



LIGAND EXCHANGE REACTION BETWEEN CYANIDE ION AND SULPHANILAMIDE IN DMF SOLVENT CATALYZED BY MERCURY (II) : A SPECTROPHOTOMETRIC STUDY

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ABSTRACT

The reaction mixture containing potassium ferrocyanide in 40% dimethyl formamide (DMF), sulphanilamide at pH 4 in the presence of mercury (II) developed a reddish brown colored species. Appreciable color development occurs at 10 minutes. The color formation is monitored spectrophotometrically under the optimum conditions of 40% DMF, pH 4, wave length 510 nm, 2 fold excess hexacyanoferrate (II) to sulphanilamide and mercury (II) at 1×10^{-5} M. The color reaction is successfully investigated for the spectrophotometric determination of sulphanilamide in the range 0.086 mg/mL - 0.043 mg/mL, when mercury concentration is kept fixed. In the same way, when the concentration of SN is fixed the method is successfully explored for the spectrophotometric determination of Hg (II) in the range 0.2 μ g/mL to 1.2 μ g/mL. The proposed method can be suitably applied for the spectrophotometric estimation of the drug sulphanilamide and also Hg (II).

Key words: Spectrophotometric, Dimethyl formamide (DMF), Potassium hexacyanoferrate ($K_4Fe(CN)_6$), Sulphanilamide (SN), Mercury (II).

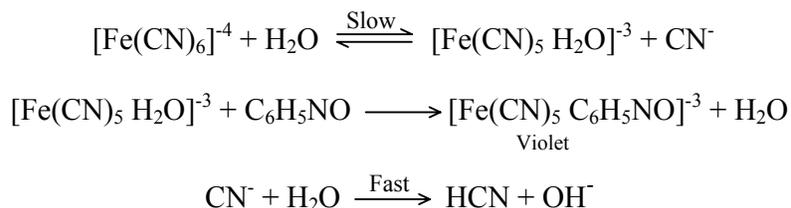
INTRODUCTION

Aqueous solution of potassium hexacyanoferrate (II) is stable on in the dark or in diffused sunlight. A survey of the chemical literature¹⁻⁶ revealed that the solution when exposed to light of wavelength less than 500 nm or to high temperatures decomposes at a measureable rate. It is reported by Asperger⁷ that the photoreaction of the ferrocyanide gives $[Fe(CN)_5 H_2O]^{-3}$ and CN^- first and that the absorption of $[Fe(CN)_5 H_2O]^{-3}$ does not differ

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much from that of the ferrocyanide ion. It is also reported that the penta cyanides of iron give coloured complexes with several aromatic compounds such as nitroso benzene⁸, 4,4 dipyridyl⁹, p-nitroso diphenylamine^{10,11} and iso nicotinoyl hydrazide¹² etc. Sulphanilamide has also been spectrophotometrically determined using a few other methods¹³⁻¹⁵.

For Example: The ligand exchange reaction with nitroso benzene can be shown as:



Asperger (loc.cit.) further reported that the colour formation takes place quickly in the presence of small quantities of Hg (II) ions even in the absence of UV light or high temperatures.

The above observations prompted the present authors to investigate and explore the ligand exchange reaction between hexacyano ferrate (II) and sulphanil amide (SN) in the presence of Hg (II) ions as catalyst. Since sulphanilamide is not freely soluble in water the spectrophotometric behavior of the aqueous solution of ferrocyanide is studied in the presence of suitable buffer solution and the solvent dimethyl formamide (DMF) and catalyst Hg (II) ions. The detailed results obtained are presented in this communication.

Preliminary studies have shown that the SN prepared in DMF forms a reddish brown color with an aqueous solution of $\text{K}_4\text{Fe}(\text{CN})_6$ in weakly acidic medium (pH 2-4). For complete color development, it takes nearly six hours but in the presence of Hg (II) solution the reddish brown color formation is rapid. In order to establish favorable conditions for this reaction between SN and $\text{K}_4\text{Fe}(\text{CN})_6$ in presence of Hg (II) experiments are conducted and the results obtained are presented in this paper.

