The Anion Exchange of Metal Complexes

The Silver — Thiosulphate System

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The silver thiosulphate system has been studied by an anion exchange method. Batch equilibrations and column elutions gave silver distribution data between Dowex-1-thiosulphate resin and solutions of $\text{Na}_2\text{S}_2\text{O}_3$ in the concentration range 0.01–4 M. The thiosulphate concentrations in the resin in excess over its capacity were measured, and the activity of thiosulphate ion in the resin calculated. This together with the distribution data yielded the "ideal" distribution curve, whence it appears that if the resin species is RAgS_2O_3 , then $\text{Ag}(\text{S}_2\text{O}_3)_3^{5-}$ will predominate in the solution. For the reaction $\text{Ag}(\text{S}_2\text{O}_3)_3^{5-} + \text{S}_2\text{O}_3^{2-} \rightleftharpoons \text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$ the concentration quotient at 1–2 M ionic strength is $k' = 2.5 \pm 0.5$, while for $\text{Ag}(\text{S}_2\text{O}_3)_3^{5-} + 1/2 \text{R}_2\text{S}_2\text{O}_3 \rightleftharpoons \text{RAgS}_2\text{O}_3 + 5/2 \text{S}_2\text{O}_3^{2-}$ the constant is $K'' = 5$.

The complex systems previously studied in this laboratory were of the type in which a neutral complex could form. The anion exchange method developed for studying complex systems may, however, also be applied to systems in which neutral complexes are unable to form. This has already been demonstrated by the calcium citrate system¹, for which, however, the data are rather scant. It was thought, therefore, that it would be of interest to work out a similar system in detail.

The silver thiosulphate system was chosen, as it has already been studied by a number of authors^{2–4}, and complexity constants are available for comparison. The system has been shown to be mononuclear, so that in the sequence of species: Ag^+ , $\text{Ag}(\text{S}_2\text{O}_3)^-$, $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$... no neutral species appears.

Apart from the general interest in the silver-thiosulphate system (for photography), there is also a specific interest in its anion-exchange behaviour, in connection with the separation of silver from other metals or its recovery from spent photographic solutions. Lure and Perenyslova⁵ have applied the resin *m*-phenylenediamine sulphate to silver-thiosulphate solutions. The silver was absorbed (as $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$ according to the authors), but was rapidly reduced to Ag_2S , the resin functioning as catalyst.

Fig. 1. The column for elution experiments. a: dropping rate counter; b: standard taper 14/35 ground joint; c: Dowex-1-X10 thiosulphate resin; d: distance between top and bottom of column $d = 8.0 \pm 0.2$ cm; e: glass wool plugs; f: lead shield; g: G.-M. cylindrical counter; h: 3 mm diameter hole in shield; i: 1 mm diameter capillary tube; j: 4.8 mm inner diameter glass column.

In order to apply the anion exchange distribution data quantitatively to complexity calculations, it is necessary, as has been pointed out before, to know the activity of the ligand in the resin. This could not be found in the literature, and had to be determined in addition to the silver distribution.

EXPERIMENTAL

Materials. A known weight of $> 99.9\%$ pure silver wire, irradiated by A. E. R. E. Harwell, England, to produce ^{110}Ag (half life = 9 months), was dissolved in moderately concentrated nitric acid. The solution was then neutralized with ammonia and diluted with water to 1.00×10^{-4} M in silver and about 0.01 M in nitrate.

Sodium thiosulphate pentahydrate was dissolved in water to saturation (about 4 M), and from this stock solution others were prepared by dilution. No mould growth was observed in the concentrated solution during more than a month.

Dowex-1 resin, 10 % cross-linked and 100–200 mesh, was converted from the chloride to the thiosulphate state by passing a tenfold excess of 2 M sodium thiosulphate through a column of the resin. Finally, after destruction of the thiosulphate in the effluent by adding 1 M sulphuric acid, heating to coagulate the sulphur and centrifuging it off, no more chloride could be detected. The resin was then thoroughly washed with water, and a portion shaken with 1 M ammonium nitrate showed no remaining chloride.

