A thermometric enthalpy titration study of the cadmium/ferricyanide system

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Abstract

A thermometric enthalpy titration study of the cadmium/ferricyanide system in aqueous solution has revealed that in the presence of excess cadmium ion, a single cadmium/ferricyanide complex species predominates in solution with a stoichiometry of $[Cd_{10}(Fe(CN)_6)_7]^-$. In the presence of excess ferricyanide, a single cadmium/ferricyanide complex species again predominates but with a stoichiometry of $[Cd(Fe(CN)_6)_2]^{4-}$. It is apparent that the relative concentrations of Cd^{2+} and $[Fe(CN)_6]^{3-}$ control the number and stoichiometry of cadmium/ferricyanide species formed in aqueous solution.

INTRODUCTION

Thermometric enthalpy titrimetry (TET) is acknowledged as a very versatile analytical technique for the study and determination of a wide variety of chemical species in solution. The diverse applications of TET have been reviewed comprehensively by Grime [1]. In terms of application to metal coordination compounds, TET is particularly useful for monitoring sequential reactions between metal ion and ligand in solution and for the determination of the number and stoichiometry of the complex species formed. For example, Hill and Korce [2] have applied TET to the study of the Fe^{3+}/SCN^- and Ag^+/SCN^- systems in aqueous solution. For the Fe^{3+}/SCN^- system, a thermometric enthalpy 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, corresponding to the sequential formation of a series of complex species of stoichiometry $[Fe(SCN)_n(H_2O)_{6-n}]^{(3-n)+}$, where $n = 1$–4. A similar study of the Ag^+/SCN^- system revealed one "end-point" corresponding to the formation of the insoluble species AgSCN.

The cadmium/ferricyanide interaction in aqueous solution is known to be particularly complicated, and the number and stoichiometry of the complex species formed remains uncertain.

Fernando and Freiser [3] report that the interaction of potassium ferro-cyanide and a cadmium(II) salt in aqueous solution yields a precipitate of variable composition; and the interaction between potassium ferricyanide and a cadmium(II) salt in aqueous solution results in a yellow precipitate of variable composition due to hydrolysis and adsorption. Bhattacharya and Gaur [4,5] have studied the cadmium(II)/ferrocyanide system in aqueous and non-aqueous media by thermometric, potentiometric and conductometric methods. The major species formed appears to be $[CdFe(CN)_6]^{2-}$ which is associated with hydrolysis and adsorption phenomena. Similar studies of the cadmium(II)/ferricyanide system [6,7] indicate that the major species formed is $[Cd_{10}(Fe(CN)_6)_7]^-$, with some evidence for the species $[Cd_3(Fe(CN)_6)_2]$: the extent of hydrolysis and adsorption effects appears to be less than those associated with the cadmium(II)/ferrocyanide system. An early potentiometric study of the cadmium(II)/ferricyanide system by Paris and Le Chatelier [8] suggests that at least one stoichiometric complex species is formed.

The present study re-investigates the cadmium(II)/ferricyanide system in aqueous and mixed solvent media by direct and reverse TET methods. The number and stoichiometry of the complex species formed is derived together with the relevant reaction molar enthalpies.

EXPERIMENTAL

TET system and accessories

The TET system used and the associated data analysis procedures have been described in detail by bin Ahmad et al. [9,10]. The thermochemical data derived refer to 298 K and the relevant uncertainty is quoted as the standard deviation from the mean.

Analytical procedures

The 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, ΔT (mV), for the relevant quantitative calorimetric reaction and the associated average heat capacity, $\bar{C}_p$ (kJ mV^{-1}), determined from the measured heat capacities of the calorimeter and contents before (C_{pB}) and after (C_{pA}) the thermometric titration

$$Q_R = -\bar{C}_p \, \Delta T = n_p \, \Delta_R H_m^\ominus \qquad (1)$$

where n_p is the number of moles of product formed. Titrant dilution heats, determined by titration of ferricyanide into titrate solutions without metal, were found to be less than the overall experimental error of $\pm 5 \times 10^{-5}$ mV in the ΔV determination.

Calibration

Two test reactions were employed: NaOH/HCl and THAM/HCl. The derived $\Delta_R H_m^{\ominus}$ values for these reactions was -55.26 ± 1.99 kJ mol^{-1} (-55.75 kJ mol^{-1} in ref. 11) and -47.28 ± 0.67 kJ mol^{-1} (-47.36 kJ mol^{-1} in ref. 12) respectively.

Titrants and titrates

Cadmium sulphate stock solution (0.1 M) was prepared by dissolution of cadmium sulphate (7.6956 g) in deionised distilled water (100 cm^3). Potassium ferricyanide stock solution (0.2 M) was prepared by dissolution of potassium ferricyanide (65.852 g) in deionised distilled water (1000 cm^3). These stock solutions were subsequently diluted to the appropriate concentrations.

