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# A THERMOMETRIC TITRIMETRY STUDY OF $Fe^{3+}/SCN^-$ AND $Ag^+/SCN^-$ SYSTEMS *

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## ABSTRACT

Thermometric titrimetry data for the $Fe^{3+}/SCN^-$ system show that, for a titrate concentration in the range 0.0020–0.0024 mol $dm^{-3}$ and a titrant concentration of 0.1000 mol $dm^{-3}$, the measured molar reaction heat corresponding to the first end-point formation is $-4.42 \pm 0.52$ kJ $mol^{-1}$ and the corresponding mean mole ratio factor, $n_{Fe^{3+}}/n_{SCN^-}$, is $1.04 \pm 0.04$. However, for titrate concentrations in the range 0.0010–0.0020 mol $dm^{-3}$, this factor is less than unity but progressively approaches unity as the titrant concentration nears 0.0020 mol $dm^{-3}$. This phenomenon is explained in terms of a thermal bleaching effect and is demonstrated by the use of an inhibitor in these thermometric titrations. $Al^{3+}$ and $Mn^{2+}$ cause no measurable interference effect in the $Fe^{3+}/SCN^-$ thermometric titration.

A thermometric titration with $Ag^+$ (0.0007–0.0030 mol $dm^{-3}$) as titrate and $SCN^-$ (0.1000 mol $dm^{-3}$) as titrant reveals one end-point—the corresponding measured molar reaction heat is $-86.65 \pm 3.85$ kJ $mol^{-1}$ and $n_{Ag^+}/n_{SCN^-}$ is $0.97 \pm 0.02$. $Al^{3+}$ causes no measurable interference effect in this titration.

The overall thermoanalytical data obtained for these two systems suggest that thiocyanate can be used as a reagent for the determination of $Fe^{3+}$ and $Ag^+$ in aqueous solution by thermometric titrimetry.

## INTRODUCTION

The mutual interaction of ferric and thiocyanate ions has long been used as the basis of qualitative differentiation of ferrous and ferric ions in aqueous solution [1] and of the colorimetric determination of ferric ions by measurement of the absorbance of aqueous ferric/thiocyanate systems at 480 nm [2]. This interaction is also the indicator reaction in the Volhard procedure for the determination of halide ions in aqueous solution [2]. These analytical procedures are dependent on the intense red colour of aqueous ferric/thiocyanate complex species. Ferric ions react sequentially with thiocyanate ions to give a series of complex species, $[Fe(SCN)_n(H_2O)_{6-n}]^{(3-n)^+}$, with a maximum value of $n = 6$. The stability constant $K_1$ (298 K) for $[FeSCN(H_2O)_5]^{2+}$ was determined potentiometrically by Yal-

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* Dedicated to Professor James J. Christensen in memory of his contribution to innovation in calorimetry.

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man [3] as 142.6 ($\mu = 0.5$) and 1070 ($\mu = 0$). Frank and Oswalt [4] state $K_1 = 138$ ($\mu = 0.5$) and 236 ($\mu = 0.128$), based on spectrophotometric measurements. Betts and Dainton [5] report $K_1 = 114$ ($\mu = 1.28$) and 865 ($\mu = 0$), based on a kinetic study. Laurence [6] gives $K_1 = 139$ ($\mu = 0.5$) based on potentiometric data and Edmonds and Birnbaum [7] give $K_1 = 127$ ($\mu = 1$). Lister and Rivington [8] spectrophotometrically determined $K_1$ as 130.2 ($\mu = 1.2$). Mironov and Rutkouskii [9] report $K_1$ values for $[Fe(SCN)(H_2O)_5]^{2+}$ corresponding to a range of $\mu$ values in complex ionic media. For $[Fe(SCN)_2(H_2O)_4]^+$, Yalman [3] reports $K_2 = 13.2$ ($\mu = 0.52$), Laurence [6] gives $K_2 = 20.4$ ($\mu = 0.5$) and Lister and Rivington [8] state $K_2 = 15$ ($\mu = 1.2$). For $[Fe(SCN)_3(H_2O)_3]$, Lister and Rivington [8] calculated $K_3 = 1$. An average formation enthalpy (298 K) [3,5,6] for aqueous $[Fe(SCN)(H_2O)_5]^{2+}$ is $-6.3$ kJ mol$^{-1}$ and the standard formation enthalpy is tabulated as 23.4 kJ mol$^{-1}$ [10]. Although difficult to compare at different ionic strengths, these stability constant data confirm the stepwise formation of ferric thiocyanate complex species and the estimated formation enthalpy data suggest that, in an $Fe^{3+}/SCN^-$ thermometric titration, clear end-points should be discernable for at least the first three complex species in the sequence.