Pyrex glass was ground to a powder of 100–200 mesh, washed with dilute nitric acid and water and dried.

All other reagents were of analytical grade.

Procedure. The column for the elution studies consisted of a narrow glass tube (Fig. 1), of inner diameter 0.48 cm (cross section $A = 0.180 \pm 0.003$ cm²). It contained a weight $w = 0.725 \pm 0.002$ g of air dried resin to a height $d = 8.0 \pm 0.2$ cm above a glass wool plug. A G.-M. counter surrounded by a thick lead shield was mounted with a window in the shield opposite the bottom of the resin column. On top of the resin was another, narrow, glass wool plug, on top of which was placed a small portion of resin (50.0 ± 1.0 mg), previously saturated with radioactive silver (absorbed from 0.05 M sodium thiosulphate). Thiosulphate solutions were passed through the column to elute the silver.

The active zone passed the distance d cm from the top of the column to the counter at the bottom at a known volume of eluant, V ml, obtained from the maximum in a plot of counting rate *vs.* volume. Similar arrangements are described by Forsling⁶ and Kraus and Moore⁷.

Batch experiments were made by shaking resin with solution for 16–20 h, which was shown to be two to three times in excess of that needed for equilibration. The dipping G.-M. tube used for radioassay counted only the gamma rays owing to its rather thick walls.

For measuring the excess thiosulphate in the resin, portions of resin or glass were shaken for 2 h with aliquots of thiosulphate solutions. The solid was then quantitatively filtered off, and thiosulphate was determined in the filtrate by titration with iodine solutions standardized against pure solid arsenic(III) oxide. The powder on the filter was washed thoroughly with water, then shaken for 2 h with a hundred times excess, on an equivalent basis, of 5 % sodium chloride. The selectivity coefficient value of Wheaton and Bauman²¹ for the sulphate-chloride exchange was taken as indicative of that of the thiosulphate-chloride exchange. On this basis it was calculated that at equilibrium with the 5 % sodium chloride (0.85 M), no more than 0.2 % of the thiosulphate will remain on the resin. The sodium chloride solution was filtered away and the powder was again washed. In the combined filtrate and washing, thiosulphate was determined. In this way both the solution and the resin thiosulphate concentration were known for equilibrium.

All experiments were repeated and agreed within ± 1.5 %. They were made at room temperature, about 25–30 °C.

RESULTS

No significant influence of silver concentration on the anion exchange distribution in the silver concentration range 2×10^{-6} to 2×10^{-4} M with a thiosulphate concentration of 0.64 M could be found. The value of the distribution obtained from eight measurements was $D = 180 \pm 15$. The formation of polynuclear complexes in the solutions is thus very unlikely.

Batch equilibrations, using 4×10^{-3} to 1.28 M thiosulphate solutions, with equilibrium concentration of silver less than 5×10^{-6} M and loading less than 1 % of the capacity, gave the distribution values D in Table 1.

Elution experiments using 0.10 to 4.24 M thiosulphate solutions gave the distribution values appearing in Table 2. They were calculated in the following way, based on the method of Kraus and Moore⁷.

Table 1. Anion exchange distribution of silver as function of thiosulphate concentration; batch method.

Thiosulphate concentration M	$-\log$ $a_{\text{Na}_2\text{S}_2\text{O}_3}$	$\log D$ (ml/g)	Thiosulphate concentration M	$-\log$ $a_{\text{Na}_2\text{S}_2\text{O}_3}$	$\log D$ (ml/g)
0.004	2.43	> 5.15	0.080	1.45	3.90 ± 0.20
0.008	2.20	> 5.15	0.128	1.29	3.36 ± 0.02
0.016	1.98	4.64 ± 0.10	0.16	1.22	3.23 ± 0.05
0.032	1.75	4.48 ± 0.08	0.32	0.99	2.71 ± 0.05
0.040	1.67	4.10 ± 0.25	0.64	0.76	2.25 ± 0.02
0.064	1.51	3.79 ± 0.05	1.28	0.53	1.49 ± 0.02

Fig. 2. The distribution of silver as function of thiosulphate activity. ■ and □ experimental points with margins of error for column and batch, methods. — — — — Curves calculated with the constants $\log K = 2.1 \pm 0.1$ and $\log k_3 = 1.7 \pm 0.2$. — — — — Straight line with slope $-5/2$.

