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A thermometric enthalpy titration study of the silver/thiosulphate system

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Abstract

A thermometric enthalpy titration study of the silver thiosulphate system in aqueous solution has revealed that in a titration of thiosulphate with Ag^+, three silver/thiosulphate complex species are formed, with stoichiometries $[Ag(S_2O_3)_2]^{3-}$, $[AgS_2O_3]^-$ and $Ag_2S_2O_2$, whereas in the reverse titration, $Ag_2S_2O_3$ is the exclusive species formed. A similar titration of either freshly precipitated silver chloride or silver bromide with thiosulphate revealed that the species $[Ag(S_2O_3)_2]^{3-}$ is formed preferentially. It is apparent that the relative concentrations of Ag^+ and $S_2O_3^{2-}$ control the number and stoichiometry of silver/thiosulphate species formed in aqueous solution.

INTRODUCTION

Silver plays an important role in the manufacture of photographic products and in photographic processes in general, and thiosulphate plays a key role in film development/fixing processes. The chemistry associated with these processes is incompletely understood but many reviews of the subject exist [1–7]. The conditions necessary to obtain a well defined and well washed film within the time limits available in modern processing techniques depend on several parameters of which the most important is the composition of the fixing medium. In photographic fixation processes, the most commonly used silver halide solubilising agent for the diffusion transfer process is sodium thiosulphate, which does not create the excessive corrosion or gelatine softening phenomena apparent with other solubilising agents such as thiourea and thiocyanate. The sodium thiosulphate may be present either in the processing solution or in the positive material but in either case, the solubilising agent must be maintained at a relatively low concentration such that the weaker silver thiosulphate complexes are formed preferentially. Excess thiosulphate in the positive material must also be avoided and it is well known that the fixing bath silver content influences the fixing rate. Thus the interaction of Ag^+ and thiosulphate in aqueous

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media is of intrinsic interest in the context of understanding the chemistry of photographic processing.

A variety of silver thiosulphate salts have been reported, but it is generally agreed that only four of these are stable under ordinary conditions: $Na_3Ag(S_2O_3)_2 \cdot 2H_2O$, $Na_5Ag_3(S_2O_3)_4 \cdot 2H_2O$, $Na_5Ag_3(S_2O_3)_4 \cdot H_2O$ and $NaAg_3(S_2O_3)_2 \cdot H_2O$. The stability of silver/thiosulphate species in solution is less certain. The solubility of the four known silver thiosulphate salts decreases as the silver content increases, and it has been reported that no species richer in silver than $[Ag(S_2O_3)_2]^{3-}$ exists in solution. In terms of photographic fixing, tests have indicated that the $Ag^+ : S_2O_3^{2-}$ ratio for a stabilised print should be at least 1 : 5 and, hence, the silver present should exist in complex ion form with a relatively high thiosulphate content and sufficient time should be allowed in the stabilisation process for such complexation to occur. For print stability, an excess of thiosulphate should persist to prevent dissociation of the silver thiosulphate complex ions present. Subsequent washing of a thiosulphate-stabilised image ultimately produces the semi-soluble salt $NaAg(S_2O_3) \cdot H_2O$, which slowly decomposes to silver sulphide. Dissociation constants for two silver/thiosulphate species are known: $[AgS_2O_3]^-$, 1.4×10^{-9}; and $[Ag(S_2O_3)_2]^{3-}$, 5.4×10^{-15}.

Thus, it is apparent that in the fixing process, the number and stoichiometry of the silver/thiosulphate complex species existing in solution is uncertain and the relative concentrations of Ag^+ and $S_2O_3^{2-}$ are key factors controlling such complexation phenomena.

Thermometric enthalpy titrimetry (TET) is a well known, versatile analytical technique for the study and determination of a wide variety of chemical species and for the derivation of the number and stoichiometry of the metal complexes existing in solution. Such diverse applications of TET have been reviewed comprehensively by Grime [8]. In the present study, TET is applied to investigate the $Ag^+/S_2O_3^{2-}$ interaction in terms of the relevant species distribution phenomena in aqueous solution and is a complimentary study to that of Elsayed [9].