Silver ions have long been known to react quantitatively with thiocyanate ions in aqueous solution to form a 1 : 1 AgSCN insoluble species and this interaction is the basis of the Volhard quantitative determination of halide ions in aqueous solution via dissolution of silver halide in excess thiocyanate [2]. Golub [11] reviewed the early literature on the stoichiometry of the silver/thiocyanate complex species formed on dissolution of AgSCN in excess thiocyanate and also reported the solubility product of AgSCN as $4.14 \times 10^{-12}$. Furthermore Golub [11] confirmed by potentiometric measurements that the predominant soluble silver thiocyanate species is $[Ag(SCN)_4]^{3-}$. Jaenicke and Hauffe [12] gave the formation enthalpy of aqueous AgSCN as $-118$ kJ mol$^{-1}$ (0–45 °C). The standard formation enthalpy of AgSCN is tabulated as 182.0 kJ mol$^{-1}$ [10]. These data suggest that in an $Ag^+/SCN^-$ thermometric titration, one distinct end-point should be observed corresponding to the formation of AgSCN.

This paper reports thermometric titrimetry studies of the $Fe^{3+}/SCN^-$ and $Ag^+/SCN^-$ systems. The thermochemical data obtained are discussed in terms of potential analytical procedures for the determination of $Fe^{3+}$ and $Ag^+$ in aqueous solution. Enthalpies of interaction of $Fe^{3+}$ and $Ag^+$ with $SCN^-$ to give 1 : 1 complex species are also reported.

## EXPERIMENTAL

### *Calorimeter and accessories*

The thermometric titrimetric system used and associated data analysis procedures were described in detail by bin Ahmad et al. [13,14]. The thermochemical data derived refer to 298 K and the relevant uncertainty is quoted as the standard deviation from the mean.

## *Analytical procedures*

Reaction heat $Q_R$ and molar reaction enthalpy $\Delta_R H_m^\ominus$ (kJ $mol^{-1}$) are calculated on the basis of the determined temperature variation, $\Delta T$ (mV) for the relevant quantitative calorimetric reaction and the associated average heat capacity, $C_p$ (kJ $mV^{-1}$), determined from the measured heat capacities of the calorimeter and contents before ($C_{p_B}$) and after ($C_{p_A}$) the thermometric titration:

$$Q_R = -C_p\ \Delta T = n_p\ \Delta_R H_m^\ominus$$

where $n_p$ is the number of moles of product formed. $\Delta_R H_m^\ominus$ is determined on the assumption of a 1 : 1 titrant : titrate reaction. $Q_R$ was corrected for the heat effect associated with the measured pH change of the system during titrations. Titrant dilution heats, determined by titration of thiocyanate into titrate solutions without metal were found to be less than the overall experimental error of $\pm 5 \times 10^{-5}$ mV in $\Delta T$ determination.

Interference studies were conducted on the basis of a 1 : 1 $Fe^{3+}$ or $Ag^+$ interferant mole ratio. The interference effect is expressed as the ratio $Q'_R/Q_R$, where $Q'_R$ is the $Fe^{3+}$ or $Ag^+/SCN^-$ reaction heat in the presence of an interfering ion. The extent of interference of a particular ion is interpreted in terms of the corresponding deviation of $Q'_R/Q_R$ from unity.

## *Calibration*

Two test reactions were employed: NaOH/HCl and THAM/HCl. The derived $\Delta_R H_m^\ominus$ for these reactions was $-55.17 \pm 0.94$ kJ $mol^{-1}$ ([15] $-55.75$ kJ $mol^{-1}$) and $-47.01 \pm 0.75$ kJ $mol^{-1}$ ([16] $-47.36$ kJ $mol^{-1}$) respectively.

## *Titrants and titrates*

The titrant stock solution was a 0.1 M $SCN^-$ solution (KSCN, BDH AnalaR grade). Titrate solutions used were acidified 0.01 M $Fe^{3+}$ ($FeNH_4(SO_4)_2 \cdot 12\ H_2O$, May and Baker, AnalaR grade), 0.002 M $Al^{3+}$ ($Al_2(SO_4)_3 \cdot 18\ H_2O$, May and Baker, AnalaR grade), 0.002 M $Mn^{2+}$ ($MnSO_4 \cdot 4\ H_2O$, May and Baker, AnalaR grade), 0.01 M $Ag^+$ ($AgNO_3$, AVLO, BP quality) and 0.01 M $Al^{3+}$ ($Al(NO_3)_3 \cdot 9H_2O$, May and Baker, AnalaR grade). Titrants and titrates were diluted as required with deionised water.