Direct thermometric titrations involved CdSO$_4$ (0.0524 and 0.1071 M) as titrant and K$_3$Fe(CN)$_6$ (3.408×10^{-5}–1.022×10^{-4} moles in 90 cm^3) as titrate. Reverse thermometric titrations involved K$_3$Fe(CN)$_6$ (0.01–0.2 M) as titrant and CdSO$_4$ (4.280×10^{-5}–5.355×10^{-4} moles in 90 cm^3) as titrate.

RESULTS AND DISCUSSION

The results for the thermometric enthalpy titration of ferricyanide with Cd^{2+} in aqueous solution are given in Table 1 and a typical thermogram is shown in Fig. 1. Similar data, but referring to titrations in 25 : 75 v/v

TABLE 1

Thermometric enthalpy titration of ferricyanide with Cd^{2+} in aqueous solution

Cd^{2+} (moles)	Fe(CN)$_6^{3-}$ (moles)	ΔT (mV)	C_p (J mV^{-1})			$-Q_R$ (J)	$-\Delta_R H_m^{\ominus}$ [a] (kJ mol^{-1})	Mole ratio (at end point) [b] nCd^{2+}/ nFe(CN)$_6^{3-}$
			C_{pB}	C_{pA}	$\bar{C}_p$			
[CdSO$_4$] = 0.0524 M								
4.743×10^{-5}	3.408×10^{-5}	0.0168	144.9	149.0	146.9	2.47	52.08	1.38
4.804×10^{-5}	3.408×10^{-5}	0.0178	147.1	150.3	148.7	2.65	55.16	1.41
4.806×10^{-5}	3.408×10^{-5}	0.0172	147.5	152.8	150.1	2.58	53.68	1.41
[CdSO$_4$] = 0.1071 M								
9.973×10^{-5}	6.816×10^{-5}	0.0336	147.5	152.7	150.1	5.04	50.54	1.46
9.340×10^{-5}	6.816×10^{-5}	0.0330	146.5	151.0	148.8	4.91	52.57	1.37
1.415×10^{-4}	1.022×10^{-4}	0.0526	145.8	151.1	148.5	7.81	55.19	1.38
1.399×10^{-4}	1.022×10^{-4}	0.0533	145.5	152.0	148.8	7.93	56.68	1.37

[a] Mean $-\Delta_R H_m^{\ominus} = 53.45 \pm 2.21$ kJ mol^{-1}.
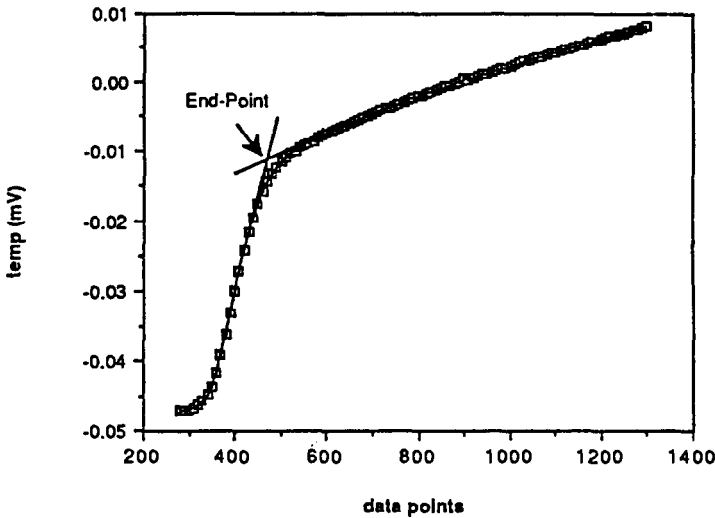[b] Mean mole ratio $= 1.40 \pm 0.03$.

Fig. 1. A typical TET thermogram for the titration of ferricyanide with Cd^{2+} in aqueous solution.

alcohol:water, are given in Table 2. The results for the thermometric enthalpy titration of ferricyanide with Cd^{2+} in aqueous solution are given in Table 3 and a typical thermogram is shown in Fig. 2. For the direct titrations in either aqueous solution or in the mixed solvent, the overall data are consistent with one well defined slope change over the duration of the reaction, indicating the formation of a single species in solution, which from the determined mean mole ratio factor of 1.4, has the stoichiometry $[Cd_{10}(Fe(CN)_6)_7]^-$. This is consistent with the thermometric titrimetry study of the cadmium/ferricyanide system, as reported by Gaur and Bhattacharya [6,7], who concluded that this polymeric anion is the major species present. From the composite data given in Tables 1 and 2 it appears that the nature of the solvent has no effect on the course of the cadmium/fer-

TABLE 2

Thermometric enthalpy titration of ferricyanide with Cd^{2+} in 25:75 v/v alcohol:water, mixed solvent medium