EXPERIMENTAL

Stock solutions of $\text{K}_4\text{Fe}(\text{CN})_6$ (0.1 M) and Hg (II) (5×10^{-2} M) are prepared by dissolving the requisite amount of the salts in double distilled water. The Hg (II) solution is standardized using standard procedure (loc.cit.Ref. 11). A solution of 2×10^{-2} M SN is prepared in DMF. A sodium Acetate trihydrate-HCl buffer solutions of pH 1-3, sodium acetate trihydrate-acetic acid buffer solutions of pH 4-6 is used in the studies. All substances used are of AR grade. Required dilutions of the solutions are made as and when necessary.

Apparatus

A Systronics Spectrophotometer Model-106 with wavelength range 300-900 nm is used for measuring absorbances. A pH meter model LI-10 manufactured by Elico is used for pH measurements. A toluene Hg thermostat is used for maintaining the temperature of the reaction mixture constant.

Recommended procedure

Determination of Hg (II)

The following procedure is recommended for the quantitative estimation of Hg (II) spectrophotometrically using the initial rate method.

4 mL of buffer solution of pH 4, 0.5 mL of $K_4Fe(CN)_6$ solution (0.1 M), 3 mL of DMF (20%) solvent and known aliquots of mercury (II) solution and 1 mL of SN solution are taken in each of the 10 mL standard flask and the resulting solution is made up to the mark in the 10 mL standard flasks with double distilled water. The absorbance of each solution is recorded at 510 nm after 2 minutes and 8 minutes against the buffer solution. The results show that a linear curve is obtained between the amount of Hg (II) and absorbance. This suggests that suitability of the method for the spectrophotometric determination of Hg (II) in the range 0.2 $\mu\text{g/mL}$ to 1.2 $\mu\text{g/mL}$. The initial rate kinetic method can also be followed to get the same results. The procedure followed in the initial rate method is that the absorbance of the test solutions containing known aliquots of Hg (II) under optimum experimental conditions is recorded at different times and the initial rate is calculated from the absorbance - time graph. A linear graph is obtained between the amount of Hg (II) and the initial rate in the range 0.2 $\mu\text{g/mL}$ to 1.2 $\mu\text{g/mL}$ suggesting the suitability of the method for the determination of Hg (II) ions.

Determination of SN

4 mL of buffer solution of pH 4, 1 mL of $K_4Fe(CN)_6$ solution (0.1 M), 1 mL of Hg (II), different known aliquots of SN are taken in 10 mL standard flask. The flasks are made up to the mark using DMF solvent. The absorbance of the test solutions are recorded at 510 nm after 2 minutes and 8 minutes against the buffer solution. The results show a linear increase in the intensity of the color in the concentration range (0.5×10^{-3} M to 2.5×10^{-3} M). This suggests the SN can be determined spectrophotometrically in the range 0.5×10^{-3} M to 2.5×10^{-3} M (or 0.086 mg/mL to 0.43 mg/mL).

RESULTS AND DISCUSSION

Absorption spectra

The absorption spectra of the test solution containing 4 mL of buffer solution (pH 4), 1 mL of $K_4Fe(CN)_6$ ($5 \times 10^{-2} M$), 1 mL of SN ($2.5 \times 10^{-2} M$), 1 mL of Hg (II) ($5 \times 10^{-5} M$), 2 mL of DMF and 1 mL water and a blank solution containing 4 mL buffer solution (pH 4), 1 mL of $K_4Fe(CN)_6$ ($5 \times 10^{-2} M$) and 5 mL water, total volume in each case 10 mL are recorded as shown in Fig. 1. It is observed from the figure that both the test solution and the blank solution show absorption maxima at 410 nm. However difference in absorbance (ΔA) of the two solutions is found to be maximum at 510 nm. Hence the absorption spectrum of the test solution is recorded against the blank solution and the curve obtained is shown in Fig. 2. For further studies a wavelength of 510 nm is fixed.