## RESULTS AND DISCUSSION

### *The $Fe^{3+}/SCN^-$ system*

A thermometric titration of $Fe^{3+}$ (0.0025 mol $dm^{-3}$) as titrate with $SCN^-$ (0.1000 mol $dm^{-3}$) as titrant reveals four distinct slope changes at approximately equal titrate volume increments. The most well-defined slope change corresponds to the quantitative formation of the 1:1 species $[Fe(SCN)(H_2O)_5]^{2+}$ and hence an analytical procedure for the determination of $Fe^{3+}$ in aqueous solution is suggested. The thermometric titrimetry data relating to subsequent runs terminated immediately after the appearance of the first end-point are given in Table 1. For a titrate concentration in the range 0.0020–0.0024 mol $dm^{-3}$ and a titrant concentration of 0.1000 mol $dm^{-3}$, the measured molar reaction heat corresponding to the first end-point formation is $-4.42 \pm 0.52$ kJ $mol^{-1}$ and the corresponding mean mole ratio factor, $n_{Fe^{3+}}/n_{SCN^-}$ is $1.04 \pm 0.04$. However, for titrate concentrations in the range 0.0010–0.0020 mol $dm^{-3}$, this factor is less than unity but progressively approaches unity as the titrant concentration nears 0.0020 mol $dm^{-3}$. This phenomenon is shown in Fig. 1 and is explained in terms of a thermal bleaching effect, previously described by Betts and Dainton [5] to explain the fading of the red $[FeSCN]^{2+}$ species at relatively low $[Fe^{3+}]$ and high $[SCN^-]$. The thermal bleaching effect is thought to involve the $(SCN)_2^-$ ion radical. Betts and Dainton [5] showed that the thermal bleaching effect can be eliminated by use of an inhibitor such as benzyl alcohol and this is verified by the present thermoanalytical data. A thermometric titration of $Fe^{3+}$ (0.0013 mol $dm^{-3}$) with $SCN^-$ (0.1000 mol

TABLE 1

Thermometric titration of $Fe^{3+}$ with $SCN^-$ (0.1000 M)

| $[Fe^{3+}]$ (mol $dm^{-3}$) | $\Delta T_R$ (mV) | $C_{p_B}$ (kJ $mV^{-1}$) | $C_{p_A}$ (kJ $mV^{-1}$) | $\bar{C}_p$ (kJ $mV^{-1}$) | $-Q_R$ (J) | $-\Delta_R H_m^{\ominus}$ (kJ $mol^{-1}$) | $\frac{n_{Fe^{3+}}}{n_{SCN^-}}$ |
|---|---|---|---|---|---|---|---|
| 0.0011 | 0.00431 | 147.5 | 159.1 | 153.3 | 0.661 | 6.67 | 0.60 |
| 0.0013 | 0.00558 | 147.8 | 153.5 | 150.6 | 0.841 | 7.18 | 0.71 |
| 0.0018 | 0.00570 | 147.3 | 153.9 | 149.1 | 0.850 | 5.25 | 0.90 |
| 0.0020 | 0.00558 | 147.6 | 152.4 | 150.0 | 0.837 | 4.65 | 0.97 |
| 0.0021 | 0.00630 | 146.8 | 151.9 | 149.3 | 0.941 | 4.98 [a] | 1.03 [b] |
| 0.0022 | 0.00576 | 146.1 | 151.9 | 149.0 | 0.858 | 4.33 [a] | 1.05 [b] |
| 0.0024 | 0.00571 | 146.3 | 152.8 | 149.5 | 0.854 | 3.95 [a] | 1.05 [b] |
| 0.0013 [c] | 0.00469 | 146.4 | 151.7 | 149.1 | 0.699 | 5.98 | 0.82 |
| 0.0013 [c] | 0.00439 | 146.1 | 152.2 | 149.2 | 0.655 | 5.60 | 0.87 |

[a] Mean $\Delta_R H_m^{\ominus} = -4.42 \pm 0.52$ kJ $mol^{-1}$.

[b] Mean $n_{Fe^{3+}}/n_{SCN^-} = 1.04 \pm 0.04$.

[c] 1% benzyl alcohol present.