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. [10,11]. 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 thiosulphate into titrate solution without metal, were found to be less than the overall experimental error of $\pm 5 \times 10^{-5}$ mV in the ΔT determination.

Calibration

Two test reactions were employed: NaOH/HCl and THAM/HCl. The derived $\Delta_R H_m^{\ominus}$ values for these reactions were -55.26 ± 1.99 kJ mol^{-1} (-55.75 kJ mol^{-1} given in ref. 12) and -47.28 ± 0.67 kJ mol^{-1} (-47.36 kJ mol^{-1} in ref. 13) respectively.

Titrants and titrates

Sodium thiosulphate stock solution (0.1 M) was prepared by dissolution of $Na_2S_2O_3 \cdot 5H_2O$ (12.40 g) (B.D.H., A.R. grade) in deionised distilled water (100 cm^3). Silver nitrate stock solution (0.1 M) was prepared by dissolution of $AgNO_3$ (16.989 g) in deionised distilled water (1000 cm^3). This solution was stored in the dark to prevent photo-decomposition.

The direct thermometric titrations involved 2.5×10^{-3} M $AgNO_3$ as titrant and 2.778×10^{-2} M $Na_2S_2O_3$ (2.5×10^{-5} moles in 90 cm^3) as titrate. Reverse thermometric titrations involved 5×10^{-3} M $Na_2S_2O_3$ as titrant and 5.556×10^{-4} M $AgNO_3$ (5×10^{-5} moles in 90 cm^3) as titrate.

Thermometric titrations of AgCl and AgBr as titrate with sodium thiosulphate solution (0.0998 M) as titrant were also conducted. The silver halide precipitates were prepared in situ in the calorimeter vessel by adding excess 0.01 M KX (X = Cl or Br) solution to a known mole quantity of $AgNO_3$.

RESULTS AND DISCUSSION

The overall study was based on silver and thiosulphate concentrations typical of those relevant to photographic fixing processes.

The results obtained for the thermometric titration of thiosulphate with Ag^+ are given in Table 1 and a typical thermogram for this system is shown in Fig. 1. It is apparent from the overall data that there are two well defined slope changes over the duration of the reaction; a third, less well defined,

TABLE 1

Thermometric enthalpy titration of $S_2O_3^{2-}$ with Ag^+ [a]

Slope change	Ag^+ (moles $\times 10^{-5}$)	$S_2O_3^{2-}$ (moles $\times 10^{-5}$)	ΔT (mV)	C_p (J mV^{-1})			$-Q_R$ (J)	$-\Delta_R H_m^{\ominus}$ [b] (kJ mol^{-1})	mole ratio [c] $nAg^+/nS_2O_3^{2-}$ (at end point)
				C_{pB}	C_{pA}	$\bar{C}_p$			
1	1.210	2.500	0.5×10^{-2}	146.8	150.6	148.7	0.744	61.49	0.48
2	2.760	2.500	1.0×10^{-2}				1.510	54.71	1.10
3	5.192	2.500	2.6×10^{-2}				3.866	148.92	2.08
1	1.300	2.500	5.10×10^{-3}	146.7	150.6	148.1	0.755	63.96	0.52
2	2.805	2.500	6.88×10^{-3}				1.619	57.72	1.12
3	5.190	2.500	2.44×10^{-2}				3.714	143.12	2.33
1	1.374	2.500	5.05×10^{-2}	147.2	149.5	148.4	0.749	60.60	0.55
2	2.780	2.500	6.95×10^{-3}				1.607	57.59	1.10
3	4.843	2.500	2.50×10^{-2}				3.710	153.21	2.20

[a] $[Ag^+] = 2.5 \times 10^{-3}$ mol dm^{-3}.

