SPECTRAL BEHAVIOR OF AN AZOPYRAZOLONIC DERIVATIVE OF HYDROXYSULFANILIC ACID AND ITS USE AS A NEW METAL INDICATOR FOR Ti(IV)

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Abstract

The present paper describes a spectrometric study on the acid – base characteristics of the reagent obtained by coupling 3-methyl-1-phenylpyrazolin-5-one with diazotized amino-aryl-sulfonic acid. The apparent pK_a values were evaluated. The reagent is recommended as metal – indicator for the complexometric determination of Ti(IV) in buffered solutions at pH = 5.00, without separation as well as pH indicator for the alkaline titration of mixtures of acids, bases and salts.

Introduction

The azopyrazolonic derivatives synthesized by coupling 3-methyl-1-phenyl pyrazolin-5-one with diazotized amino-aryl-sulfonic acid were first used for the quantitative determination of Zr(IV).[1-3] Spectrometric investigations on the systems containing Fe(III) and the sodium salt of the reagent obtained by coupling 3-methyl-1-phenylpyrazolin-5-one with diazotized 3 amino-4-hydroxybenzensulfonic acid showed the significant influence of the pH on the absorbance of both complex and reagent. Thus, the characteristic of the reagent to twice shift the color depending on the pH variation was noticed; it shifts from yellow to red when the medium turns from weakly acid to weakly alkaline and back to yellow at pH greater than 11. On this basis two methods for the spectrometric determination of Fe(III) in alkaline solution without neutralization and at pH 5.00 – 6.20 respectively, were reported.[4,5] A spectrometric method for the Ti(IV) determination at pH = 5.60 was also reported.[6]

The present paper reports a spectrometric study on the acid – base behaviour of the reagent and their use as metal indicator. The formula of the reagent (further noted by **R**) is given in Figure 1. The evaluation of the pK_a values has been carried out using different methods, theoretically based on the Henderson – Hasselbach equation.[7] The reagent is recommended for the complexometric determination of Ti(IV) at pH = 5.00. The reagent may be used as color indicator in acid-base titration.

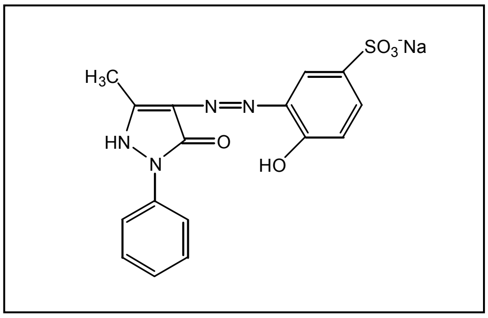

Fig.1 Formula of the reagent **R**

Results and discussion

The spectra of the reagent **R** recorded for pH range 1.00 – 8.00 show the existence of an isosbestic point at λ = 450 nm. This indicates that the reagent is present in two conjugated acid –base forms characterized by maximum absorbance at 423 nm (yellow color) and 468 nm (red color). The spectra are shown in figure 2a.

Further pH increase in the alkaline range (pH > 10.35) marks the appearance of a new isosbestic point at 448 nm corresponding to the shift of the reagent from the red form (λ_{max} = 465 nm) to the yellow one (λ_{max} = 440 nm). The spectra recorded for this pH range is presented in figure 2b.

