*Food Chemistry* **44** (1992) 165–171

# Infrared and ultraviolet spectra of sulphur(IV) oxospecies in water-non-electrolyte mixtures

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(Received 18 April 1991; accepted 23 May 1991)

Ultraviolet spectra of solutions containing $NaHSO_3$ in water-non-electrolyte (ethanol, glycerol, polyethylene glycol, sucrose) mixtures show a decrease in the intensity of the peak due to $S_2O_5^{2-}$ with increasing non-electrolyte concentration. Infrared spectroscopy in water-glycerol mixtures is consistent with the possibility that addition of glycerol reduces the concentration of $S_2O_5^{2-}$. It is possible that $S_2O_5^{2-}$ ions may be less important in partially dehydrated foods than expected from the known behaviour of $NaHSO_3$ in simple aqueous solution.

## INTRODUCTION

When used in the context of a food additive, the term sulphur dioxide or sulphite(s) denotes a mixture of oxospecies of sulphur in oxidation state IV, i.e. $SO_2$, $HSO_3^-$, $SO_3^{2-}$ and $S_2O_5^{2-}$. Collectively, these species will be referred to here as S(IV). These are all in equilibrium with one another, and equilibrium is rapidly re-established if the concentration of the species or the pH is altered. At the pH of food the predominating species is $HSO_3^-$ in dilute systems but, when solutions of this ion are concentrated, the equilibrium

$$2\,HSO_3^- \rightleftharpoons S_2O_5^{2-} + H_2O$$

is significantly displaced to the right. Thus, using known equilibrium constants (Connick *et al.*, 1982) and the law of mass action, the proportion of the total S(IV) present as $S_2O_5^{2-}$ is 1% (mol/mol) and 14% (mol/mol) at total S(IV) concentrations of 0·1M and 1M, respectively (Wedzicha & Goddard, 1991). There is no knowledge of the way in which the equilibrium is affected by a reduction of water activity; a simple consideration of the law of mass action suggests that the equilibrium may be displace to the right in a low-water activity environment.

Interest in the species $S_2O_5^{2-}$ stems from the fact that it is a poor nucleophile (Wedzicha & Goddard, 1991). The ability of sulphites to inhibit non-enzymic browning arises from the nucleophilicity of the sulphite ion, and the possible conversion of $HSO_3^-$ to $S_2O_5^{2-}$ in concentrated foods (e.g. dehydrated and partially dehydrated fruits and vegetables) has prompted speculation (Wedzicha, 1987) that the high demand for the additive to control browning in such foods is the result of it being converted to a relatively unreactive form. Additionally, it has been shown that sulphites catalyse the early stages of the Maillard reaction (Wedzicha & Vakalis, 1988) and this has been ascribed to general acid-base catalysis. Whereas $SO_3^{2-}$ and $HSO_3^-$ are good acid-base catalysts, it is possible that $S_2O_5^{2-}$ might be considerably more effective (Slae & Shapiro, 1978). If this speculation is correct, the formation of such a catalyst in concentrated, sulphited foods could be another reason for the need of high levels of use of the additive in such products.

Data on the fate of S(IV) in vegetable dehydration, however, provide no support for large scale formation of $S_2O_5^{2-}$ in this situation (Wedzicha & Goddard, 1989) and it is necessary to appraise this possibility in detail. In the present investigation it was decided to examine the effect of non-electrolytes (ethanol, glycerol, polyethylene glycol PEG 400 and sucrose), which may also act as humectants, on the ultraviolet (UV) spectra of solutions containing $NaHSO_3$ because absorbance due to $S_2O_5^{2-}$ at 255 nm ($E_{max}$ = 5790 $M^{-1}$ $cm^{-1}$; Connick *et al.*, 1982), at which wavelength $HSO_3^-$ has negligible absorbance, offers a convenient approach to measuring the extent of formation of $S_2O_5^{2-}$. In the case of experiments using glycerol, infrared (IR) spectra were also recorded to support deductions made from the electronic spectra.

*Food Chemistry* 0308-8146/92/$05.00

## MATERIALS AND METHODS

Wherever possible, reagents were of AnalaR grade and were obtained from BDH Chemicals Ltd (Poole, UK). Solutions containing S(IV) were standardised iodimetrically. Ultraviolet spectra were obtained using a Cecil 292 spectrophotometer (1 cm silica cells) and IR spectra recorded from an ATR assembly (zinc selenide crystal) attached to a Nicolet Instruments 510 FTIR spectrometer and data processing computer. In all cases, FTIR data were accumulated from 20 scans.

