



The State of Sulphur Dioxide at High Concentration and Low Water Activity

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(Received 17 January 1990; revised version received and accepted 10 May 1990)

ABSTRACT

The apparent pK of HSO_3^- is lowered by the addition of salts ($NaCl$, $NaNO_3$, Na_2SO_4) but increased by addition of ethanol, glycerol or polyethylene glycol. Sucrose (0–60 wt%) has little or no effect. The pK of sulphurous acid is similarly affected by salts ($NaCl$, $NaNO_3$) but only ethanol and polyethylene glycol give rise to a substantial increase in value. The effect of salts can be modelled by the extended Debye-Huckel theory. In the case of the 1:1 electrolytes, graphs of pK versus ionic strength pass through minima; for sulphurous acid the pK in the presence of 3 M $NaCl$ is actually greater than that at zero ionic strength for this reason. The equilibrium constant for the formation of the ion-pair $NaSO_3^-$ is estimated to be of the order $6 M^{-1}$ and evidence is given for the formation of a weak complex between SO_2 and Cl^- .

The nucleophilic reactivity of sulphur(IV) oxospecies in equilibrium with HSO_3^- was assessed kinetically by measuring rates of reaction with malachite green. The data indicate that $S_2O_5^{2-}$ ion does not behave as a nucleophile in comparison with the nucleophilicity of SO_3^{2-} . The relevance of the results to the use of 'sulphur dioxide' as a preservative in concentrated foods and in the presence of humectants is considered.

INTRODUCTION

When used in the context of a food additive, the term 'sulphur dioxide' is generally taken to mean a mixture of oxospecies of sulphur in oxidation state IV; namely, SO_2 , HSO_3^- , SO_3^{2-} and $S_2O_5^{2-}$. The proportions of these

species present at equilibrium depend on pH, ionic strength and concentration.

Solutions of SO_2 in water behave as solutions of a dibasic acid with $\text{p}K_1 = 1.86$ (Ellis & Anderson, 1961; Huss & Eckert, 1977) and $\text{p}K_2 = 7.18$ (Tartar & Garretson, 1941) at 25°C and corrected to zero ionic strength. Values of $\text{p}K_1$ as low as 1.37 (Schroeter, 1966) and of $\text{p}K_2 = 6.25$ (Shapiro, 1977) have been reported at high ionic strength. A critical appraisal of the low value of $\text{p}K_2$ shows that it could include a contribution from the effect of salt on the response of the pH-measuring electrode and Wedzicha & Goddard (1988) find that in concentrated NaNO_3 solutions the value of $\text{p}K_2$ falls only to *c.* 6.8.

Hydrogen sulphite ion also exists in equilibrium with $\text{S}_2\text{O}_3^{2-}$ ion. This is normally considered to be derived by the elimination of a molecule of water from two HSO_3^- ions and an equilibrium constant for the reaction, in the presence of excess water, is given by:

$$K = [\text{S}_2\text{O}_3^{2-}]/[\text{HSO}_3^-]^2 \quad (1)$$

The most reliable values of K , as a function of ionic strength, I , are illustrated in Fig. 1 (Connick *et al.*, 1982), from measurements of the intensities of the

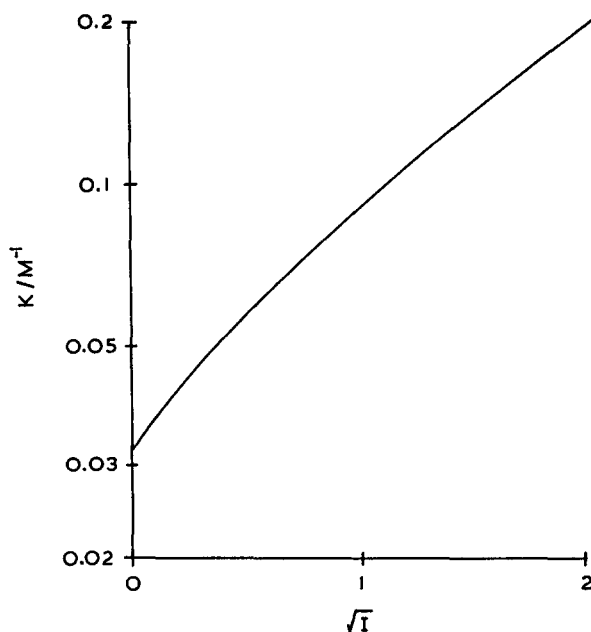


Fig. 1. Effect of ionic strength, I , on the equilibrium constant, K , at 25°C for the formation of $\text{S}_2\text{O}_3^{2-}$ from HSO_3^- , plotted as K versus \sqrt{I} . Solutions contained $[\text{HSO}_3^-] = 10\text{--}100 \text{ mM}$ and ionic strength was controlled by the addition of NaCl and NaClO_4 . Adapted from Fig. 2 of the paper by Connick *et al.* (1982).

Raman peak due to HSO_3^- and the UV absorbance due to $\text{S}_2\text{O}_5^{2-}$. Previously, Bourne *et al.* (1974) reported a value of 0.076 M^{-1} corrected to zero ionic strength from UV measurements alone but it seems as if the extinction coefficient of $\text{S}_2\text{O}_5^{2-}$ used in the calculation ($1980 \text{ M}^{-1} \text{ cm}^{-1}$ at 255 nm) is somewhat lower than that ($5790 \text{ M}^{-1} \text{ cm}^{-1}$) found in the more detailed work of Connick *et al.* (1982). It is evident that the value of K increases with ionic strength and, from the data shown in Fig. 1, the variation is described approximately by

$$K = 10^{(-1.398 + 0.35\sqrt{I})} \text{ M}^{-1} \quad (2)$$

at 25°C for $0.15 \text{ M} < I < 4 \text{ M}$ when I is varied by the addition of NaCl or NaClO_4 . If one takes a series of solutions of, say, sodium hydrogen sulphite, of concentration in the range $0.5\text{--}3.3 \text{ M}$, the percentage of HSO_3^- remaining in equilibrium with $\text{S}_2\text{O}_5^{2-}$ is found by application of the law of mass action to be as shown in Table 1. It is assumed that the equilibrium constant data