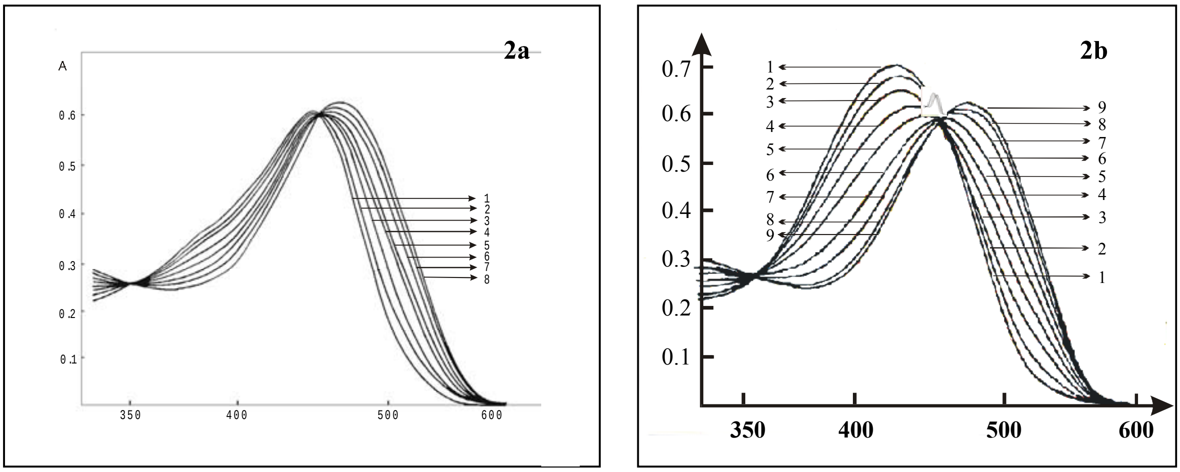

Fig. 2 The spectra of the reagent **R** recorded for pH range: **2a**. 1.00 – 8.00 (1-pH = 5.65, 2-pH = 5.92, 3-pH = 6.28, 4-pH = 6.50, 5-pH = 6.81, 6-pH = 7.08, 7-pH = 7.12, 8-pH = 7.80); **2b**. 10.00 – 12.00 (1-pH = 10.35, 2-pH = 10.47, 3-pH = 10.90, 4-pH = 11.40, 5-pH = 11.47, 6-pH = 711.60, 7-pH = 11.80, 8-pH = 11.91)

The evaluation of pK_a is performed as described below. The first pK_a designates the constant of the equilibrium between the yellow form present in acid medium and the red form existent in weakly alkaline medium, while the second pK_a value indicates the constant of the equilibrium in which, at $pH > 11.00$ the red form shifts to a new form, but also of yellow color. Results obtained were correlated with the ones reported in IR and UV studies performed on 1-phenyl-3,4-dimethyl pyrazolin-5-one and 1-phenyl-3-methyl pyrazolin-5 one.[9,10,11] In buffer aqueous solutions (pH ~ 5.00) very little of CH– form is present and the compound exists essentially in the –NH– form with about 10% of the OH- form in equilibrium (figure 3). In these conditions a pK_{a_1} the value of 7.38 ± 0.13 was determined for the acid – base equilibrium involving the – NH– group. The $pK_{a_2} = 11.34 \pm 0.03$ value characterizes the OH acidities (fig 3).