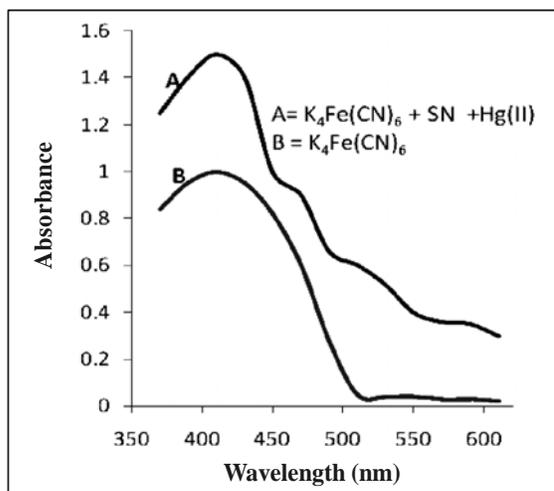


Fig. 1: Absorption spectra

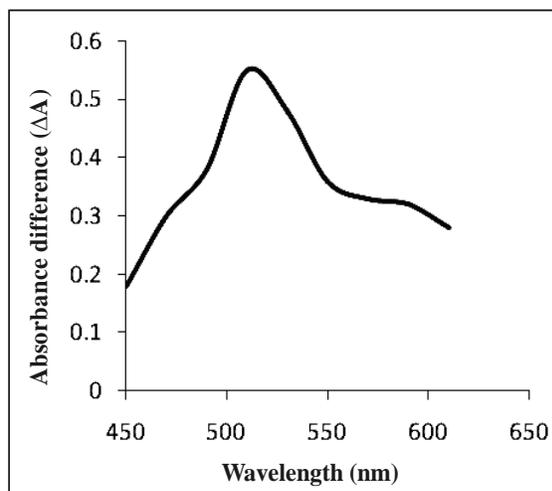


Fig. 2: Absorption spectrum

Effect of pH

With a view to establish the optimum pH of the buffer solution to be used in the detailed investigation, the test solutions are prepared in different buffer solutions in the pH range 1-6 and the absorbance values are recorded at 510 nm. The results obtained are present in Table 1. The data in Table 1 shows that the absorbance of the test solution is maximum at pH 4. Hence buffer solution of pH 4 is fixed for further studies.

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

4 mL Buffer Solution of pH 4, 2 mL of water, 1 mL of DMF solvent, 1 mL of Hg (II) (5×10^{-5} M) 1 mL of $K_4Fe(CN)_6$ (5×10^{-2} M), 1 mL of SN (2.5×10^{-2} M), Total test solution mixture = 10 mL.

pH	Absorbance at	
	2 min.	10 min.
1.0	0.02	0.04
2.0	0.04	0.08
3.0	0.07	0.14
4.0	0.08	0.17
5.0	0.04	0.06
6.0	0.02	0.04

Effect of solvent

SN is not readily soluble in water but easily soluble in DMF solvent. The effect of volume percentage of the DMF solvent on the absorbance of the test solution is fixed at 40% v/v on the basis of the data presented in Table 2.

Table 2: Effect of Volume percentage of DMF solvent on Absorbance at 510 nm

4 mL Buffer Solution of pH 4, (4-x) mL of water, X mL of DMF solvent, 0.5 mL of Hg (II) (1×10^{-4} M) 0.5 mL of $K_4Fe(CN)_6$ (0.1 M), 1 mL of SN (2.5×10^{-2} M), Total volume of test solution = 10 mL.

% DMF (v/v)	Absorbance at	
	2 min.	10 min.
10	0.01	0.03
20	0.03	0.10
30	0.05	0.17
40	0.06	0.18
50	0.06	0.18

Effect of $K_4Fe(CN)_6$

From the results in Table 3, it is clear that a minimum of 2 fold excess of $K_4Fe(CN)_6$ to SN is essential to have maximum color development. Further studies are therefore carried out with 2 fold excess of $K_4Fe(CN)_6$.

