

## METAL ION PROMOTED LIGAND-EXCHANGE OF $\text{CN}^-$ IN POTASSIUM-HEXACYANOFERRATE (II)—II

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(Received 16 December 1982)

Ag(I) promoted abstraction of  $\text{CN}^-$  from Potassium hexacyanoferrate(II) in the presence of excess Nitrosobenzene forms the violet coloured Pentacyano nitrosobenzene iron(II) complex. This has been found suitable for the spectrophotometric determination of  $\text{Ag}^+$  in microquantities ranging from 0.6-11.0  $\mu\text{g}/\text{ml}$ . The reaction is complete in 4 min at  $85^\circ\text{C}$  or 4 hours at  $40^\circ\text{C}$ . The effect of temperature, concentration of reactants and tolerance limit of diverse ions were discussed.

**Key Words :** Potassium Hexacyanoferrate(II); Silver Nitrate; Nitrosobenzene; Violet Complex; Determination

### INTRODUCTION

ASPERGER *et al.* (1953, 1954) reported the formation of violet nitrosobenzene pentacyano iron complex by the interaction of potassium-hexacyanoferrate (II) and Hg (II) in the presence of nitrosobenzene and its use in the determination of micro quantities of Hg (II) at pH 3.5. Being a Class 'b' metal ion, Silver also abstracts  $\text{CN}^-$  from hexacyanoferrate (II) to give  $\text{Fe}(\text{CN})_5$   $\text{PhNO}^{\ominus}$  in the presence of excess nitrosobenzene. The reaction is exploited for determination of Ag (I) in microgram level ranging from 0.6-11.0  $\mu\text{g}/\text{ml}$ . The effect of temperature, concentration of reactants and tolerance limits of diverse ions are also discussed.

### MATERIALS AND METHODS

#### *Apparatus*

A Spectronic-21 UV Visible spectrophotometer equipped with 1 cm matched quartz cells was used for measuring the absorbance.

#### *Reagents*

AR grade chemicals were used for preparing aqueous solutions of desired concentrations of  $\text{K}_4\text{Fe}(\text{CN})_6$ ,  $\text{AgNO}_3$  and nitrosobenzene. Nitrosobenzene was supplied by Sigma Chemical Co., and used without further purification. All solutions were

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prepared fresh and were not used beyond twelve hours and were kept protected from light. All glass double distilled water was used throughout the experiment.

### Procedure

*Determination of Ag<sup>+</sup>*: Aliquots from stock solutions of K<sub>4</sub>Fe(CN)<sub>6</sub> (2 ml, 10<sup>-2</sup>M), Nitrosobenzene (4 ml, 10<sup>-2</sup>M) and AgNO<sub>3</sub> (6 × 10<sup>-5</sup> to 1 × 10<sup>-3</sup>M), were mixed and volume made upto 10 ml to give the desired Ag<sup>+</sup> concentrations. The reaction mixture was heated at 40°C for 4 hours or 85°C for 4 min and absorbance measured at 528nm the  $\Lambda_{\max}$  for the product. Under similar conditions identical blanks minus Ag<sup>+</sup> were maintained to compensate for thermal and photodecomposition of Fe(CN)<sub>6</sub><sup>4-</sup> which also gives rise to small quantities of the violet complex and this absorbance was subtracted to get net absorbance of the complex formed by the Ag<sup>+</sup> abstraction of CN<sup>-</sup> only.

To observe the tolerance limits of diverse cations and anions in the estimation of Ag<sup>+</sup>, 2ml 10<sup>-2</sup>M K<sub>4</sub>Fe(CN)<sub>6</sub>, 4 ml 10<sup>-2</sup>M nitrosobenzene, 1 ml 10<sup>-3</sup>M AgNO<sub>3</sub> and 1 ml of the water soluble nitrates or sulphates of the cations or sodium salts of the anions were mixed, volume made upto 10ml, heated at 85°C for 4 min and the absorbance measured after cooling the reaction mixture to room temperature in a waterbath. Absorbance of identical blanks were subtracted as detailed before.