[b] Mean $-\Delta_R H_m^{\ominus}$: 1, 61.98 ± 1.78; 2, 56.67 ± 1.70; 3, 148.42 ± 5.06.

[c] Mean mole ratio: 1, 0.52 ± 0.04; 2, 1.10 ± 0.01; 3, 2.20 ± 0.13.

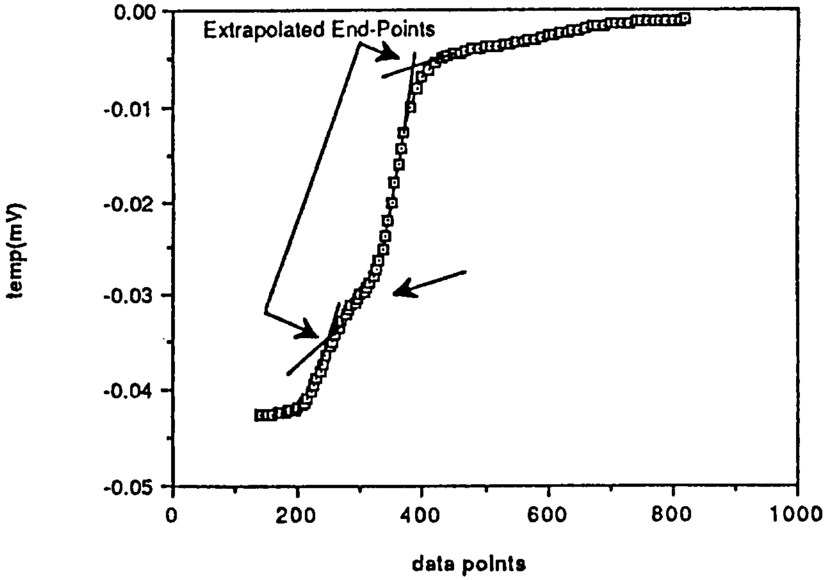

Fig. 1. A typical TET thermogram for the titration of $S_2O_3^{2-}$ with Ag^+ in aqueous solution: $S_2O_3^{2-}$ (moles) = 2.500×10^{-5}.

slope change was revealed by a regression analysis. Thus, three silver/thiosulphate complex species exist in solution with mole ratios of 0.52, 1.10 and 2.20, which correspond to the species $[Ag(S_2O_3)_2]^{3-}$, $[AgS_2O_3]^-$ and $Ag_2S_2O_3$ respectively. The corresponding step-wise formation enthalpies of these species are calculated as −61.98 ± 1.78, −56.67 ± 1.70 and −148 ± 5.06 kJ mol^{-1} respectively.

The results obtained for the thermometric titration of Ag^+ with thiosulphate are given in Table 2 and a typical thermogram for this system is shown in Fig. 2. It is apparent from the overall data that there is only one well defined slope change over the duration of the reaction, corresponding to the formation of one complex species with a mole ratio of 2.00, which

TABLE 2

Thermometric enthalpy titration of Ag^+ with $S_2O_3^{2-}$ [a]

Ag^+ (moles $\times 10^{-5}$)	$S_2O_3^{2-}$ (moles $\times 10^{-5}$)	ΔT (mV)	C_p (J mV^{-1})			$-Q_R$ (J)	$-\Delta_R H_m^{\ominus}$ (kJ mol^{-1})	Mole ratio [c] $nAg^+/nS_2O_3^{2-}$ (at end point)
			C_{pB}	C_{pA}	$\overline{C}_p$			
4.980	2.415	3.55×10^{-2}	146.0	150.8	148.4	5.268	211.60	2.08
4.981	2.480	3.55×10^{-2}	147.3	150.9	149.1	5.293	212.27	1.96
4.980	2.540	3.53×10^{-2}	146.6	150.8	148.7	5.249	210.80	1.96

[a] $[S_2O_3^{2-}] = 4.980 \times 10^{-3}$ mol dm^{-3}.
[b] Mean $-\Delta_R H_m^{\ominus} = 211.56 \pm 0.74$.
[c] Mean mole ratio = 2.00 ± 0.07.