## RESULTS AND DISCUSSION

The effect of glycerol concentration of the UV spectrum in the region 230–300 nm, of a nominally 50 mM solution of $NaHSO_3$ is shown in Fig. 1. The reduction of absorbance at 255 nm, with increase in glycerol content, is striking and it can be seen that no shift in wavelength and no new absorption peak is obtained. This result is typical of the effects of ethanol, sucrose and PEG 400 but, in these cases, the absorbance is not seen to fall to zero. The relative effects of the four non-electrolytes investigated are illustrated in Fig. 2. It can be seen that the relative effects are very different but, contrary to initial expectation, the effect of the non-electrolyte appears to be one of reducing the tendency for $S_2O_5^{2-}$ formation, despite the fact that these substances reduce the water activity, $a_w$, and any precipitated solid obtained when an excessive amount of non-electrolyte is added has an IR spectrum indistinguishable from that of solid $Na_2S_2O_5$. The main disadvantage of UV spectroscopic data is that the extinction coefficient of the solute could depend on the medium in which it is dissolved and, therefore, the authors sought to confirm these observations by running IR spectra of the glycerol-containing mixtures.

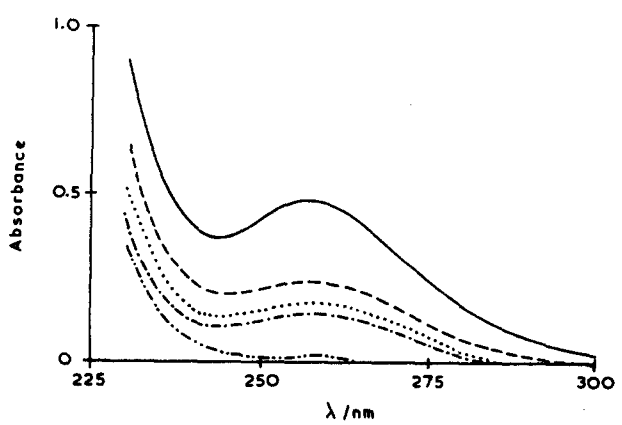


**Fig. 1.** Effect of increasing glycerol content on the ultraviolet spectrum of a 50 mM solution of $NaHSO_3$. Glycerol content: nil ———; 19·5% (w/w) — — —; 30·5% (w/w) ········; 40·0% (w/w) — · — · —; 53·0% (w/w) – ·· – ·· –.

Reference IR spectra of S(IV) oxospecies were obtained from 0·1 M solutions at pH 1 (Fig. 3(a)), pH 5·5 (Fig. 3(b)) and pH 9 (Fig. 3(c)). Thus, $SO_2.H_2O$ absorbs at 1151 cm$^{-1}$ (peak B, symmetric stretch) and 1331 cm$^{-1}$ (peak A, non-symmetric stretch) (Davis & Chatterjee, 1975), the weak feature at 1052 cm$^{-1}$ (peak C) possibly being due to a trace of $HSO_3^-$, in equilibrium with $SO_2.H_2O$. Solutions in which the predominating species is $HSO_3^-$ give peaks at 1210 cm$^{-1}$ (peak D, $S_2O_5^{2-}$, non-symmetric S–O stretch), 1054–1065 cm$^{-1}$ (peak E, $S_2O_5^{2-}$) and 1023 cm$^{-1}$ (peak F, $HSO_3^-$) (Herlinger & Long, 1969; Davis & Chatterjee, 1975) whilst $SO_3^{2-}$ gives a weak broad peak at 1098 cm$^{-1}$ (peak G, symmetric stretch) and an intense absorbance at 938 cm$^{-1}$ (peak H, non-symmetric stretch). Sulphate ion gives a single peak at 1100 cm$^{-1}$ (Fig. 3(d), non-symmetric stretch), the symmetric mode being only Raman-active. It can be seen that the solution of S(IV) at pH 5·5 shows no evidence of containing $SO_2.H_2O$ or $SO_3^{2-}$ ions. It is probably relatively free from $SO_4^{2-}$ ion because this absorbs at least twice as strongly as the S(IV) and there is no evidence of a shoulder on the high frequency side of the peak at 1054–1065 cm$^{-1}$ in Fig. 3(b).