TABLE 1

Calculation of the Percentage (mol/mol) of HSO_3^- Remaining in Equilibrium with $\text{S}_2\text{O}_5^{2-}$, in a Solution Initially Consisting of Hydrogen Sulphite Ion of Concentration s .
 I is the Ionic Strength at Equilibrium

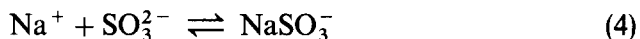
s/M	0.5	1.0	1.5	2.0	2.5	3.0	3.3
I/M	0.52	1.07	1.66	2.28	2.93	3.60	4.01
mole % HSO_3^-	93.7	86.3	78.9	72.0	65.7	60.1	57.0

when ionic strength is adjusted with NaCl and NaClO_4 are applicable to solutions in which the only contributors to ionic strength are sulphur(IV) oxoanions. Thus, we see that at high concentrations significant amounts of HSO_3^- may exist in the form of $\text{S}_2\text{O}_5^{2-}$; an even greater conversion is expected as water activity is reduced to such an extent that it is not possible to neglect the presence of water in the law of mass action expression, i.e.

$$K' = [\text{S}_2\text{O}_5^{2-}][\text{H}_2\text{O}]/[\text{HSO}_3^-]^2 \quad (3)$$

Much of the chemical reactivity of sulphur dioxide in food stems from the nucleophilicity of SO_3^{2-} (Wedzicha, 1984) and any interactions which affect the activity of this species are of interest. The structure of $\text{S}_2\text{O}_5^{2-}$ is that of an S—S bonded species where the lone pair responsible for the nucleophilic reactivity of SO_3^{2-} is used to form the inter-sulphur link. Conversion of HSO_3^- to $\text{S}_2\text{O}_5^{2-}$ reduces the concentration of the former in equilibrium with SO_3^{2-} . The question as to whether $\text{S}_2\text{O}_5^{2-}$ is capable of acting as a nucleophile is relevant and of some importance in dehydrated and partially dehydrated sulphited foods.

Another way in which the activity of sulphite ion may be reduced is through ion-pair formation with cations as illustrated here for Na^+ :



There is very little information regarding the values of dissociation constants of ion pairs involving SO_3^{2-} although NaSO_4^- and KSO_4^- ($\text{pK} = 0.72$ and 0.85 , respectively) and NaS_2O_3^- and KS_2O_3^- ($\text{pK} = 0.68$ and 0.92 , respectively) (Sillen, 1964) are well known. Thiosulphate ion appears to be the better model of the behaviour of SO_3^{2-} in solution (Wedzicha, 1984) and the pK values given above could well apply. The pK for KSO_3^- has been measured ($\text{pK} 0.51$, $I = 1.0\text{M}$, 25°C) (Young & Jencks, 1977).

In relatively acid solution, where significant concentrations of SO_2 are present, and in the presence of halide salts, nucleophilic addition of halide ion to SO_2 could lead to a reduction of SO_2 activity in concentrated systems. Thus, Br^- and I^- form weak complexes ($\text{pK} -0.66$ and -0.41 , respectively) (Salama & Wasif, 1975), SO_2Br^- and SO_2I^- , respectively, but there is yet no evidence of interaction with Cl^- .

This review of the literature shows that there exists a complex series of interacting ionic equilibria which determine the distribution of sulphur(IV) oxospecies in concentrated foods. This paper marks the start of a new and detailed investigation of the factors affecting the chemical reactivity of 'sulphur dioxide' in such systems and deals with the problems of reporting pK values, measurement of the activity of SO_3^{2-} , ion-pair formation and the nucleophilicity of $\text{S}_2\text{O}_5^{2-}$. Preliminary studies of the effect of ionic strength on the pK of HSO_3^- have already been published (Wedzicha & Goddard, 1988) and form the basis of the approach to pK measurements reported here.

MATERIALS AND METHODS

All reagents were of AnalaR grade with the exception of polyethylene glycol 400 (PEG-400) (Laboratory Grade) and malachite green (microscopy material), and were obtained from BDH Chemicals Ltd, Poole. Solutions of sulphur(IV) oxospecies contained 1 vol% ethanol to prevent oxidation and were standardised iodimetrically. Values of pK were obtained by pH titration at 30°C , monitoring the pH with a Jenway 3020 pH meter with a combined glass and calomel electrode. Solutions of SO_2 were prepared by bubbling the gas through water to give stock solutions in the range 45–75 mM. The pH-electrode response was corrected as described previously (Wedzicha & Goddard, 1988). Absorbance measurements were carried out using a Cecil CE292 digital spectrophotometer.

The nucleophilic reactivity of solutions of sulphur(IV) oxospecies was

assessed by measuring the rate of reaction with malachite green in a stop-flow kinetic apparatus (Hi-Tech Scientific SF51). Unbuffered solutions of sulphur(IV) oxospecies ($[S(IV)] = 0.01-4.0M$) were allowed to react with an equal volume of malachite green solution ($10\mu M$) at $30^\circ C$ and pseudo-first order rate constants calculated. The pH of the solutions of S(IV) diluted (1 + 1) with water and of reaction mixtures after the reaction had gone to completion was measured.

RESULTS AND DISCUSSION

Dissociation constant of HSO_3^-

The effect of addition of $NaNO_3$, $NaCl$ and Na_2SO_4 on the apparent pK of HSO_3^- is illustrated in Fig. 2 where equilibrium constants are defined in terms of concentrations and pK values have been corrected for the response of the pH meter electrode as described previously (Wedzicha & Goddard, 1988). It is seen that the ionic environment has a large effect on the value of the pK. Even the two 1:1 electrolytes ($NaNO_3$ and $NaCl$) show different behaviour, the greatest discrepancy between the salts being 0.2 units at c .

