

# Spectrophotometric Study of the Complexation Equilibria of Vanadium(V) with 3,5-Diamino-4-[*o*-hydroxyphenylazo-]pyrazole

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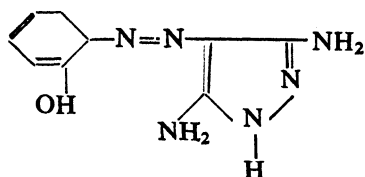
The acid-base characteristics of 3,5-diamino-4-[*o*-hydroxyphenylazo-]pyrazole (DAAZP) were studied spectrophotometrically in water dimethylsulphoxide media. The complexes of vanadium(V) with this reagent liable to occur in solutions are described and evaluated. The study of the behaviour of vanadium in the presence of equimolar concentrations or in solutions containing metal or ligand excess gave evidence for the formation of two types of species with stoichiometric ratios 1 : 2 (M : L) depending on the pH of the medium. A spectrophotometric method for the determination of microamounts of vanadium (V) with DAAZP has been established at pH = 4.0 ( $\lambda_{\max} = 450$  nm,  $\epsilon = 3.5 \times 10^4$  l mol<sup>-1</sup> cm<sup>-1</sup>).

## INTRODUCTION

The fact that several organic dyes are now of wide applications in analytical chemistry has created renewed interest in investigating their analytical properties such as the acid-base properties and their behaviour as metallochromic or chromophoric indicators with the emphasis stressed on specificity, selectivity, stoichiometry and sensitivity. Although a large number of metal-dye complexes have been used in dyeing, only a few of such compounds were characterized and reported<sup>1,2</sup>. Arylazo heterocyclic compounds have been directed the attention as chelating agents to various metal salts forming excellent dye-stuffs<sup>3-7</sup>. The present work aims to study the spectral, acid-base properties of 3,5-diamino-4-[*o*-hydroxyphenylazo-]pyrazole (DAAZP) in 20% (v/v) DMSO and the complexation equilibria of the reagent with vanadium(V). The fundamental conditions favouring the direct spectrophotometric determination of trace levels of vanadium(V) using DAAZP have also been investigated.

## EXPERIMENTAL

The azo-compound under consideration which has the formula:



was prepared according to the method reported<sup>8</sup>. A stock solution  $10^{-2}\text{M}$  of the reagent was prepared by dissolving the weighed amount in 20% (v/v) dimethylsulphoxide.  $10^{-3}\text{M}$  Solution of vanadium(V) was prepared from the analytical pure ammonium metavanadate and standardized complexometrically<sup>9</sup>. All the working solutions were prepared in doubly distilled water and DMSO of BDH grade. The pH values of solutions were adjusted by the addition of either dilute sulphuric acid or sodium hydroxide and measured by Fischer Accument pH meter model 800 at  $25^{\circ}\text{C}$ . The partially aqueous solutions were corrected as given by Douheret<sup>10</sup>. The electronic absorption spectra were recorded on a UV-vis. Shimadzu-240-Recording Spectrophotometer using 1 cm matched quartz cells.

## RESULTS AND DISCUSSION

### Acid-Base Equilibria of DAAZP in 20% DMSO

The absorption spectra of  $4 \times 10^{-5}\text{M}$  of the reagent in 20% (v/v) DMSO at different hydrogen ion concentration adjusted by  $\text{H}_2\text{SO}_4$  or  $\text{HNO}_3$  are shown in Fig. 1. The two main bands observed in the visible region

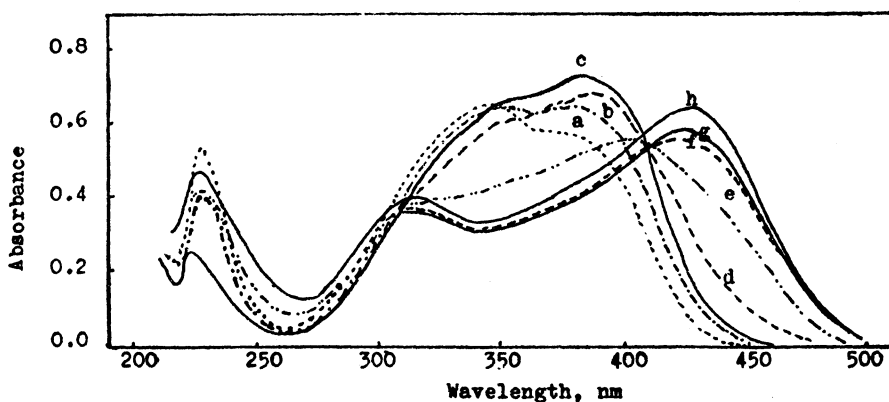


Fig. 1 Absorption spectra of  $3.8 \times 10^{-5}\text{M}$  of DAAZP in 20% (v/v) DMSO at pH: (a) 2.2; (b) 3.6; (c) 5.5-8.1; (d) 9.5; (e) 10.3; (f) 11.3; (g) 12.1; (h) 12.4

