

# Spectrophotometric Studies of the Complexation of $\text{Hg}^{+2}$ , $\text{Ag}^+$ and $\text{VO}^{+2}$ with Pyrocatechol Violet

MUHAMMAD ABDUL RAUF\*, MUHAMMAD IKRAM AND NASEEM RAUF  
*Department of Chemistry*  
*Quaid-I-Azam University*  
*Islamabad, Pakistan*

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**Summary:** Pyrocatechol violet (PV) has been used as reagent for complexation studies with  $\text{Hg}^{+2}$ ,  $\text{Ag}^+$  and  $\text{VO}^{+2}$  by spectroscopic method. The spectra of the complexes were monitored under optimized conditions. The values of stability constants for the  $\text{Hg}^{+2}$ ,  $\text{Ag}^+$  and  $\text{VO}^{+2}$  complexes with PV were found to be of the order of  $7.2 \times 10^6$ ,  $1.9 \times 10^4$  and  $2.0 \times 10^{13}$  respectively

## Introduction

In reaction with organic reagents, metal ions are generally transformed into a colored complex [1]. Such complexes can be formed easily and also be monitored in terms of their metal to ligand ratio by using various methods [2]. The stability constants of the complexes formed can be of significance as it can be used in many chemical processes such as isolation, extraction or preconcentration methods [3-6]. Many elements present in trace amounts can be isolated by complexing reagents and later on used for other purposes. The present study aims at the conditions of complexation of pyrocatechol violet (PV) with  $\text{Hg}^{+2}$ ,  $\text{Ag}^+$  and  $\text{VO}^{+2}$ . The structure of PV is given in Fig. 1. Such conditions were optimized and the stability constants of the complexes formed were determined. The effect of foreign ions on complexation was also studied.

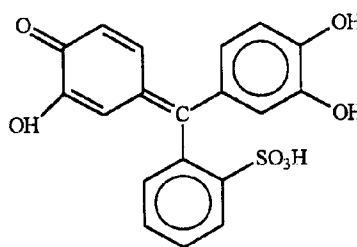


Fig. 1 Molecular structure of pyrocatechol violet (abbreviated as PV)

## Results and Discussion

The absorption spectra of pyrocatechol violet (PV) with  $\text{Hg}^{+2}$ ,  $\text{Ag}^+$  and  $\text{VO}^{+2}$  were recorded and showed their maximum at 575, 407 and 621 nm

\*To whom all correspondence should be addressed.

respectively. This is shown in Fig. 2. Their spectra were obtained in aqueous media against blank solution. The aqueous solution was adjusted to various pH values with buffer solutions and the optimized conditions were obtained at which the complexation took place. The stoichiometry of the complexes formed in each case with the dye was determined by applying Job's method [7]. The results are shown in Table-1. In each case of complexation, the values of molar extinction coefficients were also determined and are included in the above-mentioned table.

Table-1: Various properties of the complexes formed between  $Hg^{+2}$ ,  $Ag^+$ ,  $VO^{+2}$  and pyrocatechol violet.

Metal Ions	Stoichiometry of the complex	Molar Absorbivity*	Stability constant
$Hg^{+2}$	1:1	$1.3 \times 10^4$	$7.2 \times 10^6$
$Ag^+$	1:1	$2.8 \times 10^4$	$1.9 \times 10^4$
$VO^{+2}$	1:2	$4.3 \times 10^4$	$2.0 \times 10^{13}$

\*L/mole/cm.