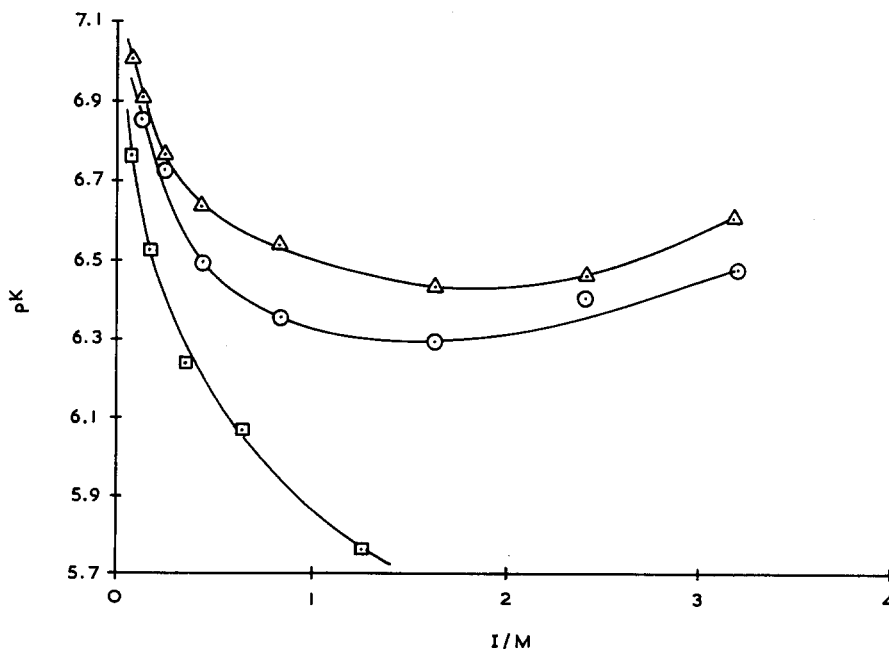


Fig. 2. Effect of ionic strength, I , on the pK of a 50 mM solution of HSO_3^- at $30^\circ C$. Ionic strength adjusted using \odot $NaCl$, \triangle $NaNO_3$, \square Na_2SO_4 .

1.2M salt. The effect of Na_2SO_4 is much greater. The value of the pK in terms of activities pK(a) is related to that in terms of concentrations by

$$\text{pK} = \text{pK(a)} + \log y_{\text{SO}_3^-} - \log y_{\text{HSO}_3^-} + \log y_{\text{H}^+} \quad (5)$$

where y denotes activity coefficients. Application of the Debye-Huckel theory and use of constants for 30°C , gives

$$\text{pK(a)} = \text{pK} + 1.56\sqrt{I}/(1 + \sqrt{I}) - \log y_{\text{H}^+} \quad (6)$$

Unfortunately, it is not possible to reliably predict y_{H^+} and values of the mean ionic activity coefficients of H^+Cl^- , H^+NO_3^- and $(\text{H}^+)_2\text{SO}_4^{2-}$ (Robinson & Stokes, 1965) were used instead. Calculated values of pK(a) for HSO_3^- in the presence of the three salts are as shown in Table 2. These results

TABLE 2

Calculated Values of the pK of HSO_3^- at Zero Ionic Strength Obtained from Data for Apparent pK Values in the Presence of NaCl , NaNO_3 and Na_2SO_4 at the Ionic Strengths, I , shown

I/M	0.08	0.12	0.24	0.43	0.83	1.63	2.41	3.19
NaCl	7.44	7.36	7.36	7.25	7.21	7.21	7.31	7.34
NaNO_3	7.45	7.42	7.41	7.40	7.43	7.43	7.49	7.64
I/M	0.08	0.17	0.35	0.64	1.25			
Na_2SO_4	7.60	7.51	7.42	7.44	7.35			

are remarkably constant as ionic strength is varied over a wide range and it is evident from application of eqn (6) that the main reason for the difference in the effects of the three salts rests on the way in which the mean ionic activity coefficients of the corresponding acids change with I . There is no need, therefore, to postulate specific interactions between HSO_3^- or SO_3^{2-} and the three anions in question, which is reassuring in view of the expected mutual repulsion between the species. The mean value of all the data is 7.40 ± 0.11 . Whilst it is greater than the published value of 7.18, the latter was obtained using dilute solutions and the agreement with the present results is most encouraging. It implies that the procedure for correcting for electrode response and the trends illustrated in Fig. 2 are likely to be reliable, at least to a first approximation.

It is pertinent to consider whether any interaction between SO_3^{2-} and Na^+ could contribute to the effect of salts on the pK of HSO_3^- . The near UV spectrum of SO_3^{2-} shows no peak but the extinction coefficient decreases with increasing wavelength (Hayon *et al.*, 1972). It was found that an increase in the concentration of Na_2SO_3 or the addition of NaCl to a solution of Na_2SO_3 caused a decrease in this absorbance at all wavelengths as

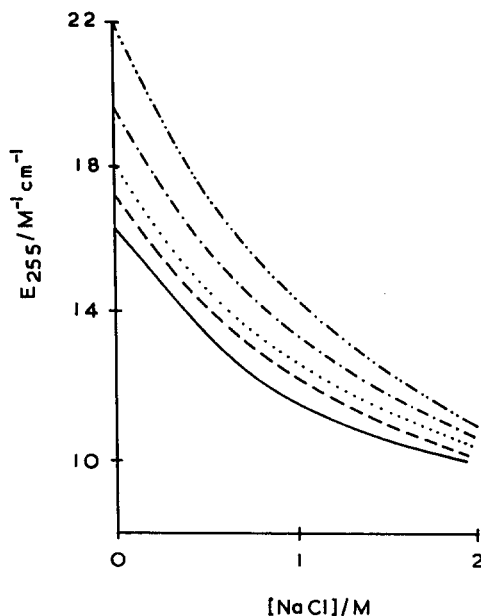


Fig. 3. Effect of concentration of Na_2SO_3 and added NaCl on the apparent extinction coefficient of SO_3^{2-} at 255 nm, E_{255} , and 30°C . $[\text{Na}_2\text{SO}_3] = 10 \text{ mM}$ ———, 30 mM ————; 50 mM; 70 mM - - - -; 90 mM ———.

