Spectrophotometric Determination of Sulphur Dioxide and Thiosulphate in Aqueous Solutions of Hydrogen Sulphite

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A spectrophotometric method for the determination of SO_2 aq and $S_2O_3^{2-}$ in aqueous solutions containing hydrogen sulphite in great excess is described. The concentration ranges investigated are $[HSO_3^-]$, $5 \times 10^{-3} - 5 \times 10^{-1}$; $[S_2O_5^{-2}]$, $5 \times 10^{-5} - 10^{-3}$; $[SO_2$ aq $]$, $5 \times 10^{-5} - 10^{-3}$ M.

A number of investigations of ultraviolet absorption spectra of sulphurous species have been published.[1-7] Albu and Goldfinger[1] report that the absorption of SO_2 aq starts at 327 nm and shows a maximum at 280 nm. A careful study of the ultraviolet spectra of hydrogen sulphite ions in aqueous solutions at the pH-range $3.5 - 5.5$ has been carried out by Golding.[4]

At low concentrations ($< 3 \times 10^{-3}$ M) the spectrum shows a single peak (λ_{max} 205.2 nm; log ε apparent 2.75) which has been ascribed to the isomer $HO.SO_2^-$. As the total sulphur concentration is increased, the peak does not obey Beer's law but the wavelength maximum shifts towards 215 nm and the extinction coefficient decreases. The peak at 215 nm has been ascribed to the HSO_3^- isomer (λ_{max} 215 nm; log ε 1.78). At higher concentrations ($> 10^{-2}$) a peak appears with maximum at 255 nm (log ε apparent 3.75). The peak has been ascribed to the species $S_2O_5^{2-}$, from the equilibrium $2HSO_3^- = S_2O_5^{2-}$ ($K = [S_2O_5^{2-}]/[HSO_3^-]^2 \approx 7 \times 10^{-2}$ M^{-1}).

Thiosulphate ions ($S_2O_3^{2-}$) show a single peak (λ_{max} 215 nm $\varepsilon \approx 3700$).[8]

The total absorbance of n species with overlapping bands can, if the assumption of additive absorbance is made, at any wavelength within the overlapping region be expressed as

$$A_s = l \sum \varepsilon_{sn} \times C_n$$

where l is the length of the absorption cell, C_n the concentration of species n and ε_{sn} the extinction coefficient of the species n at the wavelength λ_s.

To determine the concentrations of n species, absorbances must be measured at n wavelengths within the overlapping region. Thus a system of n linear equations is to be solved and can be written in matrix notation, $A = CE$, *i.e.*

$$\begin{pmatrix} A_1 \\ \cdot \\ \cdot \\ A_n \end{pmatrix} = \begin{pmatrix} C_1 \\ \cdot \\ \cdot \\ C_n \end{pmatrix} \begin{pmatrix} \varepsilon_{11} & \cdots & \varepsilon_{1n} \\ \cdot & & \cdot \\ \cdot & & \cdot \\ C_{n1} & \cdots & C_{nn} \end{pmatrix}$$

The solution is given by $C = AE^{-1}$.

The absorbances are, however, in many cases not additive, e.g. due to complex formations, interactions between species in the system studied (cf. hydrogen sulphite above) and hence each system should be tested for linearity in the concentration range of interest. The aim of the present investigation was to study the absorbances of $SO_{2\ aq}$ and $S_2O_3{}^{2-}$ in aqueous solutions of hydrogen sulphite containing low concentration of $SO_4{}^{2-}$ and if possible apply UV-spectroscopy analytically to such solutions. The concentration range of interest was $[HSO_3{}^-] = (5 \times 10^{-3} - 10^{-1})$; $[S_2O_3{}^{2-}]$ $(5 \times 10^{-5} - 10^{-3})$; $[SO_4{}^{2-}]$ $(5 \times 10^{-5} - 10^{-3})$ M.

EXPERIMENTAL

All chemicals used were of p.a. quality except $Na_2S_2O_3$ which was of *supra* pure quality. The solutions were prepared by dissolving $Na_2S_2O_5$, $Na_2S_2O_3$, and H_2SO_4 in doubly distilled water. Different pH values were achieved by addition of NaOH.