When spectra were recorded from a 1 M solution of S(IV) at pH 5·5 an additional weak feature was seen at

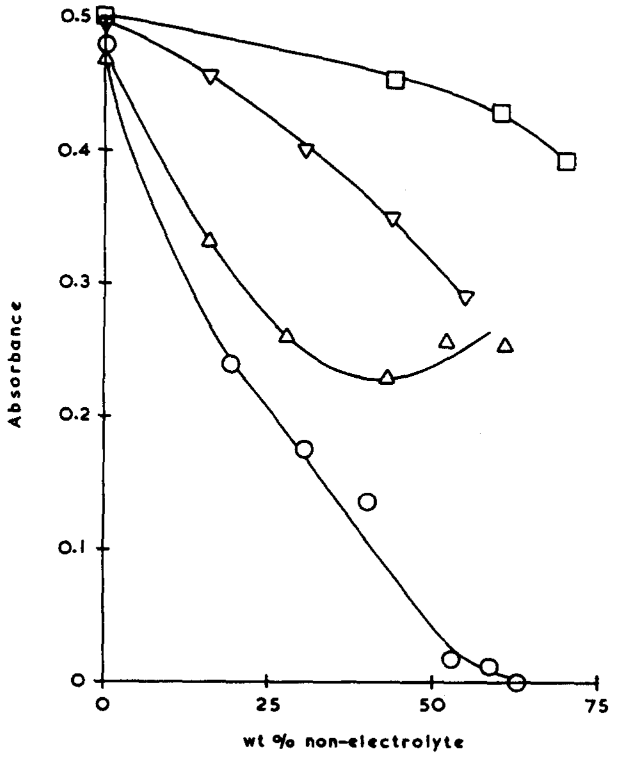
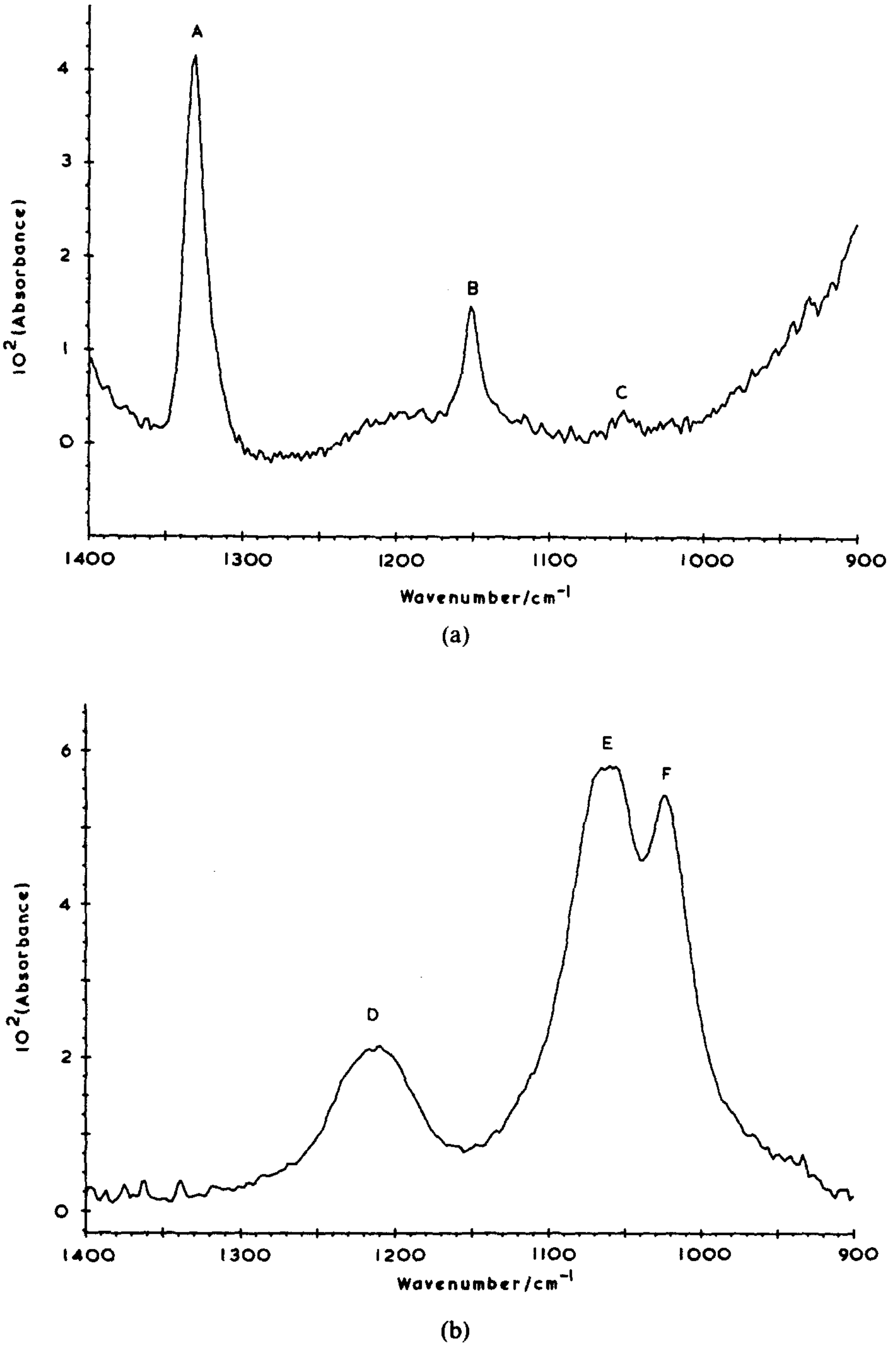