illustrated for 255 nm in Fig. 3. This wavelength was chosen arbitrarily but is one at which the absorbance due to HSO_3^- is negligible. Let us assume that the change in absorbance is indicative of formation of a complex between the cation and SO_3^{2-} and that this takes the form of an ion-pair. A reasonable starting value for the equilibrium constant, K_0 , for its formation is that (4.8 M^{-1} , 25°C , $I = 0$) reported by Denney & Monk (1951) for the ion-pair NaS_2O_3^- . To a first approximation, the value of this equilibrium constant varies with ionic strength according to

$$K = K_0 y_{\text{Na}_2\text{SO}_3} \quad (7)$$

where $y_{\text{Na}_2\text{SO}_3}$ is the mean ionic activity coefficient of Na_2SO_3 at a given ionic strength. This is tabulated by Goldberg (1981). If, at any wavelength, the observed absorbance is the sum of absorbances due to SO_3^{2-} and NaSO_3^- , the apparent extinction coefficient, E_{app} (obtained by dividing absorbance by $[\text{S(IV)}]$, where $[\text{S(IV)}] = [\text{SO}_3^{2-}] + [\text{NaSO}_3^-]$) is related to the extinction coefficients of SO_3^{2-} and NaSO_3^- , $E_{\text{SO}_3^{2-}}$ and $E_{\text{NaSO}_3^-}$ respectively, by

$$E_{\text{app}} = E_{\text{SO}_3^{2-}} + [\text{NaSO}_3^-] (E_{\text{NaSO}_3^-} - E_{\text{SO}_3^{2-}}) / [\text{S(IV)}] \quad (8)$$

For a series of solutions of Na_2SO_3 with $[\text{S(IV)}] = 0.01\text{--}1.0 \text{ M}$, $[\text{NaSO}_3^-]$ was calculated using values of K predicted by eqn (7) with $K_0 = 3.8 \text{ M}^{-1}$. A plot

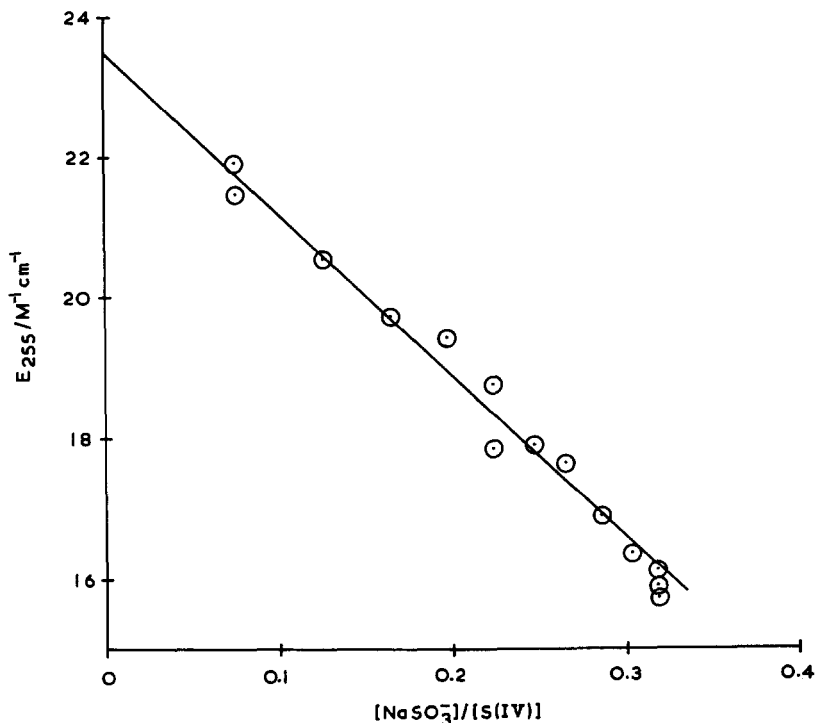


Fig. 4. Graph of apparent extinction coefficient at 255 nm, E_{255} , versus $[\text{NaSO}_3^-]/[\text{S(IV)}]$ where $[\text{NaSO}_3^-]$ was calculated assuming a formation constant of 6 M^{-1} ($I=0$) and $[\text{S(IV)}] = [\text{SO}_3^{2-}] + [\text{NaSO}_3^-]$. Raw spectrophotometric data were obtained by measurement of absorbance of solutions of Na_2SO_3 (0.01–1.0 M) at 30°C .

of E_{app} versus $[\text{NaSO}_3^-]/[\text{S(IV)}]$, for measurements made at 255 nm and using $K_0 = 6 \text{ M}^{-1}$ is shown in Fig. 4. The linear behaviour confirms that the ion association model is sensible. It is found that the plots obtained using $K_0 = 3\text{--}5 \text{ M}^{-1}$ are also linear but values of $E_{\text{NaSO}_3^-}$ are negative, and the values of K_0 are, therefore, unacceptable. Plots with $K_0 = 7\text{--}8 \text{ M}^{-1}$ become progressively nonlinear with increase in K_0 and it is suggested that the best value of K_0 is in the region of 6 M^{-1} . The data plotted in Fig. 4 give $E_{\text{NaSO}_3^-} = 0.0$ and $E_{\text{SO}_3^{2-}} = 23.5 \text{ M}^{-1}$. Similar behaviour was observed when data at 265 nm were analysed. The implication of the results obtained is that the percentage conversion of SO_3^{2-} to NaSO_3^- varies with $[\text{S(IV)}]$ as shown in Table 3. Significant concentrations of ion pair are to be expected in concentrated systems.

It was of interest to investigate the effects on pK value of nonelectrolytes, which are the components of foods often determining water activity. Here, the effects of ethanol, glycerol, polyethylene glycol PEG-400 and sucrose were considered. There are few data on the activity of strong acids such as

TABLE 3

Calculation of the Percentage Conversion (mol/mol) of Sulphite Ion to the Ion Pair NaSO_3^- in a Solution of Sodium Sulphite whose Total S(IV)-Concentration is in the Range 0.01–1.00 M

[S(IV)]/M	0.01	0.02	0.03	0.04	0.05	0.10	0.25	0.50	1.00
mole % NaSO_3^-	8	13	17	20	22	32	46	56	66

HCl in these media and it is not possible to make precise predictions of the effects of these solutes on the response of the pH electrode. Table 4 shows mean ionic activity coefficients of 0.01 molal HCl in various ethanol–water mixtures and the predicted and measured pH of such solutions. It is seen that the effect of ethanol on electrode response is small but the data were used to correct the electrode response as described previously for salt solutions (Wedzicha & Goddard, 1988). There are no published activity coefficients of HCl in the presence of the other solutes. Table 5 lists the measured pH of 10 mM HCl in aqueous solutions of ethanol, glycerol and PEG-400. Whilst pH values in PEG-400 are similar to those in ethanol, those in glycerol and sucrose are somewhat lower but there is no straight-forward way of distinguishing the effects of the solute on hydrogen ion activity from the effect of solute on the response of the electrode. In view of the relatively small scale of any effect, to a first approximation, it will be assumed that glycerol, PEG-400 and sucrose, at the concentrations used, have no effect on electrode performance. This is reasonable when one considers the fact that the theory of ion association in such mixed solvents is still poorly understood.