located at  $\lambda_{\text{max}}350$  and  $\lambda_{\text{max}}390$  nm are due to charge transfer transition. This is due to their large molar absorptivities ( $1.9 \times 10^{-4}$ ,  $2.2 \times 10^{-4} \text{ l mol}^{-1} \text{ cm}^{-1}$ ) and their high sensitivity to change in acidity of the medium. The shorter band decreases within the range pH 2.3-5.5, while the longer one increases till they reach a constant value (pH 5.5-8.1) exhibiting an isobestic point at  $\lambda_{\text{max}}350$  nm. This behaviour denotes that an equilibrium

exists between the protonated and the neutral forms of the compound. On increasing the pH beyond 8.1, the shorter band gradually disappears whilst the band located at 390 nm gets bathochromic shift to  $\lambda_{\max}$  425 nm. This is in accordance with the opinion that the electronic transition leading to this band is facilitated by an intramolecular charge transfer originated from the OH-group. Such type C.T. is easier in the ionic forms as a result of the increased negative charge density on the phenate oxygen<sup>11</sup>. A clear isobestic point is observed at  $\lambda_{\max}$  410 nm indicating the existence of an equilibrium probably between the neutral and the anionic forms.

The variation of absorbance with pH (Fig. 2) was utilized in the

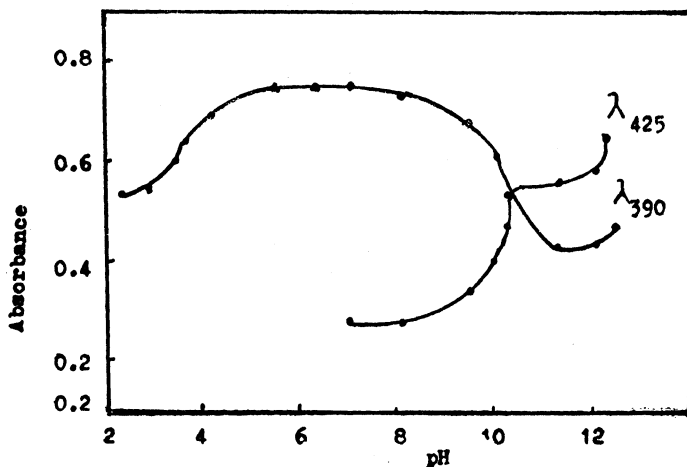
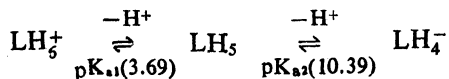


Fig. 2 Absorbance vs pH of  $3.8 \times 10^{-5}$  M DAAZP in 20% (v/v) DMSO

determination of the acid dissociation constants of the compound by the half-height<sup>12</sup>, the modified limiting absorbance<sup>13</sup> and the modified isobestic point<sup>13</sup> methods. Generally, the possible equilibria and the dissociation constants can be represented as follows:



The spectra of each of the individual acid-base forms, where the existence of a single form of the reagent can be assumed are shown in Fig. 3.

### Chelating Behaviour of DAAZP with Vanadium(V)

On comparing the electronic absorption spectra of the free ligand and its metal chelate solutions (Fig. 3), it is clear that the addition of the metal ion to the ligand causes a definite changes in the spectra of the ligand. The longer wavelength band ( $\lambda_{\max}$  390 nm) exhibits a considerable red shift on complexation ( $\lambda_{\max}$  450 nm). This behaviour can be presumably

due to easier intermolecular C.T. taking place within the chelated molecule ( $L \rightarrow M^{n+}$ ) relative to that in the free ligand<sup>14</sup>. This results from the