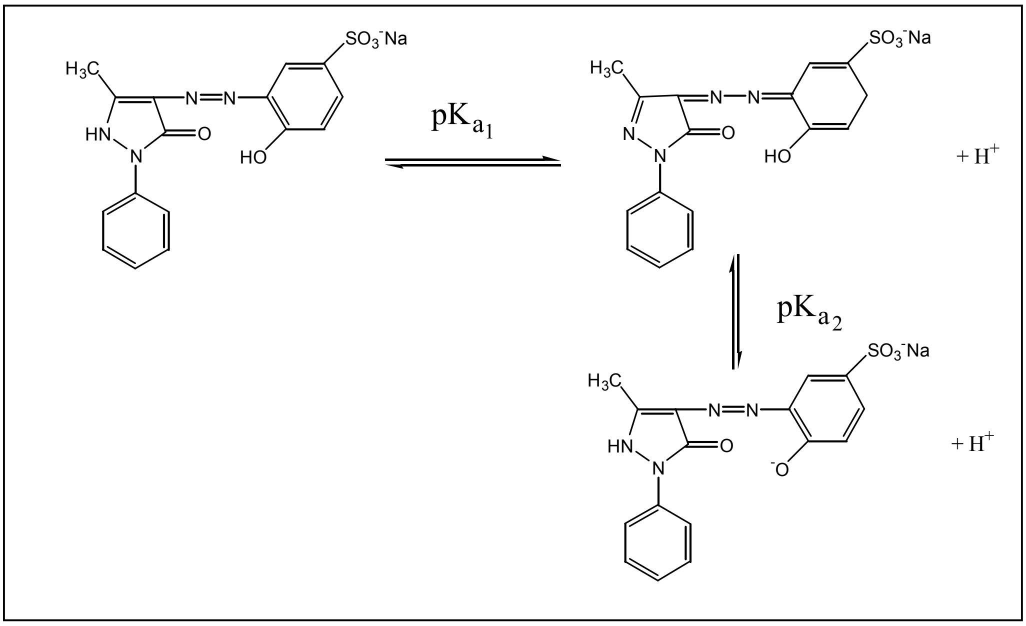

Fig. 3 Attribution of the pK_a values

The dramatic change in the reagent's color for its acid – base conjugated forms as recommend the reagent as pH indicator. The reagent **R** has two pH transition ranges in alkaline solutions. The first pH transition range is at $\Delta pH = 7.28 \pm 1.00$ and the second at $\Delta pH = 11.34 \pm 1.00$. Few pH indicators have the pH transition ranges greater than 9.20 and it is for this reason that this reagent could be used in alkaline media.

Determination of Ti(IV) by complexometric titration

The reagent can be used as metal indicator for the titration of Ti(IV) with ethylenediaminetetracetic acid, disodium salt (EDTA). Titanium (IV) forms with the reagent a stable complex[5] having the total stability constant $\beta = 10^8$ at $\lambda_{max} = 520$ nm, in the pH range of 5.00 – 6.50. A small amount of indicator is added to the sample solution buffered at pH 5.00 and Ti(IV) forms a red complex. The color of uncomplexed indicator at pH = 5.00 is yellow ($\lambda_{max} = 423$ nm). The metal-indicator complex must be less stable than the metal-EDTA complex in order to perform a complexometric titration. The stability constant of the metal – indicator complex is 10^8 and the apparent stability constant of metal – EDTA complex, at pH = 5.00 is 7.09×10^{14}. The range of pβ (pβ = logβ) is 8.00 ± 1.00. The best choice of the metal indicator in complexometric titration requires the fulfillment of two conditions: first, pM_{100} (pM_{100} = -log[M] at equivalence point, in which M is the concentration of metal ion) must be very close to pβ and second, the range of Δβ must be comprised within the range of ΔpM corresponding to the (100 – e%) and (100 + e%) EDTA added (e% represent the errors for the titrimetric method). A theoretical evaluation of the organic reagent **R** as Ti(IV)–indicator was performed. The values obtained are shown in Table 1.

As shown, the best fit between the pM_{100} and pβ is for the concentration of Ti(IV) 10^{-1} mol.L^{-1}. The second condition is fulfilled for all the concentration values considered in the above theoretical calculation.

Table 1 Results of evaluation of R as metal - indicator

Ti(IV) mol.L^{-1}	pM_{100}	pβ	ΔpM	
			± 1%	± 0.1%
10^{-1}	8.07	8.00	8.70	6.70
10^{-2}	8.57	8.00	7.70	5.70
10^{-3}	9.07	8.00	6.70	4.70

*the range of ΔpM has been calculated taken into consideration the errors at ±1% and ±0.1% of EDTA solution added

The use of the reagent **R** as indicator for Ti(IV) determination by titration with EDTA was first tested for synthetic samples. The results are show in table 2.

Table 2 Results of Ti(IV) determination in synthetic samples

No. sample	Ti(IV) mg in sample	Ti(IV) mg found	relative accuracy %
1	0.800	0.805	+0.60
2	1.500	1.490	-0.66
3	2.200	2.215	+0.68
4	3.000	3.004	+0.13
5	4.000	4.008	+0.20

The results demonstrate that there is good agreement between the sample quantities and those that were determined.