All spectra were measured on a Hitachi Perkin-Elmer Model 139 UV-spectrometer. The cells used were of 1 cm path length and the spectra were measured at $25 \pm 0.5°C$
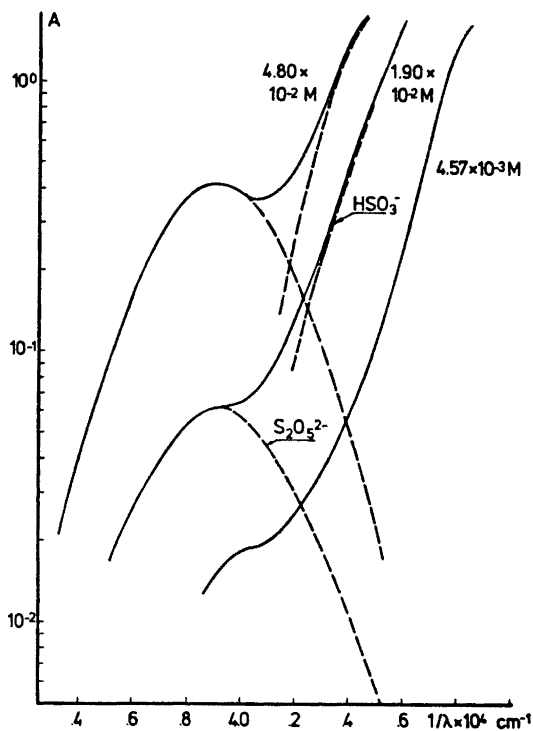

Fig. 1. Ultraviolet spectra of hydrogen sulphite.

RESULTS AND DISCUSSION

Hydrogen sulphite HSO_3^-, $S_2O_5^{2-}$. Spectra of hydrogen sulphite in the concentration range $5 \times 10^{-3} - 5 \times 10^{-2}$ are shown in Fig. 1. As seen the maximum for HSO_3^- is shifted towards longer wavelengths with increasing

Table 1. The extinction coefficients $\varepsilon(S_2O_5^{2-})$ of the bisulphite species $S_2O_5^{2-}$ at different wavelengths. (Based on Gaussian distribution.)

λ nm	$\varepsilon(S_2O_3^{2-})$
225	236
230	484
235	935 ± 35
240	1453 ± 36
245	1989 ± 89
250	2365 ± 77
255	2527 ± 65
260	2365 ± 105
265	2026 ± 87
270	1590 ± 47
275	1182 ± 4
280	852 ± 60
285	577 ± 50
290	335
295	205
300	130

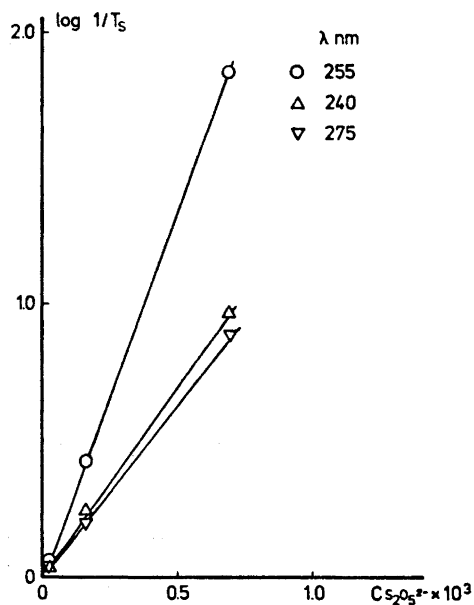*Fig. 2.* Linearity test of $S_2O_5^{2-}$ absorbancy $\log 1/T_s$ *vs.* $[S_2O_5^{2-}]$.