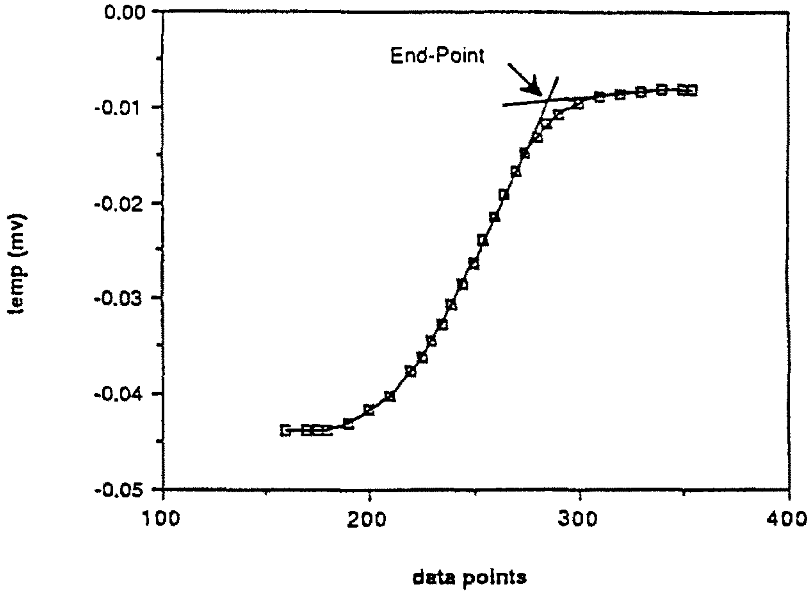

Fig. 2. A typical TET thermogram for the titration of Ag^+ with $S_2O_3^{2-}$ in aqueous solution: Ag^+ (moles) = 4.980×10^{-5}.

corresponds to a stoichiometry of $Ag_2S_2O_3$. The corresponding formation enthalpy is -211.56 ± 0.74 kJ mol^{-1}, Thus, the relative concentrations of Ag^+ and $S_2O_3^{2-}$ control the number and stoichiometry of the silver/thiosulphate species formed.

The results obtained for the thermometric titration of freshly precipitated silver bromide with thiosulphate are given in Table 3 and typical thermograms for this system are shown in Figs. 3 and 4. It is apparent from the overall data that only one well defined slope change occurs over the duration of the reaction, corresponding to the formation of one complex species with

TABLE 3

Thermometric enthalpy titration of AgBr with $S_2O_3^{2-}$

$S_2O_3^{2-}$ (moles)	AgBr (moles)	$-\Delta T$ (mV)	C_p (J mV^{-1})			Q_R (J)	$-\Delta_R H_m^\ominus$ [a] (kJ mol^{-1})	Mole ratio $nS_2O_3^{2-}/nAg^+$
			C_{pB}	C_{pA}	$\bar{C}_p$			
1.936×10^{-3}	9.96×10^{-4}	0.2150	145.9	150.7	148.3	31.885	32.01	2.37
1.920×10^{-3}	9.96×10^{-4}	0.1973	145.5	150.9	148.2	29.240	29.36	2.13
2.023×10^{-3}	9.96×10^{-4}	0.2080	146.1	150.6	148.4	30.867	30.99	2.16
1.940×10^{-3}	9.96×10^{-4}	0.2104	146.7	151.0	148.9	31.329	31.45	2.05
9.988×10^{-3}	4.98×10^{-3}	−0.0450	145.5	150.7	148.1	−6.660	−1.34	2.01
9.994×10^{-3}	4.98×10^{-3}	−0.0400	145.9	150.7	148.3	−5.932	−1.19	2.01

[a] Mean $-\Delta_R H_m^\ominus = 30.99 \pm 1$ kJ mol^{-1}.