An elution constant E is defined by eqn. (1)

$$E = d \cdot A \cdot V^{-1} \quad (1)$$

where d , A and V are the quantities defined above. E is related to the volume distribution coefficient D_v by eqn. (2)

$$E = (D_v + i)^{-1} \quad (2)$$

where i is the fractional interstitial volume, having the value 0.45 (this, however, need not be known accurately for large enough distributions). The mass distribution coefficient D is related to D_v by the specific volume of the resin $d \cdot A \cdot w^{-1}$ where w is the weight of the resin in g in the d cm long column:

$$D = d \cdot A \cdot w^{-1} \cdot D_v = w^{-1} \cdot V - (i \cdot d \cdot A \cdot w^{-1}) \quad (3)$$

Inserting the particular values for the column employed, D is obtained in terms of V directly as

$$D = 1.38 V - 0.9 \text{ ml/g} \quad (4)$$

Table 2. Anion exchange distribution of silver as function of thiosulphate concentration; column method.

Thiosulphate concentration M	$-\log a_{\text{Na}_2\text{S}_2\text{O}_3}$	$\log D$ (ml/g)	Thiosulphate concentration M	$-\log a_{\text{Na}_2\text{S}_2\text{O}_3}$	$\log D$ (ml/g)
0.10	1.37	3.45 ± 0.05	0.96	0.62	1.81 ± 0.05
0.20	1.14	2.99 ± 0.07	1.49	0.47	1.43 ± 0.06
0.30	1.00	2.79 ± 0.05	2.00	0.36	0.94 ± 0.20
0.50	0.84	2.49 ± 0.05	2.96	0.21	0.60 ± 0.06
0.72	0.72	2.08 ± 0.05	4.24	-0.05	0.16 ± 0.10
0.96	0.62	1.88 ± 0.05			

Values of the activity coefficients of thiosulphate solutions were taken from Stokes⁸ and converted from the molal to the molar scale.

A $\log D(\log a_{\text{Na}_2\text{S}_2\text{O}_3})$ plot is shown in Fig. 2 for values of both Tables 1 and 2.

The thiosulphate capacity of the resin was determined to be 1.255 ± 0.003 mmole/g. The chloride displaced from the resin amounted to 2.55 mequiv/g, which means that the thiosulphate occupies $2.55/1.255 = 2.0$ sites on the resin, as would be expected from its charge.

The water content of air-dried resin was determined in a "drying pistol" at 78°C, and was found to be 29.5 ± 0.3 % W/W.

The concentration of thiosulphate in a resin in equilibrium with a thiosulphate solution is made up of three parts: the fixed capacity, the invading electrolyte, and the surface-sorbed material, *i. e.* the part contained in a mechanically-held film on the surface, of the same concentration as the bulk of the solution, and assumed to be equal to the amount sorbed on a similar glass powder surface. Table 3 gives the thiosulphate concentrations in these three categories as functions of solution concentration in the range 0.01 to 2 M.

In cases where the excess electrolyte is small, and at low thiosulphate concentrations, the combined amounts "excess electrolyte" + "glass" were obtained directly from the difference between initial and final thiosulphate concentration in the solution. At high thiosulphate concentrations, when this becomes inexact, the thiosulphate displaced from the resin by 5 % sodium chloride, *i. e.* the "total resin" concentration was the directly measured quantity.

Table 3. Thiosulphate concentration on resin and glass as function of solution concentration.