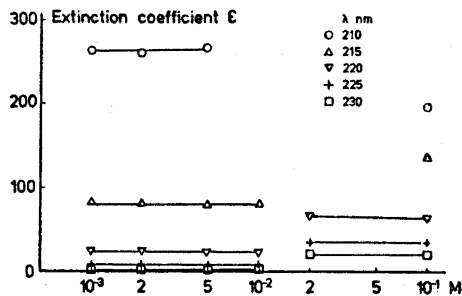*Fig. 3.* The extinction coefficient of HSO_3^- *vs.* $[HSO_3^-]$ at different wave lengths.

concentration. The peak at 255 nm (3.92×10^{-4} cm^{-1}) has been calculated assuming Gaussian distribution around the mean transition energy.[9] The calculated extinction coefficients $\varepsilon(S_2O_5{}^{2-})$ at different wavelengths are given in Table 1. The calculations are based on equilibrium constant 7×10^{-2} for the equilibrium 2 HSO$_3{}^- \rightleftharpoons$ S$_2$O$_5{}^{2-}$ given by Golding.[4] The maximum coefficient obtained $\varepsilon_{max} = 2527 \pm 65$ is much lower than ε_{max} obtained by Golding, $\varepsilon = 3980$. The linearity of the S$_2$O$_5{}^{2-}$ peak is shown in Fig. 2. The extinction coefficients for HSO$_3{}^-$ at different wavelengths are plotted in Fig. 3. As seen, in agreement with Golding, constancy is found at concentrations $< 10^{-2}$ and $> 2 \times 10^{-2}$ whereas in the intermediate region great changes in extinction coefficient occur.
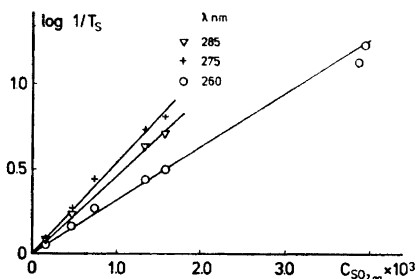

Fig. 4. Linearity test of SO$_2$ $_{aq}$ absorbancy log $1/T_s$ *vs.* [SO$_2$ $_{aq}$].
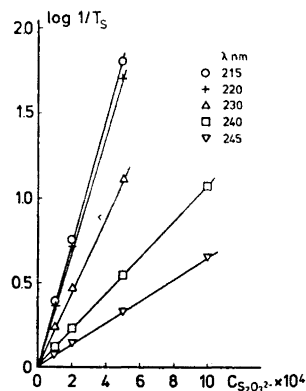
Fig. 5. Linearity test of S$_2$O$_3{}^{2-}$ absorbancy log $1/T_s$ *vs.* [S$_2$O$_3{}^{2-}$].

Sulphur dioxide, SO$_2$ $_{aq}$, shows two absorption bands (Fig. 6), one with maximum at 276 nm ($\varepsilon_{max} = 600$) and one with maximum at shorter wavelengths, $\lambda_{max} < 210$ nm. The absorbancy has been tested for linearity in the concentration range $0-4 \times 10^{-3}$ M and the results are plotted in Fig. 4. As seen, Beer's law is obeyed by the SO$_2$ $_{aq}$ species in this region.

Thiosulphate. The ultraviolet spectrum of S$_2$O$_3{}^{2-}$ is shown in Fig. 6 and the extinction coefficient at different wavelengths tabulated in Table 2. The S$_2$O$_3{}^{2-}$ ions give a single peak (λ_{max} 215 nm, ε_{max} 3678 $\pm$ 10). The absorbancy has been tested for linearity in the concentration range $0-10^{-3}$ M (Fig. 5).

Sulphate ions in the concentration range $0-10^{-3}$ M and hydrogen sulphite in the concentration range $0-5 \times 10^{-2}$ were not found to have any effect on the absorbancy.