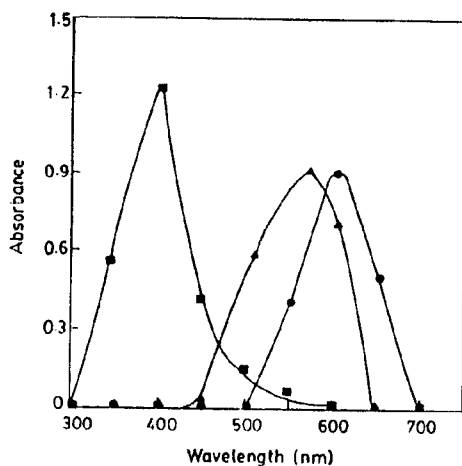


Fig. 2: Absorption spectra of  $Hg^{+2}$  ( $\sigma$ ),  $Ag^+$  ( $v$ ) and  $VO^{+2}$  ( $\lambda$ ) complexes with Pyrocatechol violet in aqueous solution.

Further studies on these complexes were done to monitor the effect of time and their stability constants. In each case of complexation, the absorption spectra were recorded with time and any variation in absorption intensity was observed. In case of  $Hg^{+2}$ , the complex formed remained stable for only one hour, whereas, the  $Ag^+$  complex showed stability for sixty-three hours and  $VO^{+2}$  complex with PV showed a stability period of twenty-three hours.

The magnitude of the stability constants of complexes in aqueous solution is important in analytical work. This indicates in particular the level of tolerance and interference by other species. By applying the equilibrium condition on a given system, one can easily obtain the value of stability constants.



$$K = [ML] / [M][L]$$

The concentration of the species in the above equation was determined spectrophotometrically and thus the values of K were determined. Table I shows such values as calculated in this particular work. From this table, one can infer that the most stable complex was formed between  $VO^{+2}$  and the dye, whereas,  $Ag^+$  formed the least stable complex. The high stability of  $VO^{+2}$  with PV can be explained on the basis of Sidgwick's classification of complexation [8], according to which  $VO^{+2}$  is included in the group which bonds strongly to oxygen rather than to nitrogen. In case of  $Ag^+$  complex with PV, silver bonds loosely with oxygen because of its filled d-orbital system.

The effect of foreign ions (both cations and anions) on the complexation of PV with  $Hg^{+2}$ ,  $Ag^+$  and  $VO^{+2}$  was also studied. These ions were added as either nitrate salts (for cations) or as potassium salts (for anions). The effect was studied under optimized conditions of pH and the concentration of the dye and the metal ion. The limiting concentration of the added foreign ions and the percentage decrease in absorbance intensity are reported in tables 2-4. From these tables, one can see that in case of  $Hg^{+2}$  and PV complexation, the effect is pronounced in the presence of  $Mg^{+2}$  and  $I^-$ , whereas,  $K^+$  and  $CH_3COO^-$  have least effect on the complexation process. Ferrous and cyanide ions have a largest depressive effect in case of  $Ag^+$  and PV complexation, whereas, the effect of nitrate ions is relatively small. Magnesium and sulfate ions reduce the absorption intensity in case of complexation of  $VO^{+2}$  and PV. The reduction in absorption intensity is a direct indication of the interference of added ions in a particular complexation process. Thus these ions should be removed from solution prior to complexation of PV and the metal ions under study.

Table-2: Effect of added ions on the Hg (PV)<sub>2</sub> complex.

Added Ions <sup>†</sup>	Limiting Conc. (M)	% decrease in intensity
Ba <sup>+2</sup>	1.0 x 10 <sup>-4</sup>	8.0
K <sup>+</sup>	8.0 X 10 <sup>-4</sup>	5.0
Pb <sup>+2</sup>	1.2 x 10 <sup>-4</sup>	42.0
Mg <sup>+2</sup>	1.7 x 10 <sup>-4</sup>	55.0
I <sup>-</sup>	1.0 x 10 <sup>-4</sup>	78.0
CH <sub>3</sub> COO <sup>-</sup>	2.7 x 10 <sup>-4</sup>	15.5
NO <sub>3</sub> <sup>-</sup>	7.9 x 10 <sup>-4</sup>	34.0
BrO <sub>3</sub> <sup>-</sup>	0.5 x 10 <sup>-4</sup>	16.0
SO <sub>4</sub> <sup>-2</sup>	1.5 x 10 <sup>-4</sup>	29.0

<sup>†</sup>Cations were added as nitrate salts and anions as potassium salts.