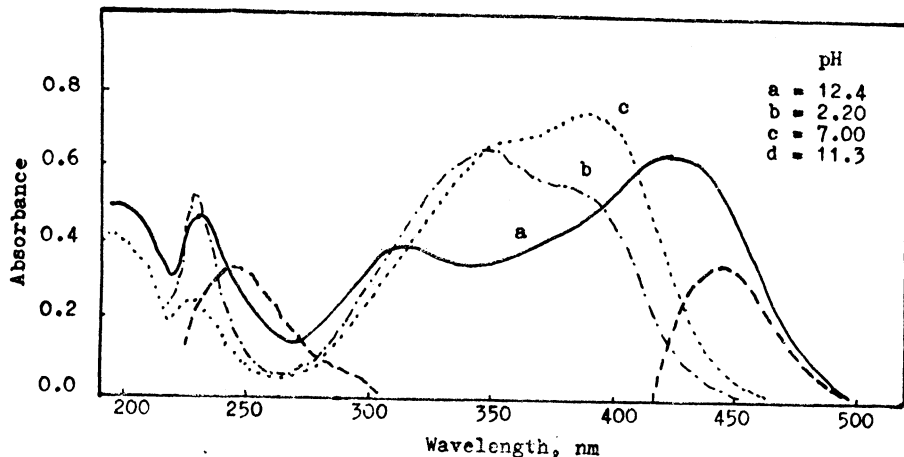


Fig. 3 Absorption spectra of individual acid-base forms of DAAZP (a,b,c and d) V-DAAZP complex (equimolar) in 20% DMSO

high acceptor character of the coordinating positively charged metal ion.

To explain the complexation and to establish the stability constants spectrophotometrically, the methods based on the relationship  $A = f(\text{pH})$  were employed<sup>15</sup>. The results presented in Fig. 4 show the absorbance-pH

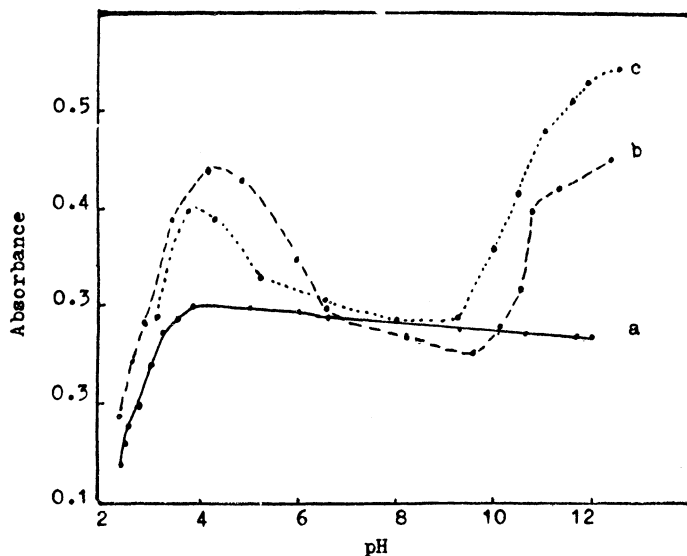


Fig. 4 Absorption -pH curves of V-DAAZP complexes in 20% DMSO at  $\lambda$  450 nm, (a)  $C_L = 2 \times 10^{-3} \text{ M}$ , (b)  $C_L = C_M = 4 \times 10^{-3} \text{ M}$ , (c)  $C_L = 2 \times 10^{-3} \text{ M}$

curves in equimolar solutions and with excess metal or with excess ligand. It is obvious from the results that two chelate equilibria are existed in the pH range 2-4 and 9.5-12.4 respectively.

The number of protons released during complexation and the equilibrium constants were calculated graphically from the curves obtained with the three metal to ligand mole ratios as follows<sup>16</sup>:

(a) For equimolar solutions, equation(1) was applied:

$$K_{eq} = \frac{AA_0 [H^+]^n}{4 C_M^2 (A_0 - A)^3} \quad (1)$$

where A is the absorbance at a given pH,  $A_0$  is the absorbance maxima,  $K_{eq}$  is the equilibrium constant and  $C_M$  is the total metal concentration. The logarithmic dependence of this equation is a straight line with a slope n and an intercept including  $K_{eq}$ :

$$\log \frac{A}{(A_0 - A)^3} = \log K_{eq} - \log \frac{A_0}{4C_M^2} + n \text{ pH}$$

(b) In the presence of excess metal ion, the following equation is valid;

$$K_{eq} = \frac{AA_0^2 [H^+]^n}{m C_M^2 (2A_0 - mA) (A_0 - A)^2} \quad (2)$$

where  $m = C_L/C_M < 1$ ,  $C_L$  is the total ligand concentration. The logarithmic transformation of this equation gives also a straight line.

(c) For solutions with excess of ligand, the logarithmic transformation of the equation;

$$K_{eq} = \frac{\Delta A [H^+]^n}{(\Delta A_0 - \Delta A) C_L^2} \quad (3)$$

was used.