**Fig. 2.** Effect of non-electrolyte concentration on the absorbance of a 50 mM solution of $NaHSO_3$ at 255 nm. Polyethylene glycol (PEG 400) □; sucrose ▽; ethanol △; glycerol ○. The data for PEG 400 are displaced upwards by 0·05 absorbance units for clarity.

965 cm$^{-1}$ and the relative heights of the peaks at 1054–1065 and 1023 cm$^{-1}$ were slightly altered. A new broad and weak absorbance was also seen at *c.* 1160 cm$^{-1}$. Both new peaks are due to an increased concentration of $S_2O_5^{2-}$ deduced from previously reported assignments (Herlinger & Long, 1969; Davis & Chatterjee, 1975).

It was decided to investigate the effect of glycerol in the concentration range 0–30% (w/w) because this gives the greatest change in UV absorbance at 255 nm. The IR spectra of aqueous glycerol solutions are shown in Fig. 4. and illustrate that, with increasing glycerol concentration, one simply obtains scaled traces with no evidence of new features arising from changes in solute–solvent interactions. However, at the highest glycerol concentration, the absorbance is in the region of 1·0 and, therefore, the glycerol–water reference has a high absorbance compared with that of S(IV) species (Fig. 3); the main problem is that the absorbance maxima shown by the reference are in the region of interest. This was found to limit the concentration of glycerol used to 30% (w/w). The appropriate reference was subtracted (1:1) from samples containing S(IV) oxospecies to obtain spectra of the desired solutes and the success of removing this background was judged by the fact that a peak due to water at 1650 cm$^{-1}$ had disappeared



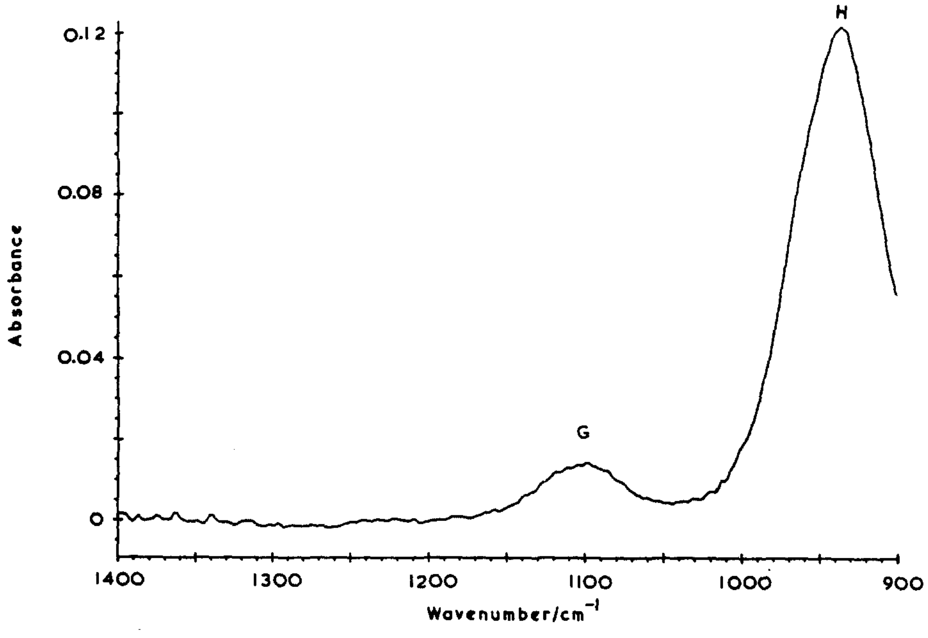
(b)