The effect of the nonelectrolytes on the pK of a 50 mM solution of NaHSO_3^- is illustrated in Fig. 5 for ethanol, glycerol, PEG-400 and sucrose.

TABLE 4

Mean Ionic Molal Activity Coefficient, γ_{\pm} , of 0.01 Molal HCl in Mixtures of Ethanol and Water. The Predicted pH Value was Calculated from the Concentration of HCl and γ_{\pm} ; the Measured pH Value was obtained during the Present Investigation. Literature sources: a, Robinson & Stokes (1965); b, Sankar *et al.* (1979); c, Longhi *et al.* (1988)

Ethanol content wt%	γ_{\pm} for HCl	pH predicted	pH measured	Literature source
0	0.912	2.04	2.06	a
10	0.894	2.05	2.06	b
20	0.887	2.05	2.07	b
40	0.851	2.07	2.15	b
70	0.771	2.11	2.21	c

TABLE 5
Measured pH of Solutions of 10 mM HCl in Aqueous Solutions of
Ethanol, PEG-400, Glycerol and Sucrose at 30°C

(a)

<i>Ethanol-content</i> wt%	<i>pH with</i> <i>ethanol</i>	<i>PEG-400</i> <i>content wt%</i>	<i>pH with</i> <i>PEG-400</i>
8	2.06	11	2.05
16	2.07	22	2.09
25	2.11	32	2.13
34	2.15	42	2.18
43	2.19	50	2.22
52	2.19	60	2.24
63	2.21	69	2.24
74	2.19		

(b)

<i>Sucrose content</i> wt%	<i>pH with</i> <i>sucrose</i>	<i>Glycerol content</i> wt%	<i>pH with</i> <i>glycerol</i>
16	1.99	10	1.98
30	1.90	20	1.93
43	1.80	31	1.88
55	1.70	42	1.83
66	1.61		

In the case of sucrose the change is no greater than the effect of sucrose on the pH of a solution of HCl. The increase in pK in the presence of ethanol, glycerol and PEG-400 could be due to the lower water activity environment favouring the formation of HSO_3^- as a result of less efficient solvation of the more highly charged SO_3^{2-} . However, a contribution from the formation of $\text{S}_2\text{O}_5^{2-}$ is likely because further addition of, say, ethanol leads to the precipitation of $\text{Na}_2\text{S}_2\text{O}_5$ and it is reasonable to imagine that the extent of association of HSO_3^- ions gradually increases with addition of solvent until the solubility of the salt is exceeded.

Dissociation constant of 'sulphurous acid'

Solutions of SO_2 in water are normally regarded as the dibasic 'sulphurous acid' but there is no evidence of significant amounts of H_2SO_3 actually being formed (Wedzicha, 1984). Conventionally, aqueous solutions of SO_2 are formulated $\text{SO}_2 \cdot \text{H}_2\text{O}$. This is a relatively strong acid and it is necessary to include the self-ionisation of $\text{SO}_2 \cdot \text{H}_2\text{O}$ in the formulation of the pH-

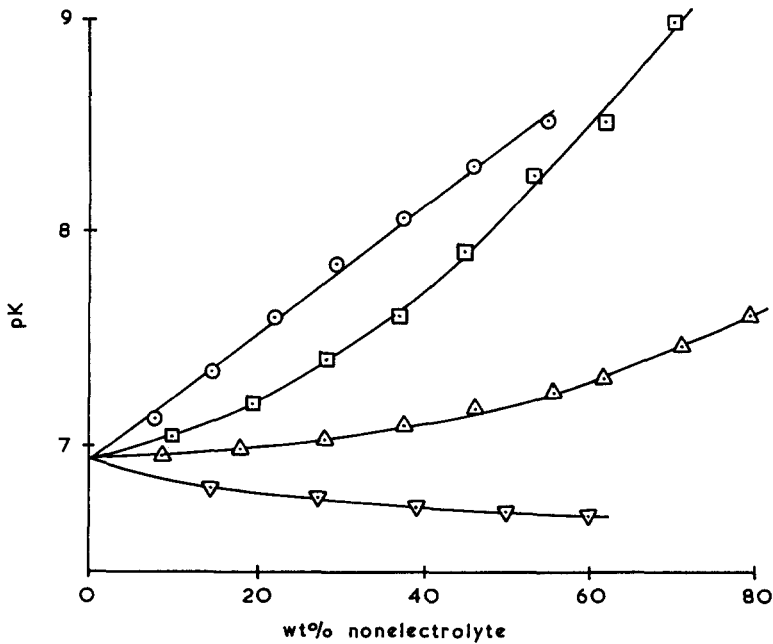
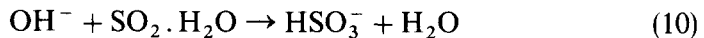
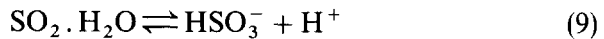


Fig. 5. Effect of concentration of nonelectrolyte on the pK of a 50 mM solution of NaHSO_3 at 30°C . \odot Ethanol; \triangle Glycerol; \square PEG-400; ∇ Sucrose.

titration curve used to determine the pK. Thus, during titration, HSO_3^- is derived from the following two reactions:



