

**INTERACTION BETWEEN POTASSIUM FERROCYANIDE AND
THE SCHIFF'S BASE DERIVED FROM ORTHO VANILLIN AND
SULPHANILAMIDE (OVSN) CATALYZED BY MERCURY(II) ION –
A SPECTROPHOTOMETRIC STUDY**

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RECEIVED : 25 March, 2016

Interaction between Potassium hexacyanoferrate (II) and the Schiff's base derived from ortho Vanillin and Sulphanilamide (OVSN) produces an intense reddish brown color in the presence of Mercury (II) which functions as a catalyst. Though there is instant color formation after mixing but the maximum color development is observed in 30 minutes. The color formation is spectrophotometrically monitored under established optimal experimental conditions which are 510 nm as wavelength of maximum absorbance, pH of buffer solution to be 4, the volume percent of DMF solvent as 30% (v/v), hexa cyanoferrate (II) concentration is fixed at 5×10^{-3} M etc. This color reaction is carefully investigated and successfully exploited for the quantitative spectrophotometric determination of OVSN in the concentration range 1×10^{-4} M to 5×10^{-4} M (0.03 mg/ml to 0.15 mg/ml) when the concentration of Hg(II) 5×10^{-6} M is kept constant. Similarly the color reaction is also suitably explored for the quantitative spectrophotometric determination of Hg(II) in the concentration range 2×10^{-6} M to 12×10^{-6} M (0.4 μ g/ml to 4.8 μ g/ml) when the concentration of OVSN is kept constant at 2×10^{-4} M. Thus the proposed method offers an advantage that it is suitable for the quantitative spectrophotometric estimation of both OVSN and Hg (II).

INTRODUCTION

Dutta and Das [1], Saroja Raman [2], Phull *et. al.* [3, 4], Kares and Pinter [5] have reported reactions involving the exchange of the cyanide ion by organic liquids in potassium ferrocyanide in the presence of Hg (II) ion. This suggested that many types of organic compounds facilitate this exchange process and such reactions are favorable for the determination of mercury (II) ion or the organic substrate. It is also reported that the penta cyanides of iron give colored complexes with several aromatic compounds such as nitroso

benzene [6], 4, 4-dipyridy [7], p-nitroso diphenylamine, isonicotinoyl hydrazide [8] and sulphanilamide [9]. This formation of colored species was successfully utilized for their spectrophotometric determinations. A survey of chemical literature indicated that sulpha drugs namely the derivatives of para amino benzene sulphonamides have not been tried for the possible exchange of the cyanide ions in $K_4[Fe(CN)_6]$. Further in view of the importance of the assay of the sulpha drugs, a systematic study of the exchange reaction with sulphamethaxazole [10], sulphanilamide [11] and the condensation product of sulphanilamide with salicylaldehyde(SASN) [12] was carried out and reported. This study prompted the authors to carry out the present investigations on the sulpha drug formed by the condensation of ortho Vanillin and Sulphanilamide(OVSN) in detail and the results are communicated herewith. To establish the analytical suitability of above interaction between $K_4[Fe(CN)_6]$ and OVSN, the optimum experimental conditions are established in a systematic way as follows.

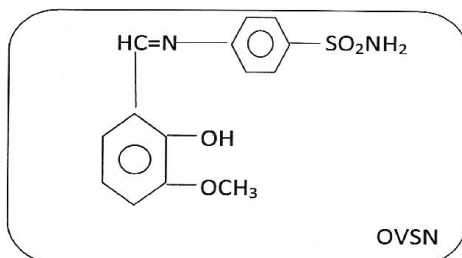
When the Schiff's base OVSN derived from ortho Vanillin and sulphanilamide is added to an aqueous solution of $K_4[Fe(CN)_6]$ in buffer solutions in the pH range 1-5, a reddish brown color species is formed. The intensity of the color is found to increase with time and reached a maximum intensity after half an hour of mixing. However addition of a dilute solution of Hg(II) hastened up the color development. No reddish brown color is obtained when Hg(II) is added separately to the solution of $K_4[Fe(CN)_6]$ or OVSN. In the view of this, the absorption spectra of the test solution is recorded after half an hour of the preparation of test solution to establish the wavelength of maximum absorbance so that further studies can be done at that wavelength.

EXPERIMENTAL

Apparatus, Reagents and Solutions:

Apparatus : A Systronics Spectrophotometer Model-106 with wavelength range 300-900 nm is used for absorbance measurements. A toluene Hg thermostat is used for maintaining the temperature of the reaction mixture constant. pH measurements are made using an Elico LI-10 digital pH meter.