**Fig. 3.** FTIR spectra of 0·1 M solutions of S(IV) at various pH and 0·1 M $Na_2SO_4$: (a) pH 1; (b) pH 5·5.

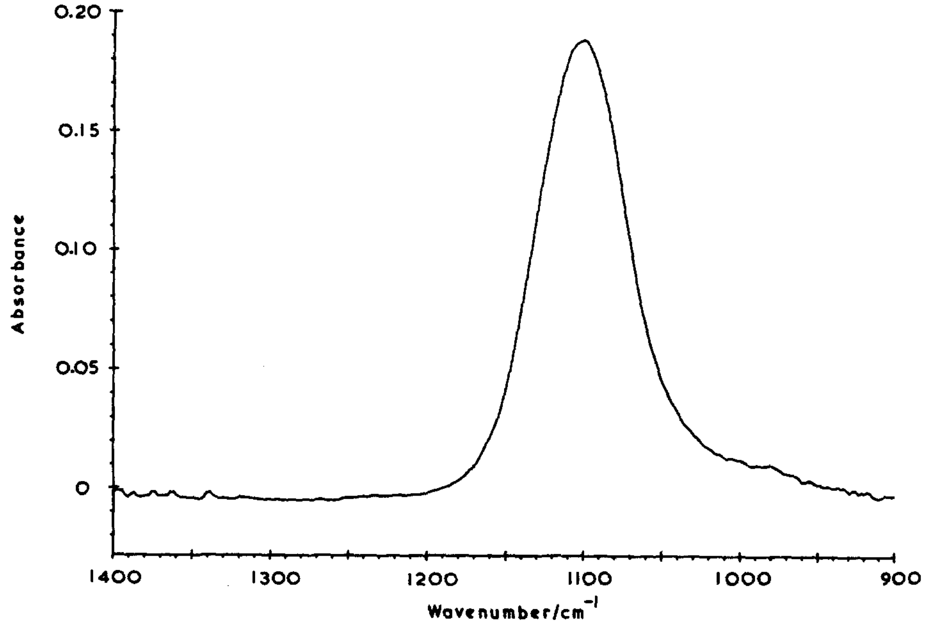
into the noise. There is no way of checking that the peaks due to glycerol had been fully subtracted. However, changing the ratio of reference to sample by ±10% did not introduce any new features into the spectra and only affected the relative heights of the resulting peaks in that region to a small extent.

Difference spectra for a constant concentration of S(IV) but a variable amount of glycerol are plotted in Fig. 5. Here, the comparison, in each case, is made with the sample dissolved in water and a positive peak denotes a higher absorbance in water than in water–glycerol mixtures. Thus, it can be seen that increase in glycerol content causes a marked increase in absorbance of the samples at 1000–1010 and 1095 cm$^{-1}$ (peaks I and J, respectively) and a decrease at 1052 and 1210 cm$^{-1}$ (peaks K and L, respectively). The changing intensity of peaks at 1052 and 1210 cm$^{-1}$ is a clear indication of a reduction in $S_2O_5^{2-}$ content with increase in glycerol content; the use of the peak at 1210 cm$^{-1}$ is particularly reliable as it is well removed from any prominent features of the water–glycerol spectra.