Table 3: Effect of $K_4Fe(CN)_6$ Concentration on the Absorbance at 510 nm

4 mL Buffer Solution of pH 4, (1.5-x) mL of water, 3 mL of DMF, 0.5 mL of Hg (II) (1×10^{-4} M) X mL of $K_4Fe(CN)_6$ (5×10^{-2} M), 1 mL of SN (2.5×10^{-2} M), Total volume of test solution = 10 mL.

$K_4Fe(CN)_6 \times 10^3$ M	Absorbance at	
	2 min.	10 min.
1.0	0.03	0.14
2.0	0.05	0.17
3.0	0.07	0.19
4.0	0.08	0.19
5.0	0.08	0.19
6.0	0.08	0.19

Calibration curve - Obedience of beer-lambert's law

Determination of SN

The effect of SN concentration on the absorbance of the test solution indicated a proportionate increase in the absorbance values up to a concentration of 2.5×10^{-3} M and thereafter the absorbance values remained almost constant. This suggests the suitability of the method for the determination of SN in the range 0.5×10^{-3} M to 3.5×10^{-3} M. However a concentration of 2.5×10^{-3} M is fixed for further studies. The data obtained is presented in Table 4 and Fig. 3.

Table 4: Determination of SN concentration based on the absorbance at 510 nm

4 mL Buffer Solution of pH 4, (4-x) mL of DMF, 1 mL of Hg (II) (5×10^{-5} M), 1 mL of $K_4Fe(CN)_6$ (4×10^{-2} M), x mL of SN (2.5×10^{-2} M), Total volume of test solution = 10 mL.

[SN] $\times 10^3$ M	Absorbance at	
	2 min.	10 min.
0.5	0.02	0.05
1.0	0.04	0.10
1.5	0.06	0.15
2.0	0.09	0.20
2.5	0.11	0.25
3.0	0.11	0.26
3.5	0.11	0.26

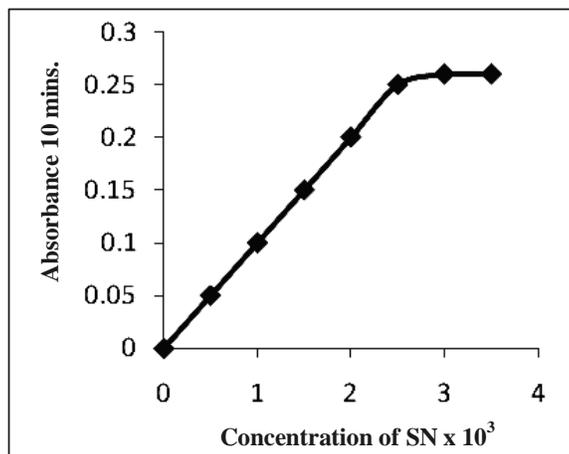


Fig. 3: Determination of SN

Determination of Hg (II) ion

The test solution containing different aliquots of Hg (II) are prepared under optimum conditions and the absorbances are measured at 510 nm. The results shown in Table 5 and Fig. 4 indicate linear relationship between the amount of Hg (II) and the absorbance of the test solutions. This indicates the possibility of the determination of Hg (II) in the range 0.2 $\mu\text{g/mL}$ to 1.2 $\mu\text{g/mL}$. Thus for further studies when Hg (II) ion is used as catalyst a minimum of 1.2 $\mu\text{g/mL}$ is fixed.

Table 5: Determination of Hg (II) amount based on the absorbance at 510 nm

4 mL Buffer Solution of pH 4, (1.5-x) mL of water, 3 mL of DMF, x mL of Hg (II) (5×10^{-5} M) 0.5 mL of $\text{K}_4\text{Fe}(\text{CN})_6$ (4×10^{-2} M), 1 mL of SN (2.5×10^{-2} M), Total volume of test solution = 10 mL.