Cd^{2+} (moles)	$Fe(CN)_6^{3-}$ (moles)	ΔT (mV)	C_p (J mV^{-1})			$-Q_R$ (J)	$-\Delta_R H_m^{\ominus}$ [a] (kJ mol^{-1})	Mole ratio [b] $n Cd^{2+}/ n Fe(CN)_6^{3-}$
			C_{pB}	C_{pA}	$\overline{C}_p$			
[CdSO$_4$] = 0.0524 M								
4.810×10^{-5}	3.408×10^{-5}	0.0761	148.0	152.6	150.4	11.45	238.0	1.41
4.816×10^{-5}	3.408×10^{-5}	0.0752	147.6	151.9	149.8	11.26	233.9	1.41
4.825×10^{-5}	3.408×10^{-5}	0.0770	148.5	153.0	150.8	11.61	240.6	1.42

[a] Mean $-\Delta_R H_m^{\ominus} = 237.9 \pm 2.7$ kJ mol^{-1}.
[b] Mean mole ratio $= 1.41 \pm 0.01$.

TABLE 3
Thermometric enthalpy titration of Cd^{2+} with ferricyanide in aqueous solution

Cd^{2+} (moles)	$Fe(CN)_6^{3-}$ (moles)	ΔT (mV)	C_p (J mV^{-1})			$-Q_R$ (J)	$-\Delta_R H_m^{\ominus}$ [a] (kJ mol^{-1})	Mole ratio (at end point) [b] $nCd^{2+}/$ $nFe(CN)_6^{3-}$
			C_{pB}	C_{pA}	$\overline{C}_p$			
$[CdSO_4] = 1.071 \times 10^{-2}$ M								
5.355×10^{-4}	1.022×10^{-3}	0.3442	147.5	152.7	150.1	51.66	96.47	0.52
$[CdSO_4] = 1.071 \times 10^{-3}$ M								
1.071×10^{-5}	2.201×10^{-5}	0.0071	148.0	152.8	150.4	1.067	99.63	0.49
4.284×10^{-5}	9.787×10^{-5}	0.0313	145.7	150.5	148.1	4.636	108.20	0.44

[a] Mean $-\Delta_R H_m^{\ominus} = 101.4 \pm 6.1$ kJ mol^{-1}.
[b] Mean mole ratio $= 0.48 \pm 0.04$.

ricyanide interaction, except that the relevant molar enthalpy change is considerably more exothermic in the mixed solvent, as a direct consequence of a reduced hydration enthalpy of the cation.

For the reverse titration of Cd^{2+} with ferricyanide in aqueous solution, the overall data are again consistent with one well defined slope change over the duration of the reaction, indicating the formation of a single species in solution, which, from the determined mean mole ratio factor of 0.48, corresponds to the stoichiometry $[Cd(Fe(CN)_6)_2]^{4-}$.

From the overall data presented, it is evident that the number and stoichiometry of cadmium ferricyanide species formed in solution is critically dependent upon the relative component concentrations. However,
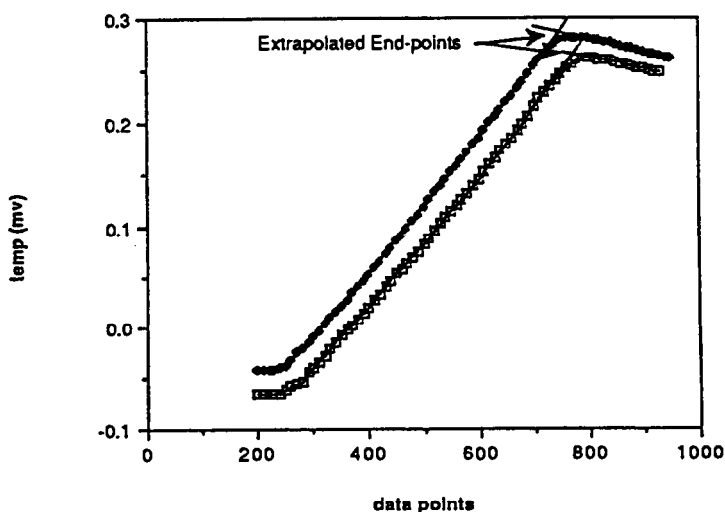

Fig. 2. A typical TET thermogram for the titration of Cd^{2+} with ferricyanide in aqueous solution.

because in both the direct and reverse thermometric titrations only one cadmium/ferricyanide species appears to be formed in well defined stoichiometry, ferricyanide can be applied in the TET analysis of Cd^{2+} in aqueous solution to a detection limit of 10^{-4} mol dm^{-3}. An extensive interference study, however, is a necessary pre-requisite, as ferricyanide is known to form complex ion species with many metals such as copper [13] and zinc [14].

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