Reagents : The Schiff's base derived from ortho Vanillin and sulphanilamide (1:1) in absolute alcohol is prepared according to procedure reported in Chemical Literature [13] Equi molar quantity of ortho Vanillin and sulphanilamide both dissolved in alcohol are mixed and refluxed for one hour, cooled, filtered and finally recrystallised from absolute alcohol. Yellow crystals formed under reflux are separated, washed and recrystallized with hexanol. The compound is readily soluble in DMF and its solution is stable for more than one month. The structure of ortho Vanillin - sulphanilamide (OVSN) is given as



Solutions: Suitable quantity of OVSN is dissolved in DMF and the solution obtained is yellow in color and is stable for more than one month. 0.306 gram of OVSN is dissolved and

diluted to 100 ml with DMF to get a stock solution of 0.01M. $K_4[Fe(CN)_6]$ solution is prepared by dissolving 4.221 gram of AR sample in distilled water and diluted to 100 ml to get a stock solution of 0.1M. Hg(II) solution is prepared by dissolving 0.2715 gram of mercury(II) Chloride in distilled water and diluted to 100 ml to get a 0.01M solution. Buffer solutions are prepared by adopting the standard procedures [14] mixing suitable quantities of the components concerned.

RESULTS AND DISCUSSION

(i) Absorption Spectra : The absorption spectra of the test solution containing 4 ml buffer pH 4, 2 ml water 1 ml DMF, 1ml Hg(II) (5×10^{-5} M), 1 ml of $K_4[Fe(CN)_6]$ (7×10^{-2} M) and 1 ml of OVSN (7×10^{-3} M) is recorded half an hour after mixing the components against $K_4[Fe(CN)_6]$ as a blank and is shown in Fig. 1. The absorption spectra of the individual constituent solutions without OVSN show negligible absorbance and so are not shown in the figure. The Fig. 1 shows that the absorbance is maximum in the wavelength range 500-520 nm. Hence 510 nm is chosen as the optimum wavelength for subsequent studies.

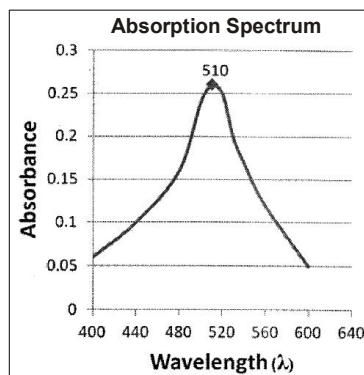


Fig 1 : Absorption Spectrum of $K_4[Fe(CN)_6]$ + OVSN + DMF + Hg (II) colored species

(ii) Effect of Time : For the complete color development, the effect of time was studied by measuring the absorbance of the test solution after every ten minutes. It is observed that there is no appreciable change in absorbance after 30 minutes of mixing the components of the test solution. This suggests that the color reaction is stable after 30 minutes of mixing. Therefore, 30 minutes time is fixed for recording the absorbance of solutions.

(iii) Effect of pH : To arrive at the optimum pH, the absorbance of the test solution is measured in the pH range 1-6 and the results are presented in Table-1.

Table 1. Effect of pH on the Absorbance at 510 nm

4 ml of Buffer Solution (pH 1 – 6), 2 ml of water, 1ml of DMF solvent, 1 ml of Hg (II) (5×10^{-5} M)

1 ml of $K_4Fe(CN)_6$ (7×10^{-2} M), 1 ml of OVSN (7×10^{-3} M), Total Test solution mixture = 10 ml

pH		1	2	3	4	5	6
Absorbance at	10 min	0.03	0.07	0.11	0.17	0.07	0.02
	30 min	0.05	0.11	0.16	0.23	0.09	0.04

The data in Table-1 indicates that the absorbance is maximum in a buffer solution of pH 4. Therefore pH 4 is chosen for further studies.

(iv) **Effect of volume percentage of DMF:** The substrate OVSN is sparingly soluble in water and readily soluble in DMF. So to fix the effect of DMF on the absorbance of the test solution, the volume percentage of DMF in the test solution is varied in the range 10% (v/v) to 50% (v/v) and the absorbance values are recorded at 510 nm and shown in Table 2.

Table 2. Effect of volume percentage of DMF on the absorbance of solution at 510 nm

Test solution : 4 ml buffer solution (pH 4), (4 - x) ml water, x ml DMF, 0.5 ml of Hg (II) 1×10^{-4} M, 0.5 ml $K_4[Fe(CN)_6]$ (1.4×10^{-2} M), 1 ml OVSN (7×10^{-3} M) Total volume = 10 ml.