The position of the $HSO_3^-$ peak at 1022 cm$^{-1}$ in water is displaced slightly to 1018 cm$^{-1}$ as the glycerol content is increased to 30% (w/w), but the absorbance



(c)



(d)

**Fig. 3.** — *contd.*: (c) pH 9; (d) $Na_2SO_4$.

due to $HSO_3^-$ remains constant (0·48 and 0·49 in water and 30% (w/w) glycerol, respectively). The lack of effect of changing glycerol content on the $HSO_3^-$ peak is illustrated well in Fig. 5 where the spectrum crosses the baseline at this location for all solvent mixtures. The increasing absorbance due to peak I, with increasing glycerol content is therefore not due to an increasing concentration of $HSO_3^-$. Figure 6 shows that the absorbances due to peaks I. J and K are well correlated to those of peak L although the lines drawn do not pass through the origin. Perhaps, peaks I and J both represent new species formed from $S_2O_5^{2-}$ with increasing glycerol content. A weak feature at 1128 cm$^{-1}$ could, likewise, be related to $S_2O_5^{2-}$. The difference peak at 1095 cm$^{-1}$ (peak J) is too close to that for $SO_4^{2-}$ (1100 cm$^{-1}$) and errors in interpretation could

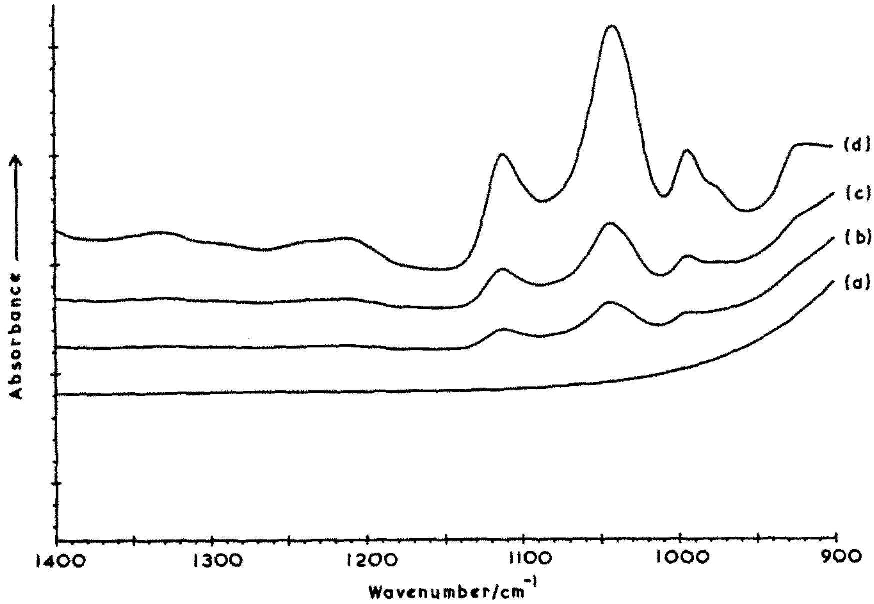


Fig. 4. FTIR spectra of water and water–glycerol mixtures: (a) water; (b) 5% (w/w) glycerol; (c) 10% (w/w) glycerol; (d) 30% (w/w) glycerol. Each division on the absorbance axis represents 0·01 absorbance units. Spectra have been displaced by arbitrary amounts along the absorbance axis for clarity.