Solution M	Total resin mmole/g	Glass mmole/g	Net resin mmole/g	Excess electrolyte mmole/g
0.010	1.265	0.005	1.260 ± 0.005	0.005 ± 0.005
0.020	1.270	0.005	1.265 ± 0.005	0.010 ± 0.005
0.050	1.290	0.005	1.285 ± 0.005	0.030 ± 0.005
0.100	1.310	0.005	1.305 ± 0.005	0.05 ± 0.01
0.300	1.375 ± 0.005	0.010	1.365 ± 0.005	0.11 ± 0.01
0.706	1.55 ± 0.01	0.010	1.530 ± 0.005	0.28 ± 0.01
1.00	1.67 ± 0.01	0.047	1.62 ± 0.01	0.37 ± 0.01
2.02	2.48 ± 0.01	0.098	2.38 ± 0.01	1.13 ± 0.01

CALCULATIONS

The resin thiosulphate activity was calculated by the method used by Kraus and Moore⁹ and by Gottlieb and Gregor¹⁰. At equilibrium the activities of sodium thiosulphate are equal in both phases:

$$(\text{Na})^2(\text{S}_2\text{O}_3) = 4[\text{S}_2\text{O}_3]_{\pm}^3 = (\text{Na})_r^2(\text{S}_2\text{O}_3)_r = [\text{Na}]_r^2[\text{S}_2\text{O}_3]_{r,\pm}^3 \quad (5)$$

where parentheses denote activities, square brackets — concentrations, suffix *r* — resin phase, no suffix — solution phase and $f_{\pm}$ the average activity coefficients.

In order to compare the two phases, resin concentrations were converted to mole/liter by the factor 3.40 kg/l, obtained from the water content of the air-dried resin. This factor was assumed to be independent of the thiosulphate concentrations because no expansion or contraction of the resin could be observed when the concentration of the eluant was changed in the column experiments.

The term $[\text{Na}]_r$ is equal to twice the "excess electrolyte" in Table 3, as this is the only sodium ion source in the resin. The term $[\text{S}_2\text{O}_3]_r$ is equal to "net resin" in Table 3. Rearranging eqn. (5), the ligand activity in the resin is obtained

$$\log (\text{S}_2\text{O}_3)_r = \log [\text{S}_2\text{O}_3]_{r/\pm r} = 2/3 \log \text{"net resin"} + \log [\text{S}_2\text{O}_3] + \log f_{\pm} - 2/3 \log \text{"excess electrolyte"} - \log 3.40 \quad (6)$$

Eqn. (6) introduces the activity of a single ion — $\text{S}_2\text{O}_3^{2-}$ — which necessitates an extrathermodynamic assumption. As the resin phase is a concentrated aqueous solution, at least 2.5 equiv. per 295 g water, *i. e.* 8.5 N, it is felt that this is a region where the Debye-Hückel term of the activity coefficient plays a minor role compared with the hydration term. Thus $f_{\text{S}_2\text{O}_3^{2-}}^r$ was assumed equal to $f_{\pm r}$. As regards the aqueous solutions, although their concentration range was mainly much lower than that of the resin, the same assumption was made, as the alternate extreme assumption: $\log f_{\text{S}_2\text{O}_3^{2-}} = 4 \log f_{\text{Na}^+}$ led to a curve concave upwards, *i. e.* representing a decreasing formation function $\bar{n}$ with increasing concentration, and this is untenable.

Values of the ligand activity calculated from eqn. (6) are given in Table 4.

Table 4. Resin ligand activity as function of solution activity.