[b] Mean mole ratio = 2.12 ± 0.06.

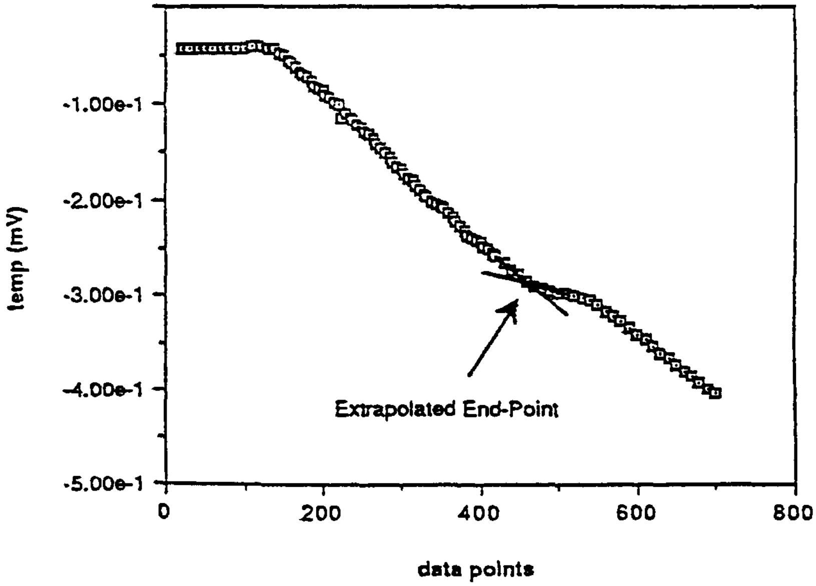

Fig. 3. A typical TET thermogram for the titration of AgBr with $S_2O_3^{2-}$ in aqueous solution: AgBr (moles) = 9.96×10^{-4}.

a mole ratio of 2.12 and, hence, a stoichiometry of $[Ag(S_2O_3)_2]^{3-}$. Further, it is apparent that the reaction is endothermic at the higher AgBr concentration employed.

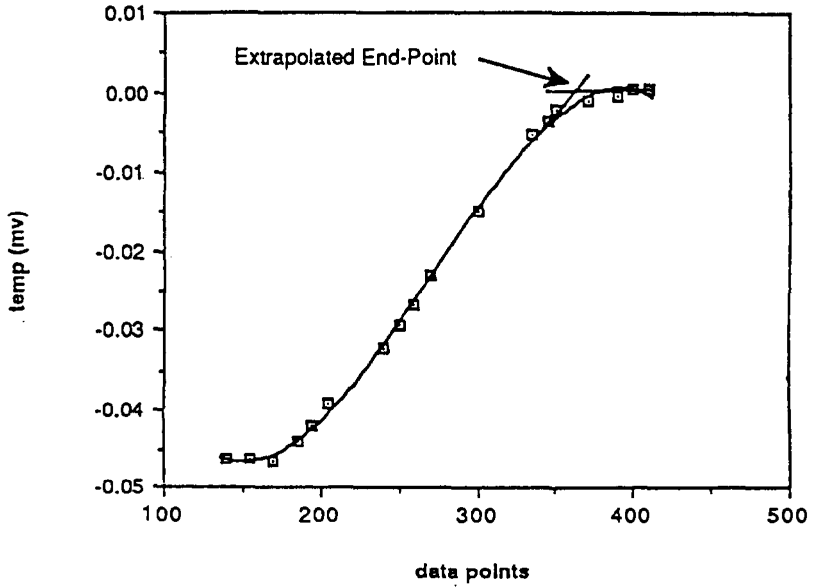

Fig. 4. A typical TET thermogram for the titration of AgBr with $S_2O_3^{2-}$ in aqueous solution: AgBr (moles) = 4.98×10^{-3}.