If a is the initial concentration of $\text{SO}_2 \cdot \text{H}_2\text{O}$, x the concentration of H^+ present at equilibrium when an amount of OH^- equivalent to a concentration b , has been added, the equilibrium concentrations of $\text{SO}_2 \cdot \text{H}_2\text{O}$ and HSO_3^- are $a - b - x$ and $b + x$, respectively. At half neutralisation $b = a/2$ and the value of the dissociation constant, K , of $\text{SO}_2 \cdot \text{H}_2\text{O}$ is, therefore, related to the corresponding hydrogen ion concentration by:

$$K = x(x + a/2)/(a/2 - x) \quad (11)$$

Values of pK, corrected for electrode response, in the presence of NaCl and NaNO_3 are illustrated in Fig. 6 whilst the corrected effect of ethanol, and uncorrected effects of glycerol, PEG-400 and sucrose are given in Fig. 7. Thus, sucrose and glycerol show little or no effect. Application of the Debye-Huckel theory to the measurements in salt solution gives a mean value of 1.86 ± 0.11 for pK(a) which agrees with that reported by Huss & Eckert

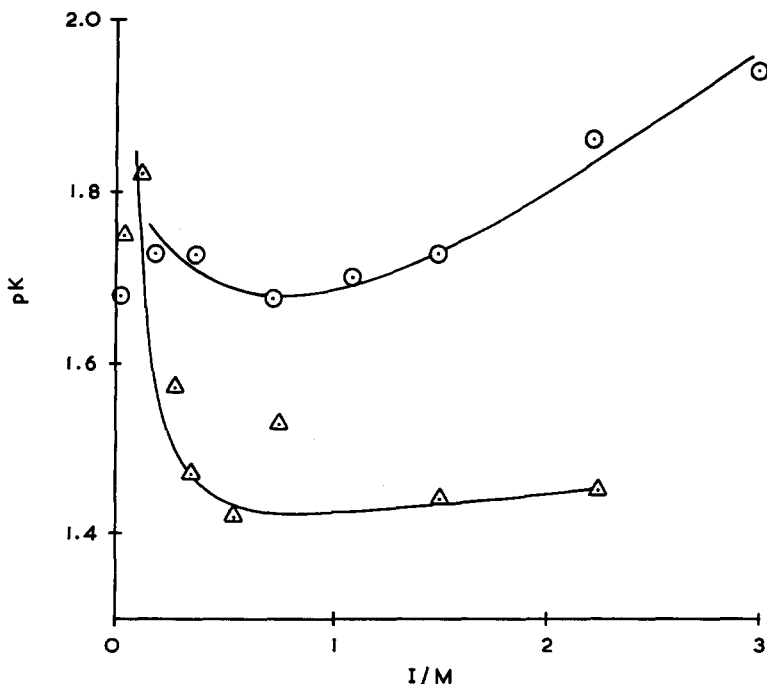


Fig. 6. Effect of ionic strength, I , on the pK of a 75 mM solution of $SO_2 \cdot H_2O$ at $30^\circ C$. Ionic strength adjusted using \odot NaCl; \triangle $NaNO_3$.

(1977). The reason why the two salts change the pK value to different extents is the same as for the pK of HSO_3^- ; that is, because of the differing mean ionic activity coefficients of H^+Cl^- and $H^+NO_3^-$, particularly at high ionic strengths. There is, however, evidence that Cl^- is involved in a specific interaction with SO_2 . Figure 8 shows the effect on the UV spectrum of $SO_2 \cdot H_2O$ of the addition of NaCl (1.0–4.0M) and a marked increase in absorbance (λ_{max} for $SO_2 \cdot H_2O$ is 277 nm (Huss & Eckert, 1977)) is accompanied by a small shift in λ_{max} to longer wavelength (283 nm). The concentration of $SO_2 \cdot H_2O$ at a given pH is:

$$[SO_2 \cdot H_2O] = [S(IV)]10^{-(pH - pK)} / (1 + 10^{-(pH - pK)}) \quad (12)$$

where $[S(IV)] = [SO_2 \cdot H_2O] + [HSO_3^-]$ and the concentration of SO_3^{2-} is negligible. Using the pK values plotted in Fig. 6 to calculate the concentration of $SO_2 \cdot H_2O$, apparent extinction coefficients at 283 nm are found to vary with NaCl concentration as shown in Table 6. The relationship between the two is linear. If one assumes that a 1:1 complex is formed between SO_2 and Cl^- , its concentration as a function of $[SO_2]$ and $[Cl^-]$, when $[Cl^-] \gg [SO_2]$, is given by:

$$[\text{complex}] = [Cl^-][SO_2] / ([Cl^-] + K) \quad (13)$$

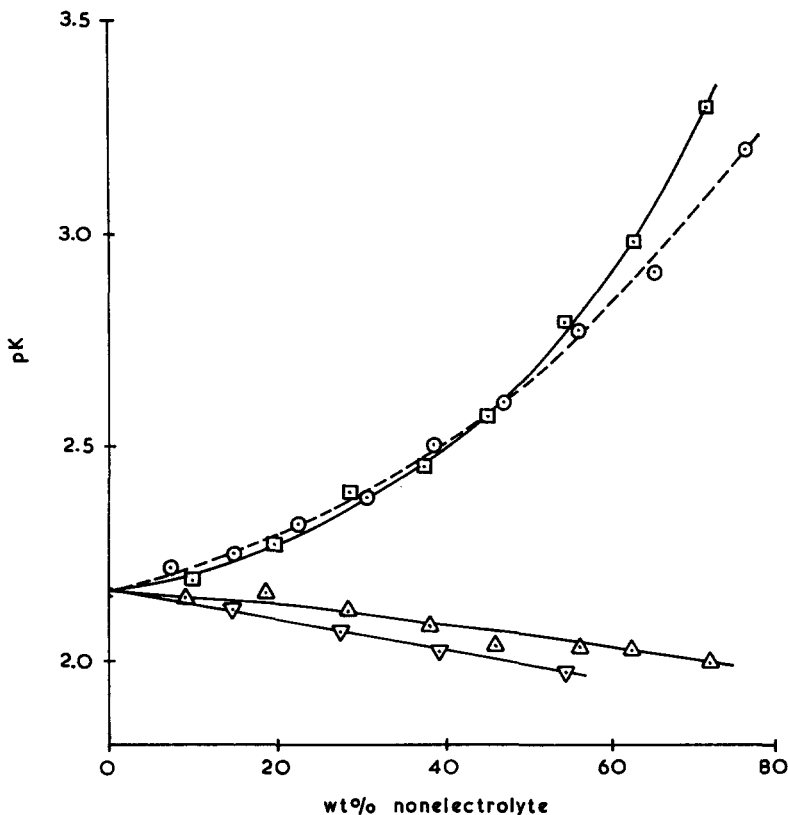


Fig. 7. Effect of concentration of nonelectrolyte on the pK of a 45 mM solution of $\text{SO}_2 \cdot \text{H}_2\text{O}$ at 30°C. \odot Ethanol; \triangle Glycerol; \square PEG-400; ∇ Sucrose.