Amount of Hg (II) in $\mu\text{g/mL}$	Absorbance at	
	2 min.	10 min.
0.2	0.02	0.04
0.4	0.04	0.08
0.6	0.06	0.12
0.8	0.08	0.16
1.0	0.10	0.20
1.2	0.12	0.24
1.4	0.13	0.25
1.6	0.13	0.25

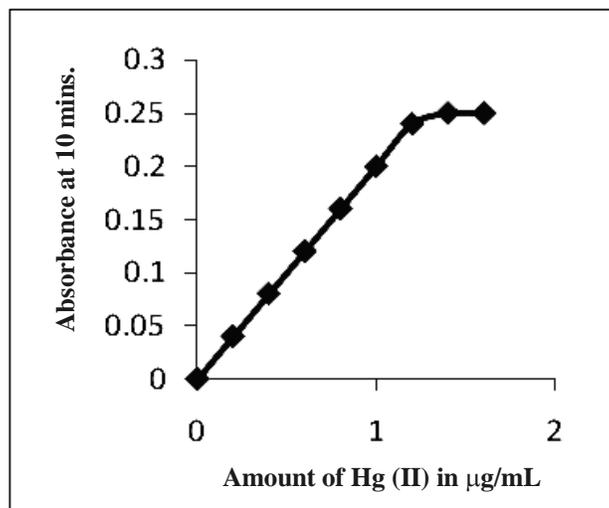


Fig. 4: Determination of Hg (II)

Initial rate method

In the kinetic initial rate method, the absorbances of the test solutions containing known aliquots of Hg (II) under optimum conditions are recorded at different times and the initial rate is computed from the absorbance-time graph. A linear graph obtained between the amount of Hg (II) and the initial rate indicates that the method can be applied for the quantitative determination of Hg (II) in the range 0.2 µg/mL to 1.2 µg/mL. The data is presented in the Table 6 and Fig. 5.

Table 6: Determination of Hg (II) using initial rate method

Amount of Hg (II) in µg/mL	Initial rate x 10 ⁴ sec ⁻¹
0.2	2.0
0.4	3.6
0.6	5.0
0.8	6.2
1.0	7.6
1.2	8.6
1.4	8.8
1.6	9.0

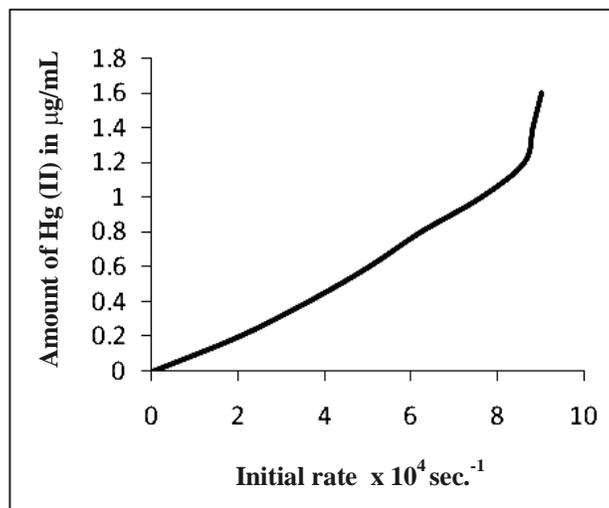


Fig. 5: Determination of Hg (II) using initial rate method

Effect of diverse ions

The effect of diverse ions on the absorbance of the test solution containing 1.0 $\mu\text{g/mL}$ of Hg (II) is recorded. The amount of the diverse ion causing a deviation of $\pm 2\%$ or more in the absorbance value is taken as the tolerance limit of the diverse ion. The tolerance limit of various diverse ions is presented in Table 7.

Table 7: Effect of diverse ions - tolerance limits

Added ions	Tolerance limit in $\mu\text{g/mL}$	Added ions	Tolerance limit in $\mu\text{g/mL}$
Barium ion	1370	Copper ion	0.64
Magnesium ion	120	Sulphate ion	2400
Aluminium ion	54	Chloride ion	1952
Lead ion	07	Bromide ion	120
Calcium ion	06	Nitrate ion	62
Zinc ion	03	Iodide ion	02
Nickel ion	03	Fluoride ion	0.2
Cobalt ion	02		

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