonding interactions. Because water has a greater tendency to donate hydrogen bonding (a hydrogen bond donor) than other organic solvents molecules[18] which are stronger H bond acceptors, the protonated terpyridine molecule is expected to be less stabilized by hydrogen bonding interaction as the amount of the organic cosolvent in the medium is increased. This will tend to decrease the pK_a in the same direction, as evident from the data given in Table 1. Therefore, one can conclude that differences in stabilization of the protonated terpyridine molecule by hydrogen bonding interaction in partially aqueous media relative to that in pure one appear to play a significant role in the acid dissociation process of this compound.

Literature Cited

(1) Smith, G. F.; Richter, F. R. *Phenanthroline and Substituted Phenanthroline Indicators*; G. Frederick Smith Chemical Company: Columbus, Ohio, 1944.
(2) Raston, C. L.; White, A. H. Crystal Structural of Bis (2,2′,6′,2″-Terpyridyl) Cobalt (II) Bromide Trihydrate. *J. Chem. Soc., Dalton Trans.* **1974**, 1803−1807.
(3) James, B. R.; Williams, R. J. P. The Oxidation−Reduction Potentials of Some Copper Complexes. *J. Chem. Soc.* **1961**, 2007−2019.
(4) Irving, H.; Rossotti, H. S. Methods for Computing Successive Stability Constants from Experimental Formation Curves. *J. Chem. Soc.* **1953**, 3397−3405.
(5) Irving, H.; Rossotti, H. S. The Calculation of Formation Curves of Metal Complexes From pH Titration Curves in Mixed Solvents. *J. Chem. Soc.* **1954**, 2904−2910.
(6) Rossotti, H. S. *The Study of Ionic Equilibria*; Longman: London, 1978.
(7) Vogel, A. I. *Text Book of Quantitative Inorganic Analysis*, 3rd ed.; Longman: London, 1961; p 245.
(8) Douheret, G. The Dissociation of Organic Compounds in Aqueous Organic Media. I. Determination of the Liquid Junction Potential and the Effect of the Medium on the Hydrogen Ion in These Systems, and the Study of the Dissociation of Some Acid−Base Couples. *Bull. Soc. Chim. Fr.* **1967**, 1412−1419.
(9) Bates, R. G. *Determination of pH*; John Wiley and Sons: New York, 1964.
(10) Coetzee, J. F.; Ritchie, C. D. *Solute−solvent Interactions*; Marcel Dekker: New York, 1969; pp 221−222.
(11) Hammam, A. M.; Ibrahim, S. A.; Abou El-Wafa, M. H.; Mohamed, A. A.; Rageh, N. M. Acidity Constants of Some Hydroxy Azopyrazolopyridines in Mixed Aqueous−Organic Solvents. *J. Chem. Eng. Data* **1993**, *38*, 63−66.
(12) Weast, R. C. *Hand Book of Chemistry and Physics*, 55th ed.; CRC Press: Cleveland, Ohio, 1975; E74.
(13) Denison, J. T.; Ramsey, J. B. Free Energy, Enthalpy and Entropy of Dissociation of Some Perchlorate in Ethylene Chloride and Ethylidine Chloride. *J. Am. Chem. Soc.* **1955**, *77*, 2615−2621.
(14) Gilkerson, W. R. Application of Free-Volume Theory to Ion-Pair Dissociation Constants. *J. Chem. Phys.* **1956**, *25*, 1199−1202.
(15) Charlot, G.; Tremillon, D. *Chemical Reactions in Solvents and Metals*; Pergemon Press: Elmsford, NY, 1969, 55−306.
(16) Douheret, G. Liquid Junction Potentials and Medium Effects in Mixed Solvents (Water-Dipolar Aprotic Solvent). Application to the Standardization of the Glass − Calomel Electrodes System in These Mixtures. *Bull. Soc. Chim. Fr.* **1968**, 3122−3131.
(17) Richardt, C. *Solvents and Solvent Effects in Organic Chemistry*, 2nd ed.; VCH: Weinhiem, Germany, 1990; pp 431−433 and references there in.
(18) Franks, F.; Ives, D. J. G. Structural Properties of Alcohol-Water Mixtures. *Inst. Technol., Bradford, Engl. Quart Rev. (London)* **1966**, *20* (1), 1−44.

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