where K is the dissociation constant. If the absorbance at 283 nm is the sum of absorbances due to $\text{SO}_2 \cdot \text{H}_2\text{O}$ and the complex, a linear relationship between apparent extinction coefficient and $[\text{NaCl}]$ can be obtained if $K \gg [\text{Cl}^-]$. Since the relationship is linear even to $[\text{NaCl}] = 4.0\text{M}$, the value of K must be well in excess of 4M. No significant contribution from such a complex to acid dissociation behaviour of $\text{SO}_2 \cdot \text{H}_2\text{O}$ is expected.

The ability of ethanol and PEG-400 to markedly increase the pK is consistent with the tendency for the nonionic $\text{SO}_2 \cdot \text{H}_2\text{O}$ to be the

TABLE 6
Apparent Extinction Coefficient of $\text{SO}_2 \cdot \text{H}_2\text{O}$ at 283 nm in Solutions of NaCl at the Concentrations Shown

$[\text{NaCl}]/\text{M}$	1.0	1.5	2.0	3.0	4.0
$E_{283}/\text{M}^{-1} \text{ cm}^{-1}$	690	800	950	1 230	1 450

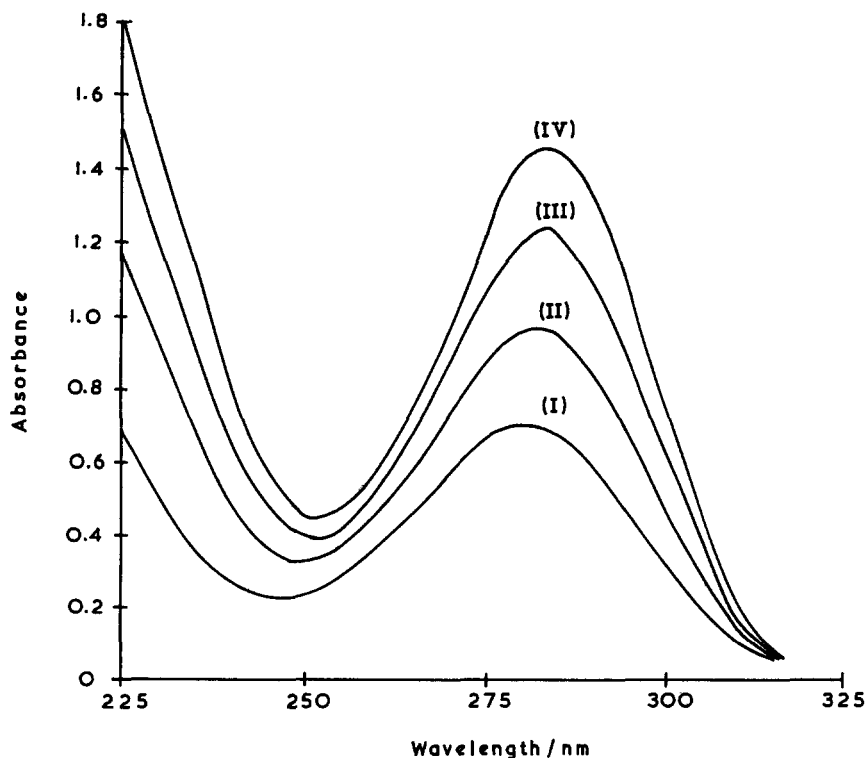


Fig. 8. Effect on UV spectrum of addition of NaCl (1.0–4.0M) to a 1 mM solution of $\text{SO}_2 \cdot \text{H}_2\text{O}$, at 30°C . $[\text{NaCl}] = 1.0\text{M}$, (I); 2.0M , (II); 3.0M , (III); 4.0M , (IV).

energetically more favourable species as the environment becomes less polar. There is no explanation for the effect of glycerol.

Kinetic measurements

Malachite green is a triphenylmethyl dye which exists as a carbocation, the positive charge being delocalised over the three rings. The dye is rapidly bleached by sulphite ion as a result of a simple, second order, nucleophilic addition reaction to the central carbon atom. The kinetics of the reaction were followed with $[\text{SO}_3^{2-}] = 0.3\text{--}330\text{ mM}$ and $[\text{dye}] = 5\ \mu\text{M}$ so that in all cases a pseudo-first order reaction may be observed. Thus, the pseudo-first order rate constant, k_1 , is related to the activity of sulphite ion by:

$$k_1 = k_2 a_{\text{SO}_3^{2-}} \quad (14)$$

where k_2 is a second order rate constant. When expressed in this way the rate constants are independent of pH. The object of the kinetic experiments was to establish whether or not $\text{S}_2\text{O}_5^{2-}$ ion showed any nucleophilic reactivity.

Their design was to prepare solutions of known initial HSO_3^- and SO_3^{2-} ion concentrations, such that the concentration of the latter was relatively small, and to measure the pseudo-first order rate constants as a function of these concentrations. Thus, using published activity coefficient data for Na_2SO_3 (Goldberg, 1981) it should be possible to calculate the second order rate constant and see if there is any relationship to the calculated concentration of $\text{S}_2\text{O}_5^{2-}$. To obtain $\text{HSO}_3^-/\text{SO}_3^{2-}$ mixtures, a solution of NaHSO_3 was titrated with NaOH and the SO_3^{2-} concentration calculated from the amount of NaOH added, neglecting any contribution from self-ionisation of HSO_3^- . The pH of reaction mixtures was in the range 5.52–5.63. Figure 9 illustrates the variation of k_1 with activity of SO_3^{2-} showing excellent first order behaviour. During the course of these experiments the concentration