The slopes of the straight lines are always about two for the three different conditions, i.e. two protons split off during complexation (Table 1). This leads to assuming the following equilibria;

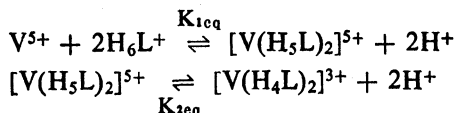


TABLE 1  
LOGARITHMIC ANALYTICAL DATA OBTAINED FROM THE STRAIGHT LINE PORTION OF THE ABSORBANCE pH-CURVES

M : L	Slope	Intercept	Log $K_{1eq}$	Log $K_{2eq}$
$C_L = C_M$	2.27	-0.6	6.7	6.38
$C_L/C_M = 0.5$	2.20	-0.7	6.9	5.98
$C_L/C_M = 2.0$	2.30	-1.0	7.1	6.22

The first equilibrium predominates over the interval pH 2–4, since at this range the protonated form  $H_6L^+$  is the only prevailing species irrespective of the ratio of the metal to ligand. The second equilibrium takes place above the pH 9.5 in which the anionic species  $H_4L^-$  predominates in condition that the components are in equimolar or of excess ligand. The stoichiometry of the complexes according to the above reactions was confirmed by continuous variation<sup>16</sup> as well as molar ratio<sup>17</sup> methods (Fig. 5) and was found to be 1 : 2 (M : L).

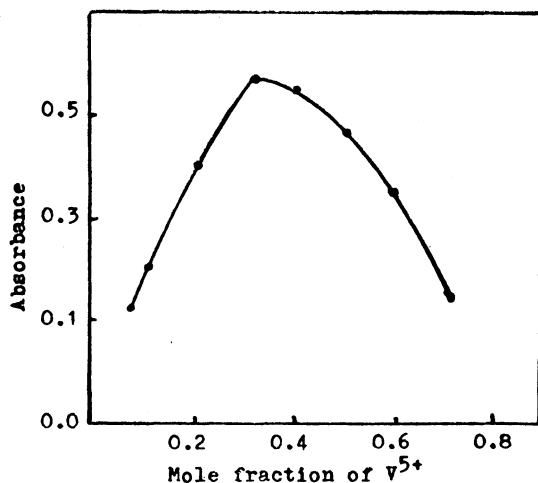


Fig. 5 Continuous variation plot for DAAZP- $V^{5+}$ ,  $C_0 = 1 \times 10^{-4}M$ ;  $\lambda_{450}$

The stability constant of the complexes were calculated using the relations<sup>18</sup>;

$$\beta_1 = K_{1eq}/K_{a1}$$

$$\beta_2 = B_1 K_{2eq}/K_{a2}$$

and represented in Table 2.

TABLE 2  
STABILITY CONSTANTS AND SPECTRAL CHARACTERISTICS OF  
 $V^{5+}$ -COMPLEXES IN 20% (v/v) DMSO AT  $\lambda_{max}$  450 nm.

Log $K_{1eq}$	Log $K_{2eq}$	Log $\beta_1$	Log $\beta_2$	$\epsilon_{max}$
6.90	6.19	9.59	26.17	$3.5 \times 10^3$

### Calibration Curve and Reproducibility

The chelating agent DAAZP has the advantage of micro determination of vanadium(V) spectrophotometrically. The calibration curves  $A = f(C_M)$

at pH 4.0 in a medium 20% (v/v) DMSO and with components of equimolar are linear upto  $7.13 \mu\text{g V}^{5+}/\text{cm}^3$  ( $C_L = 8 \times 10^{-6}\text{M}$ ) and the molar absorptivity of the complex is  $3.5 \times 10^3 \text{ l mol}^{-1} \text{ cm}^{-1}$ .

The sensitivity of the established method was calculated according to Sandell<sup>19</sup> and was found to be  $0.2 \mu\text{g}/\text{cm}^3$  of vanadium(V). Also, the reproducibility of the method was checked by measuring the absorbance of ten samples each containing  $0.5 \mu\text{g}/\text{cm}^3$  of vanadium. The relative standard deviation was 0.05%.

### Effect of Interfering Ions

The determination of vanadium(V),  $2.5 \mu\text{g}$ , by the recommended procedure was possible in the presence of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ag}^+$ ,  $\text{Sr}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Al}^{3+}$  (20 mg), EDTA, acetate,  $\text{CN}^-$ ,  $\text{Br}^-$  and  $\text{Cl}^-$  (40 mg). The presence of  $\text{Mn}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Ce}^{3+}$  interfere the determination and should be masked before working.

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