### RESULTS AND DISCUSSION

In the presence of nitrosobenzene, Ag<sup>+</sup> promotes the exchange of CN<sup>-</sup> by nitrosobenzene in Fe(CN)<sub>6</sub><sup>4-</sup> to give the violet coloured Fe(CN)<sub>5</sub>PhNO<sub>3</sub><sup>3-</sup> as the product. This was confirmed from the spectrum of the product. There is very good linear correlation between the absorbance and the concentration of Ag<sup>+</sup> used, both on heating at 40°C for 4 hours and at 85°C for 4 minutes. Linear regression analysis of the absorbance on concentration under these conditions gave equations 1 & 2 respectively. Standard deviations reported for the slope and intercept are at 95 per cent confidence level

$$A = 0.904 \pm 0.039 \times 10^4 [Ag^+] + 0.004 \pm 0.022 \quad \dots(1)$$

$$A = 0.904 \pm 0.002 \times 10^4 [Ag^+] - 0.013 \pm 0.047 \quad \dots(2)$$

The above method was tested for different quantities of Ag<sup>+</sup> mixed from synthetically prepared AgNO<sub>3</sub> solutions. The result with relative per cent error is given in Table I.

Prior to arriving at the above suitable conditions for the quantitative determination, various ratios of the concentrations of Ag<sup>+</sup> and Fe(CN)<sub>6</sub><sup>4-</sup> and nitrosobenzene were reacted and the absorbance measured. It was observed that the violet product was formed at all ratios of Fe(CN)<sub>6</sub><sup>4-</sup>/Ag<sup>+</sup> ≥ 1 and the absorbance increased continuously till the value is ≥ 20 and then reached a constant value (Fig. 1). The minimum amount of nitrosobenzene required to give maximum absorbance was established as 4 × 10<sup>-3</sup>M. Hence the concentrations of K<sub>4</sub>Fe(CN)<sub>6</sub> and nitrosobenzene and time of reaction for determination of Ag<sup>+</sup> were chosen as explained in

TABLE I

*Error in the proposed method for silver estimation* $K_4Fe(CN)_6$   $2 \times 10^{-3}M$ , Nitrosobenzene  $4 \times 10^{-3}M$ , Temperature  $85^\circ C$ , Time 4 min.

| Ag <sup>+</sup> added<br>$10^{-4}M$ | Ag <sup>+</sup> found<br>$10^{-4}M$ | *Relative error<br>% |
|-------------------------------------|-------------------------------------|----------------------|
| 0.1                                 | 0.097                               | 3.00 (-)             |
| 0.2                                 | 0.204                               | 2.00                 |
| 0.4                                 | 0.406                               | 1.40                 |
| 0.6                                 | 0.593                               | 1.20 (-)             |
| 0.8                                 | 0.794                               | 0.75 (-)             |
| 1.0                                 | 0.995                               | 0.50 (-)             |

\*Average of at least four replicates.

TABLE II

*Tolerance limit of various ions* $2 \times 10^{-3}M$   $K_4Fe(CN)_6$ ,  $1 \times 10^{-4}M$   $AgNO_3$ ,  $4 \times 10^{-4}M$  NitrosobenzeneTemperature  $85^\circ C$ , Time 4 min

| Ion                           | Concentration<br>M | *Relative error<br>% |
|-------------------------------|--------------------|----------------------|
| Hg <sup>2+</sup>              | $1 \times 10^{-7}$ | 2.00                 |
| Pt <sup>2+</sup>              | $1 \times 10^{-7}$ | 1.00                 |
| Pb <sup>2+</sup>              | $1 \times 10^{-4}$ | 0.60 (-)             |
| Mn <sup>2+</sup>              | $1 \times 10^{-4}$ | 0.50                 |
| Co <sup>3+</sup>              | $1 \times 10^{-3}$ | 6.00 (-)             |
| Zn <sup>2+</sup>              | $1 \times 10^{-4}$ | 0.50                 |
| Cd <sup>2+</sup>              | $1 \times 10^{-4}$ | 6.00 (-)             |
| Cu <sup>2+</sup>              | $1 \times 10^{-4}$ | 0.50 (-)             |
| SO <sub>4</sub> <sup>2-</sup> | $1 \times 10^{-4}$ | 0.40 (-)             |
| Cl <sup>-</sup>               | $1 \times 10^{-4}$ | 0.20 (-)             |
| I <sup>-</sup>                | $1 \times 10^{-4}$ | 5.10 (-)             |
| CN <sup>-</sup>               | $1 \times 10^{-7}$ | 6.00 (-)             |

\*Average of at least four replicates.

the procedure, so that maximum absorbance was obtained in all cases. At ratios of  $Ag^+/Fe(CN)_6^{4-} \geq 3$ , the solution was almost colourless and very little of the violet product was formed.