Analysis of solutions containing HSO$_3{}^-$, S$_2$O$_5{}^{2-}$, S$_2$O$_3{}^{2-}$ and SO$_2$ $_{aq}$. As mentioned above the total absorbance of n species with overlapping bands can, if the assumption of additive absorbances is made, be expressed as $A_s = l \sum \varepsilon_{sn} \times C_n$. Thus the concentration of the n species can be solved from the matrix system $A = CE$, *i.e.*
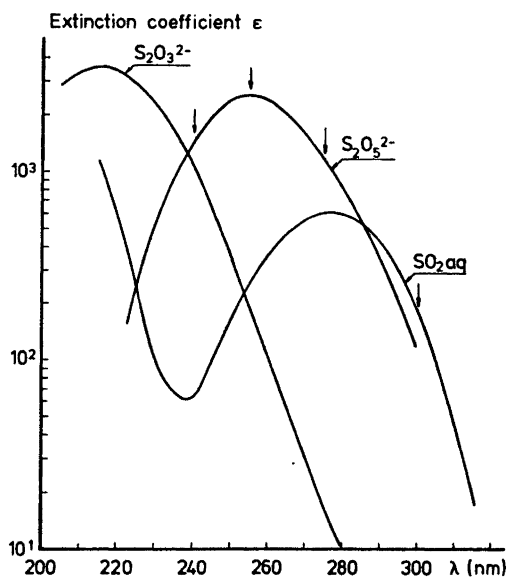
$$C = AE^{-1}$$

Fig. 6. Ultraviolet spectra of sulphur-oxyacids.

Table 2. The extinction coefficients of the thiosulphate ion $S_2O_3^{2-}$ at different wavelengths.

λ nm	$\varepsilon(S_2O_3^{2-})$
200	2552 $\pm$ 16
205	2906 $\pm$ 31
210	3366 $\pm$ 15
215	3678 $\pm$ 10
220	3478 $\pm$ 10
225	2880 $\pm$ 36
230	2202 $\pm$ 8
235	1592 $\pm$ 12
240	1055 $\pm$ 5
245	618 $\pm$ 9
250	362 $\pm$ 7
255	185 $\pm$ 5
260	107 $\pm$ 8
265	57 $\pm$ 6
270	33 $\pm$ 6
275	17.5 $\pm$ 4
280	10

The choice of wavelengths used in analysis of solutions containing HSO_3^-, $S_2O_5^{2-}$, $SO_{2\,aq}$, and $S_2O_3^{2-}$ were based on the following considerations.* As seen from Figs. 1 and 3 the absorption of HSO_3^- decreases very sharply with

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* As the absorption of HSO_3^- ions does not follow Beer's law this species is excluded from the analysis.

increasing wavelengths and is assumed to be of only slight importance at 240 nm. The wavelengths should be chosen at or near maxima in the ratios of the extinction coefficients but the magnitude of the coefficients must also be considered. Accordingly the wavelengths chosen were 240, 255, and 276 nm and thus the matrix system can be written

$$\begin{matrix} A_{240} \\ A_{255} = \\ A_{276} \end{matrix} \begin{pmatrix} C(SO_{2\ aq}) \\ C(S_2O_3{}^{2-}) \\ C(S_2O_5{}^{2-}) \end{pmatrix} \begin{pmatrix} 60 & 1055 & 1453 \\ 250 & 185 & 2575 \\ 600 & 14 & 1100 \end{pmatrix}$$

The solution is given

$$\begin{pmatrix} C(SO_{2\ aq}) \\ C(S_2O_3{}^{2-}) \\ C(S_2O_5{}^{2-}) \end{pmatrix} = \begin{pmatrix} A_{240} \\ A_{255} \\ A_{276} \end{pmatrix} \begin{pmatrix} 1.40278 & -9.55146 & 20.5061 \\ 10.63919 & -6.75044 & 1.7486 \\ -0.90056 & 5.29580 & 2.11652a \end{pmatrix} \times 10^{-4}$$

This matrix system has been used to analyse some solutions containing $HSO_3{}^-$ in great excess, $\sim 10^{-2}$ M, and low concentrations of $SO_{2\ aq}$ $(0.35 - 5 \times 10^{-4}$ M) and $S_2O_3{}^{2-}$ $(2-5) \times 10^{-4}$ M. The results are tabulated in Tables 3, 4, and 5. As seen, analyses of the species $S_2O_3{}^{2-}$ and $SO_{2\ aq}$ agree within a few per cent while the species $S_2O_5{}^{2-}$, which is present in very low concentrations $< 7 \times 10^{-6}$ M, agrees within 20 %.