$[\text{Na}_2\text{S}_2\text{O}_3]$ M	0.010	0.020	0.050	0.100	0.300	0.706	1.00	2.02
$-\log (\text{S}_2\text{O}_3)$	2.14	1.97	1.60	1.35	1.00	0.72	0.62	0.36
$-\log (\text{S}_2\text{O}_3)_r$	1.2	1.1	1.02	0.94	0.81	0.75	0.73	0.67

An arbitrary standard state will be defined as that corresponding to unit solution activity, and from extrapolation of the values of Table 4 — which, incidentally gives a linear plot — the value $\log (\text{S}_2\text{O}_3)_r^0 = -0.56$ was obtained from eqn. (7)

$$\log (\text{S}_2\text{O}_3)_r = \log (\text{S}_2\text{O}_3)_r^0 + F(\log (\text{S}_2\text{O}_3)) \quad (7)$$

The main reaction of absorption of silver by the resin may be formulated as

where p might be 1, 2, ... and R is one equivalent of resin cation. The range of variation of the resin ligand activity is not very large, so it may be assumed that only one value of p must be considered, and the total concentration of silver on the resin is $[\text{Ag}(\text{S}_2\text{O}_3)_p]_r$.

The equilibrium constant of reaction (8) will have the resin ligand activity to the $(p - 1/2)$ power. It has been shown before¹ that this means that the ideal distribution D_0 is obtained from the measured D from the relationship

$$\log D_0 = \log D - (p - 1/2) \cdot F(\log (S_2O_3)) \quad (9)$$

As in the thiosulphate range employed the function F has negative values ($\log (S_2O_3)_r^0$ greater than any value of $\log (S_2O_3)_r$), the actual "invasion" correction will give a curve $\log D_0$ ($\log (S_2O_3)_r$), above the $\log D$ curve, and with a steeper slope.

The values $p = 1, 2$ and 3 were tried and found to yield $\log D_0$ curves with limiting slopes of $-2.5, -2.9$ and -3.3 , respectively. However, only the value of $p = 1$, giving a slope of -2.5 , is consistent with the presence of $Ag(S_2O_3)_2^{3-}$ and $Ag(S_2O_3)_3^{5-}$ in the solutions under consideration, to which the evidence points^{2-4,17,18,20}. That this is so may be seen from the expression for D_0 which may easily be derived (see also Ref.¹).

$$\begin{aligned} D_0 &= k_a \beta_p (S_2O_3)_r^{0p-1/2} (S_2O_3)^{1/2} / (\beta_2 (S_2O_3)^2 + \beta_3 (S_2O_3)^3) = \\ &= K (S_2O_3)^{-3/2} (1 + k_3 (S_2O_3))^{-1} \end{aligned} \quad (10)$$

where $K = k_a \beta_p \beta_2^{-1} (S_2O_3)_r^{0p-1/2}$, and k_a is the equilibrium constant of (8). Combining eqns. (9) and (10), $\log D$ is obtained in terms of $\log (S_2O_3)$

$$\begin{aligned} \log D &= (p - 1/2) \cdot F(\log (S_2O_3)) + \log K - 3/2 \log (S_2O_3) - \\ &\quad - \log (1 + k_3 (S_2O_3)) \end{aligned} \quad (11)$$

Using $p = 1$ and the values $\log K = 2.1 \pm 0.1$ and $\log k_3 = 1.7 \pm 0.2$, the calculated solid curve in Fig. 2 is obtained, and is considered as giving the best fit with the experimental data. However, owing to the relatively large random errors in the data, especially in the low concentration range, the curvature of the plot in this range, indicating the presence of $Ag(S_2O_3)_2^{3-}$ in the most dilute solutions, may not be real. The data could also be fitted by a curve $\log D = 1/2 F(\log (S_2O_3)) + \log K - 5/2 \log (S_2O_3)$ (and even by a straight line of slope $-5/2$, which neglects the invasion correction), but these curves would mean that no $Ag(S_2O_3)_2^{3-}$ is present in this concentration range. The fit of these latter two curves is poorer than the fit obtained when unity is not neglected in comparison with $k_3 (S_2O_3)$ in this range (eqn. (11)). The value found for k_3 may be considered as the lower limit of the equilibrium constant.