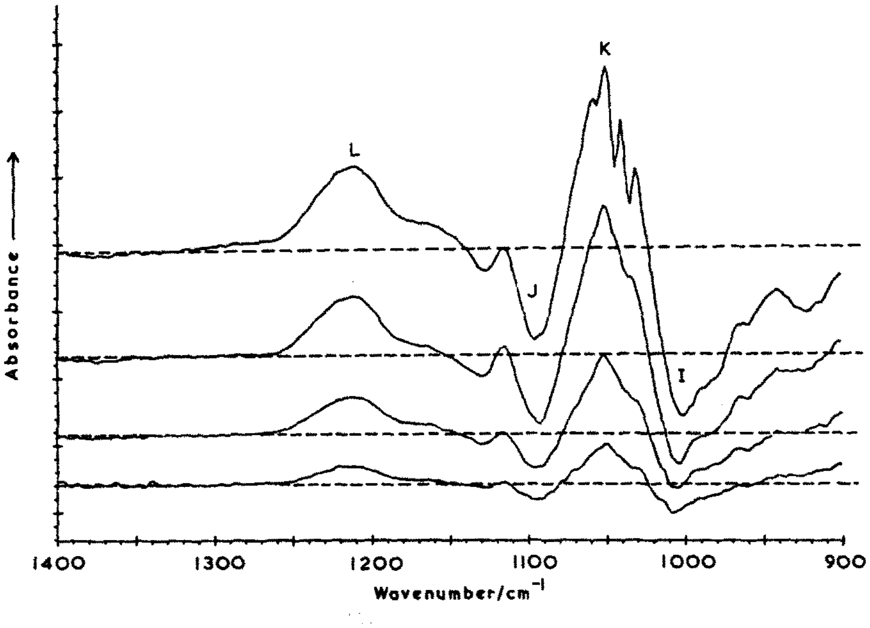


Fig. 5. Difference FTIR spectra of 1 M S(IV) in water and water–glycerol mixtures. A positive peak implies that the substance has a greater absorbance at a given wavenumber in water. Solvents: (a) 5% (w/w) glycerol; (b) 10% (w/w) glycerol; (c) 20% (w/w) glycerol; (d) 30% (w/w) glycerol. Each division on the absorbance axis represents 0·01 absorbance units. The broken line shows the baseline for each subtraction and baselines are shown displaced by arbitrary amounts along the absorbance axis.

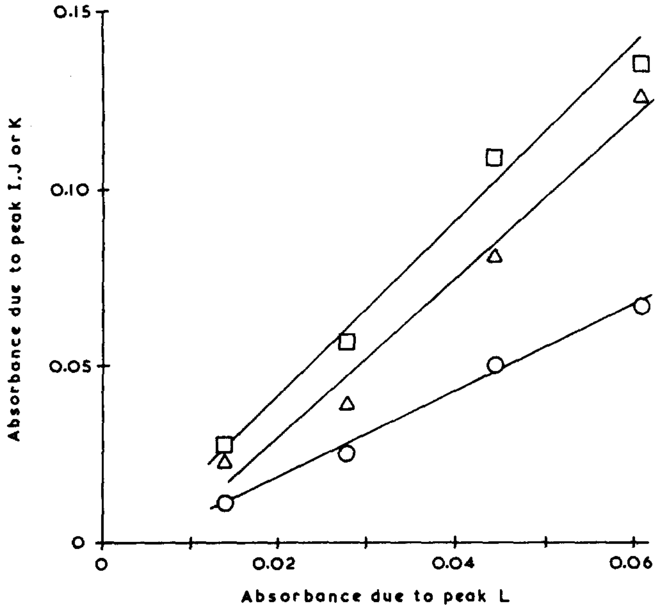


Fig. 6. Graphs of absorbance due to peaks I. J and K versus absorbance due to peak L in the difference spectra shown in Fig. 5. For each peak the absorbance is measured from the baseline and absolute values are plotted. Peak I versus peak L △; peak J versus peak L ○; peak K versus peak L □.

arise if samples were to contain small, but variable, amounts of $SO_4^{2-}$.

The Success of interpreting the difference spectra given in Fig. 5 rests with the validity of subtracting a glycerol–water reference from a glycerol–water–S(IV) sample, i.e. assuming that subtraction is perfect in all regions of the spectrum and not just where there is an isolated peak due to water at 1650 $cm^{-1}$. This must remain an assumption on which the results are conditional, though the correlations between absorbance of the peaks of interest add credence to this interpretation.

From the evidence presented here, the authors believe that addition of a non-electrolyte decreases the amount of $S_2O_5^{2-}$ present but does not change the concentration of $HSO_3^-$. In order to ascertain whether or not water activity is important in changing the UV absorbance of $S_2O_5^{2-}$, consider first the concentration of non-electrolyte required to reduce the UV absorbance due to $S_2O_5^{2-}$ by, say, 20%, i.e. 5% glycerol, 33% sucrose and 68% PEG 400. The corresponding $a_w$ = 0·99, 0·98 and 0·73 (Norrish, 1966; Sloan & Labuza, 1976; Chirifie & Fontan, 1980). Clearly, PEG 400 behaves differently from glycerol and sucrose. Secondly, consider the reduction in absorbance at $a_w$ = 0·92 (that corresponding to the most concentrated sucrose solution used). The absorbances of solutions containing the three non-electrolytes are reduced by 62, 41 and 10% respectively at this value of $a_w$. There exists, therefore, no correlation between water activity and the observed changes, and specific solute–solute or solute–solvent interactions are likely to be important.