Table 3.[a] Spectra of $SO_{2\ aq}$, $S_2O_5{}^{2-}$, $S_2O_3{}^{2-}$ and total absorbance calculated from absorbances at 240, 255, and 276 nm. For reference the experimentally obtained absorbances are given.

λ nm	$A(SO_{2\ aq})$	$A(S_2O_5{}^{2-})$	$A(S_2O_3{}^{2-})$	Calculated A_{tot}	A_{exp}	ΔA	
210					2		
215	0.592		0.670		—		
220	0.315		0.676	0.991	1.2	−0.209	
225	0.131	0.0012	0.565	0.6972	0.754	−0.0568	$HSO_3{}^-$
230	0.524	0.0025	0.436	0.4909	0.506	−0.0151	
235	0.0346	0.0048	0.313	0.3524	0.351	+0.0018	
240	0.032	0.0075	0.209	0.2485	0.248	0.0005	0.2 %
245	0.0514	0.0102	0.123	0.1846	0.087	−0.0024	−1.3 %
250	0.085	0.0122	0.0704	0.168	0.165	0.003	1.8 %
255	0.131	0.0130	0.0367	0.1807	0.181	−0.0003	−0.2 %
260	0.185	0.0122	0.0198	0.217	0.216	0.001	0.5 %
265	0.240	0.0105	0.0115	0.2620	0.260	0.002	0.8 %
270	0.293	0.0082	0.0060	0.3072	0.300	0.0072	2.4 %
276	0.315	0.0057	0.0028	0.3235	0.323	0.0005	0.15 %
281	0.303	0.0041	0.0019	0.3090	0.308	0.001	0.3 %

[a] *Solution:* 0.9602 g $Na_2S_2O_5$ dissolved in 100 ml doubly distilled water; $[S_2O_3{}^{2-}]$, 2×10^{-4} M; $[H_2SO_4]$, 10^{-3} M.

Calculated:	*Theory/exp.*
$SO_{2\ aq}$ 5.243×10^{-5} M (tested by pH-calculation)	
$S_2O_5{}^{2-}$ 5.16×10^{-6}	6.24×10^{-6}
$S_2O_3{}^{2-}$ 1.982×10^{-4}	2.00×10^{-4}
pH 2.95 (assuming $\gamma_\pm = 0.832$, Ref. 5)	2.99 ± 0.05

Table 4.[a] Spectra of $SO_{2\ aq}$, $S_2O_5^{2-}$, $S_2O_3^{2-}$ and total absorbance calculated from absorbances at 240, 255, and 276 nm. For reference the experimentally obtained absorbances are given.

λ nm	$A(SO_{2\ aq})$	$A(S_2O_5^{2-})$	$A(S_2O_3^{2-})$	Calculated A_{tot}	A_{exp}	ΔA	
210							
215	0.0419		0.6958	0.7377	1.45	0.7123	
220	0.0223		0.6573	0.6976	–	0.2404	
225	0.0093	0.0012	0.5478	0.5583	0.6460	0.0877	HSO_3^-
230	0.0037	0.0027	0.4228	0.4292	0.4610	0.0318	
235	0.0024	0.0051	0.3037	0.3112	0.327	0.0158	
240	0.0022	0.0080	0.2028	0.2130	0.2130	–	
245	0.0036	0.0109	0.1191	0.1336	0.1340	– 0.0004	– 0.3 %
250	0.0060	0.0130	0.0682	0.0872	0.0880	– 0.0008	– 0.9 %
255	0.0093	0.0139	0.0356	0.0588	0.0590	– 0.0002	– 0.3 %
260	0.0131	0.0130	0.0192	0.0453	0.042	0.003	7.1 %
265	0.0170	0.0111	0.0111	0.0392	0.0360	0.0032	8.9 %
270	0.0207	0.0087	0.0059	0.0353	0.0350	0.0003	0.8 %
276	0.0223	0.0061	0.0027	0.0311	0.031	0.0001	0.3 %
281	0.0214	0.0044	0.0018	0.026	0.024	0.002	8.3 %