DISCUSSION

The value of the complexity constant found, k_3 , is not immediately comparable with reported values, as the latter are all concentration constants, while the former is valid for zero ionic strength. However, by replotting the D_0 distribution curve against the thiosulphate concentration, instead of against its activity, a concentration quotient $k'_3 = 2.5 \pm 0.5$ is obtained, which is consistent with the experimental data. The main effect of the transition of $Ag(S_2O_3)_2^{3-}$ to $Ag(S_2O_3)_3^{5-}$ occurs in the range 0.3 to 0.7 M thiosulphate, therefore this value of k'_3 should be valid around ionic strengths of one to two.

Bodländer's values² may be regarded only as approximate, but they are of the correct order of magnitude: $\beta_2 = 10^{13}$ and $\beta_3 = 3.5 \times 10^{13}$, *i. e.* $k'_3 = 3.5$. Concentration quotients valid at 2 M ionic strength were obtained by Ölander and Adelson³, using a potentiometric method, at 25° C. They obtained $\beta_2 = 6.0 \times 10^{12}$ and $\beta_3 = 1.15 \times 10^{13}$, *i. e.* $k'_3 = 1.9$. Chateau and Pouradier⁴ assume that the activity coefficient of $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$ is equal to that of $\text{S}_2\text{O}_3^{2-}$ (obtaining $\beta_2 = 2.8 \times 10^{13}$), but that the coefficient of $\text{Ag}(\text{S}_2\text{O}_3)_3^{5-}$ is different, obtaining β_3 values in the range 1.5×10^{14} to 5.0×10^{14} , or, extrapolated to zero thiosulphate concentration, 1.4×10^{14} , *i. e.* $k_3 = 4.8$. They worked at 20° C, also employing a potentiometric method. No other determinations of k_3 are reported.

Determination of other constants in the silver-thiosulphate system were also made. Pawelka¹¹ found $\beta_2 = 2.4 \times 10^{13}$, while Ferrell and coworkers¹² obtained only an approximate estimate of 4×10^{14} for this constant. Carriere¹³ found by a conductivity method $\beta_1 = 7.4 \times 10^8$, and Chateau and Pouradier¹⁴, working at 70° C with a potentiometric method found it to be 2.75×10^7 .

The assumption of the presence of both $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$ and $\text{Ag}(\text{S}_2\text{O}_3)_3^{5-}$ in thiosulphate solutions of moderate concentrations is supported by much additional, though qualitative, evidence. Conductivity measurements of Ryabchikov and Silnichenko¹⁵ and of Saxena and Jain¹⁶ indicate the presence of $\text{Ag}(\text{S}_2\text{O}_3)^-$ and $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$ in dilute solutions. Potentiometric determinations of Ashihara and Matsuda¹⁷, Schmitz-Dumont and Schmitz¹⁸, Brehmer¹⁹ and Spacu and Murgulescu²⁰ indicate the presence of $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$ and $\text{Ag}(\text{S}_2\text{O}_3)_3^{5-}$ in more concentrated solutions. It appears that, except when the silver concentration is high (when $\text{Ag}(\text{S}_2\text{O}_3)^-$ and possibly even polynuclear complexes form), $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$ and $\text{Ag}(\text{S}_2\text{O}_3)_3^{5-}$ are the complex silver species present in thiosulphate solutions.

Using the constant K in eqn. (10), it is possible to state the main reaction with the resin not in terms of eqn. (8), which considers the exchange of the first anionic complex $\text{Ag}(\text{S}_2\text{O}_3)^-$, but in terms of the complexes actually present in the solutions. At low concentrations:

$$\log K' = \log K - 3/2 \log (\text{S}_2\text{O}_3)_r^0 = 2.38 \pm 0.10$$

and at high concentrations:

$$\log K'' = \log K' - \log k_3 = 0.7 \pm 0.2$$

Whichever of these reactions is used, it is important to realize that silver is absorbed quite strongly from dilute solutions but only weakly from concentrated ones, there being a span of five powers of ten in the distribution coefficients. Anion exchange separation from metals not absorbed from dilute thiosulphate solutions is thus possible, with subsequent elution of the silver with a concentrated thiosulphate solution.

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