%DMF (v/v)		10	20	30	40	50	60
Absorbance at	10 min	0.08	0.16	0.17	0.17	0.17	0.17
	30 min	0.14	0.22	0.23	0.23	0.23	0.23

The results in Table 2 clearly show that the absorbance of the test solution is almost constant beyond 30% (v/v) of DMF. Hence for further studies 30% (v/v) DMF is maintained.

(v) **Effect of $K_4[Fe(CN)_6]$ Concentration:** The effect of $K_4[Fe(CN)_6]$ concentration is studied by varying the $K_4[Fe(CN)_6]$ concentration in the range 1×10^{-3} M to 6×10^{-3} M in the test solution and the results obtained are shown in Table 3.

Table 3. Effect of $K_4[Fe(CN)_6]$ concentration on the absorbance of test solutions at 510 nm

Test solution : 4ml buffer solution (pH 4), (2 - x) ml water, 2 ml DMF, 1 ml of Hg (II) 5×10^{-5} M, x ml $K_4[Fe(CN)_6]$ (3×10^{-2} M), 1 ml OVSN (7×10^{-3} M) Total volume = 10 ml.

$K_4Fe(CN)_6 \times 10^3$ M		1.0	2.0	3.0	4.0	5.0	6.0
Absorbance at	10 min	0.05	0.09	0.13	0.17	0.17	0.17
	30 min	0.08	0.15	0.18	0.22	0.23	0.23

It is seen from the data in Table 3 the absorbance of the test solution is almost remaining unchanged beyond 4×10^{-3} M. Therefore $K_4[Fe(CN)_6]$ concentration is fixed at 5×10^{-3} M for further studies.

Calibration curve – Obedience of Beer-Lambert's Law:

(A) **Determination of OVSN:** The absorbance of the test solution is varying with the concentration of OVSN in the range 1×10^{-4} M to 7×10^{-4} M. This is recorded at 510nm against a blank and the data obtained is presented in Table 4 and Fig. 2.

Table 4. Effect of OVSN concentration – Determination of OVSN

Test solution : 4ml buffer solution (pH 4), 1ml water, (3 - x) ml DMF, 1 ml of Hg(II) 5×10^{-5} M, 1 ml $K_4[Fe(CN)_6]$ (5×10^{-2} M), x ml OVSN (2.5×10^{-3} M) Total volume = 10 ml.

[OVSN] $\times 10^4$ M	Absorbance at	
	10 min	30 min
1.0	0.03	0.05
2.0	0.06	0.10
3.0	0.09	0.15
4.0	0.12	0.20
5.0	0.15	0.25
6.0	0.18	0.28
7.0	0.22	0.30

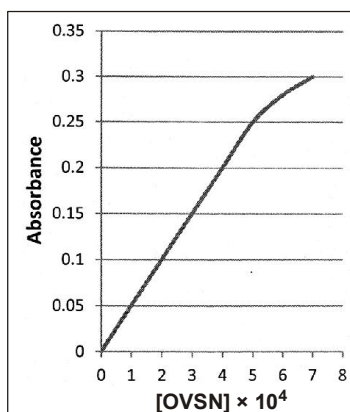


Fig. 2. Determination of OVSN

It is observed from the data in Table 4 and Fig. 2 that the absorbance increased linearly with the concentration of OVSN from 1×10^{-4} M to 5×10^{-4} M (0.03 mg/ml to 0.15 mg/ml) and thereafter it is remaining almost constant. This indicates that Beer Lambert's law is obeyed in the concentration range of OVSN from 1×10^{-4} M to 5×10^{-4} M (0.03 mg/ml to 0.15 mg/ml) and that the method is suitable for the spectrophotometric determination of OVSN in the range 1×10^{-4} M to 5×10^{-4} M (0.03 mg/ml to 0.15 mg/ml). However for further studies such as the effect of Hg (II) ion concentration, a concentration of 5×10^{-4} M OVSN may be fixed.

(B) Determination of Hg(II):

(I) To study the effect of Hg (II) concentration on the absorbance of the test solution, the solutions are prepared by varying the concentration or amounts of Hg (II) ion and the data obtained is presented in Table 5 and Fig. 3.

Table 5. Effect of Hg (II) concentration – Determination of Hg (II)

Test solution: 4ml buffer solution (pH 4), (3-x) ml water, 1 ml DMF, x ml of Hg (II) (5×10^{-5} M), 1 ml $K_4[Fe(CN)_6]$ (5×10^{-2} M), 1 ml OVSN (2.5×10^{-3} M), Total volume = 10 ml.