[a] *Solutions:* 0.9602 g $Na_2S_2O_5$ dissolved in 100 ml H_2O. $[S_2O_3^{2-}]$, 2×10^{-4} M; $[SO_4^{2-}]$, 10^{-3} M; pH (4.02 ± 0.05)

Calculated: *Theory/exp.*

$SO_{2\ aq}$ 0.371×10^{-4} (tested by pH-calculation)

$S_2O_5^{2-}$ 5.5×10^{-6} 7×10^{-6}

$S_2O_3^{2-}$ 1.922×10^{-4} 2×10^{-4}

pH 4.12 (assuming $\gamma\pm = 0.832$, Ref. 5) 4.02 ± 0.05

Table 5.[a] Spectra of $SO_{2\ aq}$, $S_2O_5^{2-}$, $S_2O_3^{2-}$ and total absorbance calculated from absorbances at 240, 255, and 276 nm. For reference the experimentally obtained absorbances are given.

λ nm	$A(SO_{2\ aq})$	$A(S_2O_5^{2-})$	$A(S_2O_3^{2-})$	Calculated A_{tot}	A_{exp}	ΔA	
225	0.0571	0.0025	1.4020	1.4616	1.499	– 0.0374	
230	0.0228	0.0044	1.0820	1.0864	1.137	– 0.0506	HSO_3^-
235	0.0151	0.0069	0.7798	0.8018	0.792	– 0.0098	
240	0.0137	0.0108	0.5191	0.5436	0.543	– 0.0006	– 0.1 %
245	0.0224	0.0147	0.3050	0.3421	0.347	– 0.0049	– 1.4 %
250	0.0372	0.0174	0.1747	0.2293	0.231	– 0.0017	– 0.7 %
255	0.0571	0.0186	0.0910	0.1673	0.167	0.0003	0.2 %
260	0.0804	0.0174	0.0526	0.1504	0.143	0.0074	5.2 %
270	0.1274	0.0117	0.0149	0.1540	0.151	0.0030	2.0 %
276	0.1370	0.0082	0.0069	0.1521	0.152	0.0001	–

[a] *Solution:* 0.5931 g $Na_2S_2O_5$ dissolved in 100 ml H_2O. $[S_2O_3^{2-}]$, 5×10^{-4} M; $[H_2SO_4] = 10^{-3}$ M; pH 3.25 ± 0.05

Calculated: *Theory/exp.*

$SO_{2\ aq}$ 2.284×10^{-4} (tested by pH-calculation)

$S_2O_5^{2-}$ 7.37×10^{-6} $\sim 7 \times 10^{-6}$

$S_2O_3^{2-}$ 4.92×10^{-4} 5×10^{-4}

pH 3.31 (assuming $\gamma\pm = 0.832$, Ref. 5)

REFERENCES

1. Albu, H. W. and Goldfinger, P. *Z. physik. Chem. (Leipzig)* **3 16** (1932) 338.
2. Shaefer, K., Niggerman, H. and Köhler, W. *Z. Elektrochem.* **21** (1915) 181; Shaefer, K. and Köhler, W. *Z. anorg. Chem.* **104** (1918) 212.
3. Simon, A. and Waldmann, K. *Z. anorg. Chem.* **281** (1955) 113, 115; **284** (1956) 36, 47; Simon, A. and Waldmann K. *Ibid.* **288** (1956) 131.
4. Golding, R. M. *J. Chem. Soc.* **1960** 3711.
5. Ratkowsky. D. A. and McCarthy, J. L. *J. Phys. Chem.* **66** (1962) 516.
6. Eremin, Yu. G. and Kiseleva, K. S. *Zh. Anal. Khim.* **24** (1969) 1201.
7. Scoggins, M. W. *Anal. Chem.* **42** (1970) 1091.
8. Teder, A. *Dissertation*, Stockholm 1969.
9. Kuhn, W. and Braun, E. *Z. physik. Chem. (Leipzig)* **8** (1930) 281.