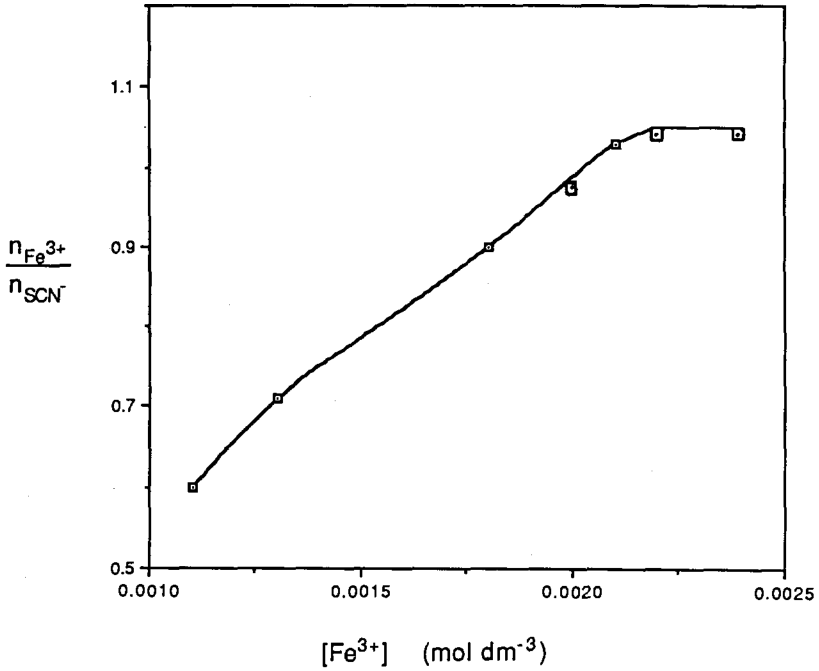

Fig. 1. Variation of $n_{Fe^{3+}}/n_{SCN^-}$ with $[Fe^{3+}]$.

dm$^{-3}$) gives $n_{Fe^{3+}}/n_{SCN^-}$ at the first end-point as 0.71. In the presence of 1% benzyl alcohol this factor increases to 0.84, which is consistent with a partial elimination of the perceived thermal bleaching effect. The variation of $\Delta_R H_m^\ominus$ at relatively low $[Fe^{3+}]$ indicates that the thermal bleaching reactions constitute a net exothermic effect.

Results of an interference study involving $Al^{3+}$ and $Mn^{2+}$ are given in Table 2. It is apparent that for systems involving a 1 : 1 $Fe^{3+}$ : $Mn^{2+}$ mole ratio, $Q'/Q$ is approximately unity and hence $Al^{3+}$ and $Mn^{2+}$ cause no appreciable interference effect.

TABLE 2

Thermometric titration of $Fe^{3+}$ with $SCN^-$ (0.1000 M) in the presence of $Al^{3+}$ or $Mn^{2+}$

| $[Fe^{3+}]$ (mol dm$^{-3}$) | $[Al^{3+}]$ | $[Mn^{2+}]$ | $\Delta T_R$ (mV) | $C_{p_B}$ (J mV$^{-1}$) | $C_{p_A}$ (J mV$^{-1}$) | $\bar{C}_P$ (J mV$^{-1}$) | $\frac{Q'}{Q}$ | $-\Delta_R H_m^\ominus$ (kJ mol$^{-1}$) | $\frac{n_{Fe^{3+}}}{n_{SCN}}$ |
|---|---|---|---|---|---|---|---|---|---|
| 0.0021 | 0.0021 | – | 0.00585 | 147.8 | 153.8 | 150.8 | 0.94 | 4.67 | 1.03 |
| 0.0021 | 0.0021 | – | 0.00545 | 157.3 | 158.3 | 157.8 | 0.92 | 4.53 | 0.98 |
| 0.0021 | – | 0.0021 | 0.00767 | 147.4 | 152.0 | 149.7 | 1.22 | 6.04 | 1.21 |
| 0.0021 | – | 0.0021 | 0.00628 | 147.3 | 152.6 | 150.0 | 1.00 | 4.96 | 1.00 |