Table-3: Effect of added ions on the Ag (PV) complex.

Added Ions <sup>†</sup>	Limiting Conc. (M)	% decrease in intensity
Fe <sup>+2</sup>	2.4 x 10 <sup>-3</sup>	87.0
Ba <sup>+2</sup>	7.6 x 10 <sup>-3</sup>	22.0
Mg <sup>+2</sup>	7.8 x 10 <sup>-3</sup>	16.0
Mn <sup>+2</sup>	3.4 x 10 <sup>-3</sup>	21.0
Pb <sup>+2</sup>	3.0 x 10 <sup>-3</sup>	31.0
K <sup>+</sup>	10	10.0
NO <sub>3</sub> <sup>-</sup>	10	10.0
BrO <sub>3</sub> <sup>-</sup>	1.0 x 10 <sup>-4</sup>	12.0
SO <sub>4</sub> <sup>-</sup>	0.1	15.0
I <sup>-</sup>	1.2 x 10 <sup>-4</sup>	46.0
CN <sup>-</sup>	3.0 x 10 <sup>-4</sup>	49.0

<sup>†</sup>Cations were added as nitrate salts and anions as potassium salts.

Table-4: Effect of added ions on the VO (PV)<sub>2</sub> complex.

Added Ions <sup>†</sup>	Limiting Conc. (M)	% decrease in intensity
Ba <sup>+2</sup>	7.6 x 10 <sup>-3</sup>	3.5
Pb <sup>+2</sup>	3.0 x 10 <sup>-3</sup>	9.0
Cu <sup>+2</sup>	1.0 x 10 <sup>-4</sup>	13.0
Mg <sup>+2</sup>	4.0 x 10 <sup>-3</sup>	30.0
K <sup>+</sup>	1.0 x 10 <sup>-3</sup>	9.0
I <sup>-</sup>	6.0 x 10 <sup>-3</sup>	7.0
NO <sub>3</sub> <sup>-</sup>	1.0 x 10 <sup>-3</sup>	9.0
SO <sub>4</sub> <sup>-2</sup>	1.7 x 10 <sup>-4</sup>	19.5
CH <sub>3</sub> COO <sup>-</sup>	2.0 x 10 <sup>-4</sup>	12.0
BrO <sub>3</sub> <sup>-</sup>	6.0 x 10 <sup>-3</sup>	17.0
CN <sup>-</sup>	6.0 x 10 <sup>-4</sup>	7.0

<sup>†</sup>Cations were added as nitrate salts and anions as potassium salts.

### Experimental

All the reagents used were of analytical grade and were procured from either E. Merck or Riedel-de-Haan. The chemicals used in this work were used from freshly opened bottles and no attempt was made

to purify them. Deionized water was prepared by standard method [9]. Stock solutions of metal salts and the dye (both 1x10<sup>-3</sup>M) were prepared by dissolving appropriate amounts in deionized water. Further dilutions were also obtained as per requirement. Buffer solutions of different compositions (pH range 1 to 13) required for this work were prepared by using the reported method [10] and were monitored on a Horriba pH meter. Absorption spectra were obtained against a blank cell on a Hitachi Spectrophotometer model No. 100-50.

### Conclusion

The absorption spectra of pyrocatechol violet (PV) with Hg<sup>+2</sup>, Ag<sup>+</sup> and VO<sup>+2</sup> were studied and their maxima were observed at 575, 407 and 621 nm respectively. The effect of time and their stability constants were also studied. The Hg<sup>+2</sup>, Ag<sup>+</sup> and VO<sup>+2</sup> complexes remained stable for one hour, 63 hours and 23 hours respectively. The effect of foreign ions, both cations and anions, revealed a decrease in absorption intensity of the complexes.

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