Preliminary consideration should be given to other possible reasons for the observed changes in UV and IR spectra. The formation of $NaS_2O_5^-$ ion-pairs is likely. It is found that ion-pair formation leads to a reduction in UV absorbance due to $S_2O_3^{2-}$ (Thomas & Monk, 1956) and $SO_3^{2-}$ (Wedzicha & Goddard, 1991). Whereas ion-pairs between 1:1 electrolytes are highly dissociated in aqueous solution, those involving 2:1 electrolytes show significant stability which is increased on addition of water-miscible organic solvents. Thus, the formation constants of $NaS_2O_3^-$ and $KS_2O_3^-$ are increased by a factor of *c.* 30 on making the solvent 50% (v/v) ethanol (Thomas & Monk, 1956). The formation constant of $NaS_2O_3^-$ in this solvent is 143 $M^{-1}$.

If one incorporates ion-pair formation in the $HSO_3^-$–$S_2O_5^{2-}$ equilibrium, the overall behaviour will be given by at least three equations, i.e.

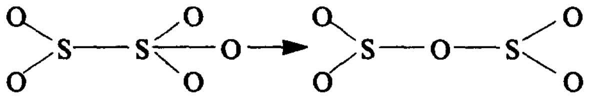
$$2\,HSO_3^- \rightleftharpoons S_2O_5^{2-} + H_2O \tag{1}$$

$$Na^+ + S_2O_5^{2-} \rightleftharpoons NaS_2O_5^- \tag{2}$$

$$Na^+ + HSO_3^- \rightleftharpoons NaHSO_3 \tag{3}$$

The formation of $NaS_2O_5^-$ would tend to reduce the activity of $S_2O_5^{2-}$ in solution and promote the 'condensation' of $HSO_3^-$, thereby causing a decrease in the concentration of $HSO_3^-$. This does not occur. The possibilities which would give rise to the observed effects include the fortuitous compensation for the formation of $NaS_2O_5^-$ by a combination of solvent effects on the reactions shown in eqs (1) and (3); the species which give rise to the new peaks observed in Fig. 5 could be speculated as one or more of the ion-pairs because their concentration would be related to the change in $S_2O_5^{2-}$ concentration.

An alternative speculation is that $S_2O_5^{2-}$ could undergo isomerisation on addition of non-electrolyte, as follows



the unsymmetrical structure being the accepted form in aqueous solution. Goodall (1984) consider that the symmetrical S—O—S bonded ion could exist in non-aqueous media to account for the facile autoxidation of S(IV) in such systems. However, this isomerisation has only been considered in anhydrous solvents and the formation of the symmetrical $S_2O_5^{2-}$ species in solvents with a high water content is a less likely possibility.

## CONCLUSIONS

The authors have presented evidence from IR and UV spectra which suggests that the addition of glycerol to a solution of $NaHSO_3$ tends to reduce the apparent concentration of $S_2O_5^{2-}$ in solution. The ion may be converted to another form and the concentration of $HSO_3^-$ is unaffected. The UV spectra of other non-electrolytes suggest that they behave similarly, the order of effectiveness in reducing the concentration of $S_2O_5^{2-}$ being PEG 400 < sucrose < ethanol < glycerol. It is suggested, therefore that, as the concentration of non-electrolyte is increased, e.g. during the dehydration of a sulphited fruit or vegetable where glucose or some other sugar could be the non-electrolyte, the predominating species remains as $HSO_3^-$. Any preservative which crystallises is the $S_2O_5^{2-}$ salt because either the solubility of the $HSO_3^-$ salt is exceeded and $S_2O_5^{2-}$ is formed during precipitation, or the solubility of traces of the $S_2O_5^{2-}$ salt is exceeded and this precipitates directly. The presence of water-miscible non-electrolytes could well make $S_2O_5^{2-}$ ions in solution less important in foods than judged from their formation in simple aqueous systems.

The possible formation of $NaS_2O_5^-$ ion-pairs suggests that one should re-examine published data for the spectroscopic measurement of the equilibrium constant for the $HSO_3^-$ – $S_2O_5^{2-}$ equilibrium and, in particular, the way the constant varies with concentration.

## ACKNOWLEDGEMENTS

The authors are grateful to the Agricultural and Food Research Council for a Research Studentship to I.B. and a Research Assistantship to S.J.G. The authors are particularly grateful to Ed Clarke, and his colleagues, of Nicolet Instruments, Warwick, for allowing them access to the FTIR instrument, for technical assistance and helpful discussion.

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