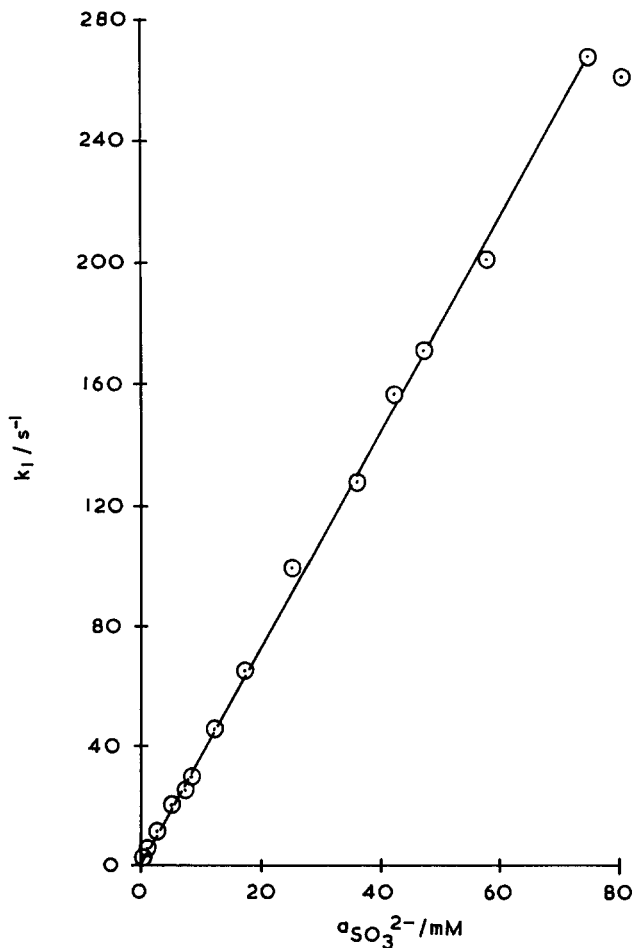


Fig. 9. Variation of pseudo-first order rate constant, k_1 , for the reaction of malachite green with SO_3^{2-} , with activity of sulphite ion, $a_{\text{SO}_3^{2-}}$, at 25°C.

of S(IV) present as species other than SO_3^{2-} increased from 4.7 mM to 1.69M. Initially, this was present as HSO_3^- , some of which is converted to $\text{S}_2\text{O}_5^{2-}$ as expected in the introduction. The relationship between the extent of conversion of HSO_3^- to $\text{S}_2\text{O}_5^{2-}$, and HSO_3^- concentration, is nonlinear and, at the highest initial concentration of HSO_3^- used here, the extent of conversion will be some 24%. Thus, the highest concentration of $\text{S}_2\text{O}_5^{2-}$, 0.41M, is somewhat greater than the accompanying activity of SO_3^{2-} and the fact that Fig. 9 is linear over the wide range of concentrations used indicates that $\text{S}_2\text{O}_5^{2-}$ makes no significant contribution to the kinetics.

CONCLUSIONS

The possible consequences of the effects of ionic strength or concentration on the distribution of sulphur(IV) oxospecies in partially dehydrated and dehydrated foods have been speculated upon (Wedzicha, 1987). Results reported here suggest that salts tend to reduce the pK and thereby cause a greater concentration of SO_3^{2-} to be present. Thus the nucleophilic reactivity of the preservative will increase. Nonelectrolytes have either no effect (as illustrated by sucrose) or tend to increase the pK (as illustrated by ethanol, glycerol and PEG-400). Thus, for example, if one has a mixture of NaHSO_3 , ethanol and NaCl in water, it is likely that at high ethanol content the large effect of ethanol will predominate and the tendency will be for the concentration of SO_3^{2-} to decrease. At low water activities one expects the species to be dominated by $\text{S}_2\text{O}_5^{2-}$ which have shown to have no significant nucleophilic reactivity compared to SO_3^{2-} . This species, itself, will not, for example prevent Maillard browning or form hydroxysulphonates with carbonyl compounds. Instead, it acts as a reservoir of preservative which is in equilibrium with HSO_3^- and a small concentration of SO_3^{2-} . The current understanding of the mechanism of the inhibition of Maillard browning by sulphur(IV) oxospecies is that the additive is involved in a zero order reaction with colour-forming intermediates (Wedzicha, 1987). Provided that the concentration of SO_3^{2-} does not fall to such an extent that it becomes rate-limiting, the apparent raising of pK by nonelectrolyte, and the conversion of HSO_3^- to $\text{S}_2\text{O}_5^{2-}$ are not likely to be significant to the inhibition of browning. The possible involvement of these species as catalysts of the Maillard reaction (Wedzicha & Vakalis, 1988) has yet to be considered and could be important. The data reported here relate to a wide range of water activities, the minimum values for the most concentrated glycerol, PEG-400 and sucrose solutions used being 0.47, 0.71 and 0.90, respectively (Norrish, 1966; Chirifie & Fontan, 1980; Sloan & Labuza, 1976). Such water activities are found in dehydrated and partially dehydrated

foods and the data therefore relate to the state of S(IV) during the course of food dehydration and in some finished products, e.g. dehydrated fruits. It is clear that water activity is not the variable which determines the pK values measured in the presence of the nonelectrolytes. Thus, for example, at nonelectrolyte concentrations corresponding to a water activity of 0.9, the measured pK values of HSO_3^- are 7.18, 8.30 and 6.66 for glycerol, PEG-400 and sucrose, respectively. The result depends very much on the nature of the non-electrolyte and our data are, perhaps, more indicative of the problems encountered when specifying the state of S(IV) in concentrated foods rather than providing a complete solution.

The effects of electrolytes and nonelectrolytes on the pK of 'sulphurous acid' are relevant to acid foods treated with the preservative. With ethanol and PEG-400 there is a tendency for the solute to encourage the formation, at a given pH, of larger amounts of sulphurous acid than expected from existing pK values in water. In wines it is unlikely that the increase in pK will be greater than 0.2 units, though it should be appreciated that even such a small change represents an increase in the ratio $[\text{SO}_2 \cdot \text{H}_2\text{O}]/\text{HSO}_3^-$ by 58%. Thus, one of the effects of the presence of ethanol could be to increase the antimicrobial activity of the preservative by increasing the concentration of the active constituent.

ACKNOWLEDGEMENT

We acknowledge generous support from the Agricultural and Food Research Council for a Research Assistantship to one of us (S.J.G.).

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