Hg(II) × 10 ⁶	Absorbance at	
	10 Min	30 Min
2.0	0.02	0.04
4.0	0.04	0.08
6.0	0.06	0.12
8.0	0.08	0.16
10.0	0.10	0.20
12.0	0.12	0.24
14.0	0.13	0.26

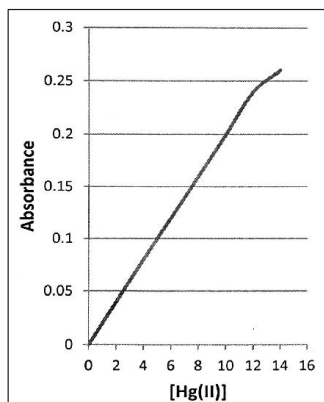


Fig. 3. Determination of Hg (II)

The data in Table-5 and Fig. 3 indicates that the absorbance is increasing linearly with the increase in the amount of Hg(II) in the range 0.4 $\mu\text{g/ml}$ to 4.8 $\mu\text{g/ml}$. This indicates that the Beer's law is obeyed in the range 0.4 $\mu\text{g/ml}$ to 4.8 $\mu\text{g/ml}$ and the method is suitable for Hg(II) spectrophotometric determination in this range.

(II) Kinetic Initial Rate Method for Hg (II) determination: It is known that better results are obtained by the initial rate kinetic method. In this method, the test solutions are prepared under optimal conditions i.e. λ_{max} 510nm, pH 4, DMF 30% (v/v) $\text{K}_4[\text{Fe}(\text{CN})_6]$ (5×10^{-3} M), [OVSN] (5×10^{-4} M), temperature 27°C with various aliquots of the Hg(II) solution (0.2 $\mu\text{g/ml}$ to 1.6 $\mu\text{g/ml}$). The absorbance of each of the test solution is measured at different time intervals and the initial rate is calculated. The results obtained are presented in Table-6.

Amount of Hg(II) in $\mu\text{g/ml}$	Initial Rate $\times 10^4 \text{ sec}^{-1}$
0.2	0.5
0.4	1.0
0.6	1.5
0.8	2.0
1.0	2.5
1.2	3.0
1.4	3.2
1.6	3.4

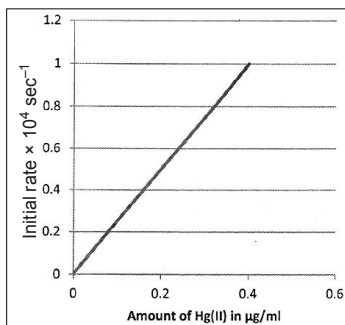


Fig. 4 : Determination of Hg(II) using Initial Rate Kinetic Method

A Linear curve is obtained between the amount of Hg (II) and the initial rate as shown in Fig. 4. It is observed from the curve that the initial rate increases linearly with the amount of Hg(II) in the range 0.2 $\mu\text{g/ml}$ to 1.2 $\mu\text{g/ml}$. This observation suggests the suitability of the method for the spectrophotometric determination of mercury.

(vi) Effect of diverse ions: To examine the effect of various diverse ions, the absorbance of the test solution containing 1 $\mu\text{g/ml}$ is recorded in the presence of these diverse ions. A deviation of $\pm 2\%$ in the absorbance is taken as the tolerance limit of the added diverse ion. The results are shown in Table-7.

Table 7. Effect of Diverse Ions: Tolerance Limit of added diverse ions

Added Diverse ion	Tolerance limit in $\mu\text{g/ml}$	Added Diverse ion	Tolerance limit in $\mu\text{g/ml}$
Ba ⁺²	216	PO ₄ ⁻³	1500
Al ⁺³	1.8	CrO ₄ ⁻²	126
Mg ⁺²	25	NO ₃ ⁻	23
Cd ⁺²	8.5	SCN ⁻	5.3
Pb ⁺²	6.2	F ⁻	70
Zn ⁺²	0.6	Cl ⁻	>1000
Ni ⁺²	1.6	Br ⁻	60
Cu ⁺²	3.2	I ⁻	0.5
Co ⁺³	0.6		
Mn ⁺²	0.3		

ACKNOWLEDGEMENTS

The authors express their gratitude to Dr. G. Abdul Huq for his keen interest in the progress of this work. One of the authors (TR) is also grateful to the authorities of G. Pulla Reddy Engineering College, Kurnool for their constant encouragement.

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