TABLE 3

Thermometric titration of $Ag^+$ with $SCN^-$ (0.1000 M)

| $[Ag^+]$ (mol dm$^{-3}$) | $\Delta T_R$ (mV) | $C_{p_B}$ (J mV$^{-1}$) | $C_{p_A}$ (J mV$^{-1}$) | $\bar{C}_p$ (J mV$^{-1}$) | $-Q_R$ (J) | $-\Delta_R H_m^{\ominus}$ (kJ mol$^{-1}$) | $\frac{n_{Ag^+}}{n_{SCN^-}}$ |
|---|---|---|---|---|---|---|---|
| 0.0007 | 0.0336 | 148.3 | 151.8 | 150.0 | 5.04 | 80.00 | 1.01 |
| 0.0013 | 0.0664 | 148.1 | 152.8 | 150.4 | 9.99 | 85.36 | 0.96 |
| 0.0024 | 0.1276 | 149.1 | 153.0 | 151.0 | 19.30 | 89.19 | 0.94 |
| 0.0024 | 0.1308 | 146.5 | 150.2 | 148.4 | 19.41 | 89.88 | 0.97 |
| 0.0027 | 0.1408 | 146.6 | 149.0 | 147.8 | 20.80 | 85.60 | 0.97 |
| 0.0030 | 0.1603 | 150.0 | 152.7 | 151.3 | 24.26 | 89.85 | 0.96 |

Mean $\Delta_R H_m^{\ominus} = -86.65 \pm 3.85$ kJ mol$^{-1}$; mean $n_{Ag^+}/n_{SCN^-} = 0.97 \pm 0.02$.

TABLE 4

Thermometric titration of $Ag^+$ with $SCN^-$ (0.1000 M) in the presence of $Al^{3+}$

| $[Ag^+]$ (mol dm$^{-3}$) | $[Al^{3+}]$ | $\Delta T_R$ (mV) | $C_{p_B}$ (J mV$^{-1}$) | $C_{p_A}$ (J mV$^{-1}$) | $\bar{C}_p$ (J mV$^{-1}$) | $\frac{Q'}{Q}$ | $-\Delta_R H_m^{\ominus}$ (kJ mol$^{-1}$) | $\frac{n_{Ag^+}}{n_{SCN^-}}$ |
|---|---|---|---|---|---|---|---|---|
| 0.0013 | 0.0013 | 0.0675 | 146.2 | 152.7 | 149.5 | 1.01 | 86.18 | 0.96 |
| 0.0027 | 0.0027 | 0.1393 | 146.3 | 153.1 | 149.7 | 1.00 | 85.82 | 1.00 |

### *The $Ag^+/SCN$ system*

The relevant thermoanalytical data are given in Table 3. A thermometric titration of $Ag^+$ (0.0007–0.0030 mol dm$^{-3}$) as titrate with $SCN^-$ (0.1000 mol dm$^{-3}$) as titrant, revealed one end-point—the corresponding measured molar reaction heat is $-86.65 \pm 3.85$ kJ mol$^{-1}$ and $n_{Ag^+}/n_{SCN^-}$ is $0.97 \pm 0.02$.

Results of an interference study involving $Al^{3+}$ are given in Table 4. It is apparent that, for systems involving a 1:1 $Ag^+ : Al^{3+}$ mole ratio, $Q'/Q$ is approximately unity and hence $Al^{3+}$ causes no appreciable interference effect.

## CONCLUSIONS

Thermometric titrimetry data obtained for the $Fe^{3+}/SCN^-$ and $Ag^+/SCN^-$ systems provisionally suggest that the corresponding 1:1 quantitative reactions identified can be used as a basis for the thermoanalytical determination of $Fe^{3+}$ and $Ag^+$, respectively, in aqueous solution. It appears that, in the case of the $Fe^{3+}/SCN^-$ system and in the absence of an inhibitor, the lower $Fe^{3+}$ concentration limit is 0.0021 mol dm$^{-3}$, since at lower $[Fe^{3+}]$ the thermal bleaching effect is significant. $\Delta_R H_m^{\ominus}$ values for the formation of aqueous $[Fe(SCN)(H_2O)_5]^{2+}$ and AgSCN are both less than the corresponding previously reported values. However, in the case of $[Fe(SCN)(H_2O)_5]^{2+}$, the previous $\Delta_R H_m^\ominus$ data are based on partially estimated stability constant/temperature data and for AgSCN, the thermochemical data leading to $\Delta_R H_m^\ominus$ are associated with a ±20 kJ $mol^{-1}$ uncertainty. The lack of interference exhibited by $Al^{3+}$ and $Mn^{2+}$ in the $Fe^{3+}/SCN^-$ system and $Al^{3+}$ in the $Ag^+/SCN^-$ system is explained in terms of the relative hardness of the cations involved.

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