TABLE 4

Thermometric enthalpy titration of AgCl with $S_2O_3^{2-}$

$S_2O_3^{2-}$ (moles)	AgCl (moles)	ΔT (mV)	C_p (J mV^{-1})			$-Q_R$ (J)	$-\Delta_R H_m^{\ominus}$ [a] (kJ mol^{-1})	Mole ratio [c] $nS_2O_3^{2-}/nAg^+$
			C_{pB}	C_{pA}	$\bar{C}_p$			
5.827×10^{-4}	2.988×10^{-4}	0.0186	145.7	153.3	149.5	2.781	9.31	1.95
6.010×10^{-4}	2.988×10^{-4}	0.0166	148.6	150.4	149.5	2.482	8.31	2.01
6.328×10^{-4}	2.988×10^{-4}	0.0171	148.7	151.5	150.1	2.567	8.59	2.12
6.270×10^{-4}	2.988×10^{-4}	0.0189	149.1	152.5	150.8	2.850	9.84	2.10
6.244×10^{-4}	2.988×10^{-4}	0.0175	145.3	150.7	148.0	2.590	8.67	2.09
4.163×10^{-3}	1.992×10^{-3}	0.1381	149.8	152.2	151.0	20.853	10.47	2.09
8.878×10^{-3}	4.395×10^{-3}	0.3084	152.1	154.3	153.2	47.250	10.75	2.02
2.764×10^{-3}	1.494×10^{-3}	0.1059	151.4	153.5	152.5	16.150	10.80	1.85

[a] Mean $-\Delta_R H_m^{\ominus} = 9.42 \pm 0.96$ kJ mol^{-1}.

[b] Mean mole ratio = 2.05 ± 0.06.

The results obtained for the thermometric titration of freshly precipitated silver chloride with thiosulphate are given in Table 4 and a typical thermogram for this system is shown in Fig. 5. It is apparent from the overall data that only one well defined slope change occurs over the duration of the reaction, corresponding to the formation of a single complex species with a mole ratio of 2.05 and, hence, a stoichiometry of $[Ag(S_2O_3)_2]^{3-}$.

Thus, it appears that the dissolution of either AgCl or AgBr in thiosulphate results in the formation of a single silver/thiosulphate complex species of stoichiometry $[Ag(S_2O_3)_2]^{3-}$; this corresponds to the ion of maximum stability in the silver/thiosulphate aqueous system.

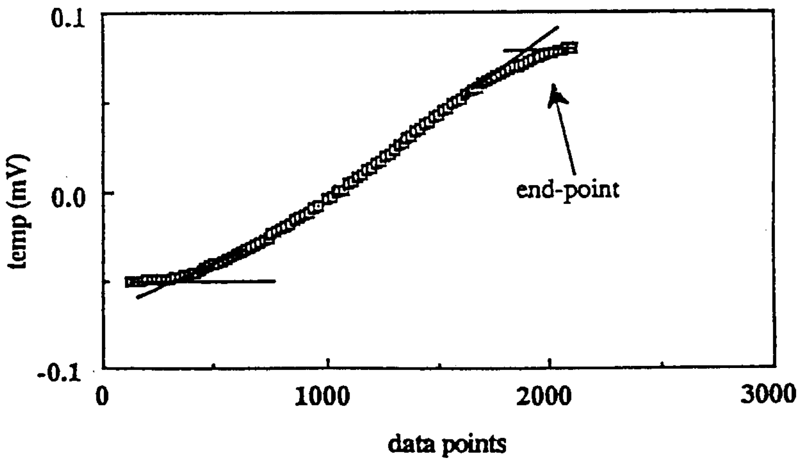

Fig. 5. A typical TET thermogram for the titration of AgCl with $S_2O_3^{2-}$ in aqueous solution: AgCl (moles) = 2.988×10^{-4}.

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