The slope of the equations 1 & 2 are in agreement with the maximum absorbance obtained when  $1 \times 10^{-4}M$   $Ag^+$  is reacted with excess ferrocyanide (Fig. 1). Asperger *et al.* 1973) reported a value of  $5.3 \times 10^3 M^{-1} cm^{-1}$  for the molar absorptivity of  $Na_3Fe(CN)_6PhNO$  complex at its  $\lambda_{max}$  of 528 nm. The result of

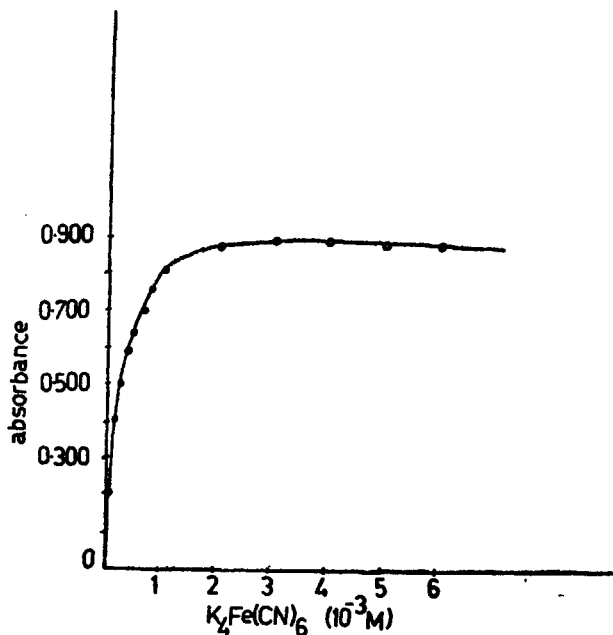
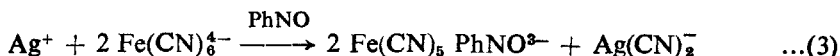


FIG. 1. Absorbance of  $Fe(CN)_6$ ,  $PhNO^{2-}$  vs.  $K_4Fe(CN)_6$  ( $10^{-3}M$ ).  $Ag^+$   $1 \times 10^{-4}M$ , 4 ml  $10^{-3}M$  nitrosobenzene, Temp  $85^\circ C$  Time 4 min.

our experiment shows that the reaction proceeds predominantly according to stoichiometry in eqn. 3.



The observed absorbance per mole of  $Ag^+$  is about 90 per cent as that required for the above stoichiometry. This is probably due to small quantities of  $AgCN$  being formed under these conditions according to eqn. 4 (Herbert, A. Laitinen, 1960).



similar behaviour was observed when bipyridine was used as the ligand exchange reagent (Reddy & Raman—*unpublished*).

Determination of  $Ag^+$  by this method is limited to an upper concentration of  $Ag^+$   $1 \times 10^{-4}M$ . When  $2 \times 10^{-4}M$  and higher concentrations of  $Ag^+$  were used, precipitation occurs possibly due to reactions 4 & 5, and the absorbance of the violet complex is low.



The effect of various added ions are given in Table II. As seen from this, many of the divalent cations present no problem at concentrations equal to that of  $Ag^+$ , very serious interference was observed in the case of  $Pt(IV)$ ,  $Hg(II)$ ,  $CN^-$  and less so

from  $\text{I}^-$  and  $\text{Cd}^{2+}$ . These are expected as  $\text{Pt(IV)}$  and  $\text{Hg(II)}$  are powerful abstractors of  $\text{CN}^-$  from  $\text{Fe(CN)}_6^{4-}$  and  $\text{CN}^-$  in turn is a very strong complexing agent for  $\text{Ag}^+$  and this lowers the concentration of  $\text{Ag}^+$  considerably.

#### ACKNOWLEDGEMENT

UGC assistance to above project and Junior Research Fellowship to B. R. R. are gratefully acknowledged. The authors thank the A. P. Agricultural University authorities for providing space and facilities for this work.

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