As the natural samples of Ti(IV) usually contain Fe(III) the most common interferent ion a study regarding its presence has been carried out. The iron (III) forms a stable complex with EDTA for pH values below 4.00 and with the reagent **R** for pH values above 5.00 and it is titrated before Ti(IV), using KSCN as indicator. The possible interference of Fe(III) could be also annuled using NaF as masking agent.

Conclusion

The reagent obtained by coupling 3 - methyl - 1- phenyl pyrazolin - 5-one with diazotized 3 amino-4–hydroxybenzensulfonic acid can exist in aqueous solutions in different structural forms depending on the pH. The variation of the absorbance with the wavelength for the reagent solutions at different pH values has shown the existence of at least three stable forms. The color of two of them is yellow, one in acid medium ($1.00 < pH < 6.80$) having $\lambda_{max} = 423$ nm and one in strong alkaline medium ($pH > 11.00$), having $\lambda_{max} = 440$ nm. The other form is red having $\lambda_{max} = 468$ nm and being stable within the pH range 7.00 –11.00, and it is in equilibrium with the two other forms of yellow color.

The reagent has been used with good results as metallochromic indicator for the determination of Ti(IV) at pH = 5.00, without separation.

Experimental

Analytical reagent grade chemicals only were used. Solutions of NaOH 1 mol.L^{-1} and HCl 1 mol.L^{-1} were obtained from standard Merck by diluting with distilled water. Aqueous solution of this reagent **R,** 10^{-3} mol.L^{-1} was obtained dissolving the accurately weighed amount of reagent in distilled water. Volumetric standard solution of EDTA, disodium salt 0.1 mol.L^{-1} and 0.05 mol.L^{-1} were obtained from Aldrich.

Procedure for pK$_a$ determination

We have adopted the Lachman and Polster procedure for the pK$_a$ determination.[12] They have demonstrated that this procedure is more accurate as the substance to establish the concentration is weighed only once. The originality of method employed in this work was the way in which the pH of the solution was adjusted: the use of two concentrated solution of NaOH and HCl, respectively, both of 1 mol.L^{-1} and the addition of small volumes of these by micropipette. In this way the dilution during the experiments is only ~ 0.5 mL (1 – 2 mL if a burette is used for titration) and the error of dilution is < 0.06%. Therefore, this error can be ignored in titration spectra recorded in analogous mode and the sharp isosbestic point is maintained. The evaluation of the apparent pK$_a$ values has been carried out using the Henderson-Hasselbach equation adapted for spectrometric titration.

$$pH = pK_a + lg[(\varepsilon' c - As)/(As - \varepsilon c)]$$

where ε' and ε are the molar absorptivity of the conjugated acid and base form of the reagent respectively, c is the reagent concentration and As is the solution absorbance at a given pH.

Absorbance measurements were carried out with a Jasco V 500 spectrometer in a 1 cm cell. The pH of the solutions was measured with the Consort P 900 pH-meter using a glass - saturated calomel combined electrode.

Procedure for Ti(IV) titration

Known volumes of 0.1 mol.L^{-1}, 0.01 mol.L^{-1} and 0.001 mol.L^{-1} solutions of Ti(IV) were transferred to a 250 mL volumetric flasks, 10 mL of buffer solution, 50 mL of distilled water and 2-3 drops of reagent **R** solution 0.001 M in water were added in each sample. The titration had been performed, using volumetric standard solution of 0.1 and 0.05 mol.L^{-1} of EDTA, disodium salt as titrant, until the color changed from red to yellow.

References and Notes

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Povzetek

Opisana je spektrofotometrična študija kislinsko–baznih lastnosti reagentov, ki so bili pripravljeni z reakcijo 3-metil-1-fenilpirazolin-5-ona z diazotiranimi amino-aril-sulfonskimi kislinami. Raziskana je bila uporabnost pripravljenih reagentov za kompleksometrično določanje Ti(IV) pri pH 5 brez predhodne ločbe in kot pH indikator za titracije kislin in baz.