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# The effects of ions and non-electrolytes on equilibria involving sulphur (IV) oxospecies in solution

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Salts of Li, Na, K and Cs are used to demonstrate and explain the effects of solute–solute interactions on the acid dissociation of 'sulphurous acid', $SO_2.H_2O$, and the conversion of $HSO_3^-$ to $S_2O_5^{2-}$. Ion-pair interactions involving the cations and $SO_3^{2-}$ and $S_2O_5^{2-}$ are identified spectrophotometrically, and are shown to perturb the generally accepted equilibria involving these oxospecies in solution. The effects of ion-pairing are greater in water–non-electrolyte mixtures. $SO_2$–halide ion interactions tend to increase the $pK_1$ of $SO_2.H_2O$.

## INTRODUCTION

The dissolution of gaseous sulphur dioxide in water results in a mixture of $SO_2.H_2O$, $HSO_3^-$, $SO_3^{2-}$ and $S_2O_5^{2-}$, which will be referred to here, collectively, as sulphur(IV) oxospecies, S(IV). The concentration of each species present in solution depends on pH, temperature, ionic strength and concentration. Sulphur(IV) oxospecies are added to a wide range of foods and beverages in order to prevent enzymic and non-enzymic browning and because of their ability to act as antimicrobial agents. The compositions of the foods to which the preservative is added vary greatly in the nature and concentration of the constituents, from dilute squash-type drinks to dehydrated vegetables. Many of the reactions which S(IV) undergo involve nucleophilic attack by $SO_3^{2-}$; this and other S(IV) species such as $S_2O_5^{2-}$ may also act as acid–base catalysts of reactions involving food components (Wedzicha, 1987; Davies & Wedzicha, 1992; Wedzicha & Allen, 1994). It is, therefore, desirable to know the concentration of the reactive S(IV) species in different food environments.

This work continues the investigation of the effects of ionic strength and non-electrolyte concentration on the pK values of $SO_2.H_2O$ and $HSO_3^-$ and the UV spectral characteristics of S(IV) to measure ion-pair interactions and the formation of $S_2O_5^{2-}$. Whilst the most important simple cations in food are $Na^+$ and $K^+$, the investigation includes the demonstration of the effects of $Cs^+$ and $Li^+$ to determine the specific nature of alkali–metal ion–S(IV) interactions. Similarly, $Cl^-$ is likely to be the most significant anion amongst many organic and inorganic anions. The type of specific anion–S(IV) interaction may be determined by compar-

ing the behaviour of species such as $Cl^-$, $Br^-$, $I^-$, $NO_3^-$ and $SO_4^{2-}$, whose properties in aqueous solution are well understood.

## MATERIALS AND METHODS

All reagents were of AnalaR grade with the exception of polyethylene glycol 400 (Laboratory Grade), and were obtained from BDH Chemicals Ltd, Poole. Solutions of S(IV) contained 1 vol. % ethanol to prevent oxidation and were standardised iodimetrically. Tetraethylammonium sulphite was prepared by bubbling sulphur dioxide through a solution of tetraethylammonium hydroxide (40 wt%) until the pH was reduced to pH 9.5 (Hayon *et al.*, 1972). Water was removed at 40°C *in vacuo* and the solid obtained was stored *in vacuo* over $P_2O_5$.
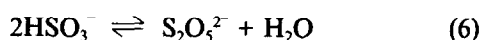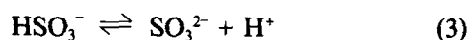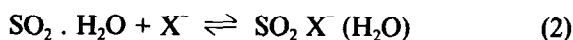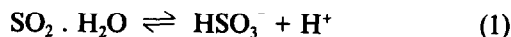
Values of pK were obtained by pH-titration at 30°C, monitoring the pH with a Jenway 3020 pH-meter and a combined glass and calomel electrode. Solutions of $SO_2$ were prepared by bubbling the gas through water to give stock solutions of around 50 mM. The pH-electrode response was corrected as described previously (Wedzicha & Goddard, 1988). Absorbance measurements were carried out using a Cecil CE292 digital spectrophotometer.

## RESULTS AND DISCUSSION

### Review of published work

A series of measurements has been made of the properties of S(IV) in solutions containing neutral salts and

non-electrolytes (Wedzicha & Goddard, 1988, 1991; Wedzicha et al., 1992, 1993), to study the following equilibria:

$$SO_2 . H_2O \rightleftharpoons HSO_3^- + H^+ \qquad (1)$$

$$SO_2 . H_2O + X^- \rightleftharpoons SO_2 X^- (H_2O) \qquad (2)$$

$$HSO_3^- \rightleftharpoons SO_3^{2-} + H^+ \qquad (3)$$

$$HSO_3^- + M^+ \rightleftharpoons MHSO_3 \qquad (4)$$

$$SO_3^{2-} + M^+ \rightleftharpoons MSO_3^- \qquad (5)$$

$$2HSO_3^- \rightleftharpoons S_2O_5^{2-} + H_2O \qquad (6)$$

$$S_2O_5^{2-} + M^+ \rightleftharpoons MS_2O_5^- \qquad (7)$$

where $X^-$ represents halide ions and $M^+$ a metal ion.

All the above equilibria involve a change in the number of charged species and/or the magnitude of charge on each species; the position of equilibrium is likely to be affected by ionic strength, $I$, and concentration. The first and second acid dissociation constants of dissolved sulphur dioxide (equilibria shown in eqns 1 and 3) are dependent on the concentrations of added neutral salts (e.g. NaCl, NaNO$_3$, Na$_2$SO$_4$) (Wedzicha & Goddard, 1991). In the case of 1:1 electrolytes, graphs of pK versus ionic strength pass through a minimum. This behaviour can be modelled satisfactorily by the extended Debye–Huckel theory (Davies, 1962). The effect of ionic strength on these acid dissociation constants is important, because a decrease in pK by only 0·3 units corresponds to a doubling of the ratio of acid:conjugate base concentrations.

The formation of ion-pairs between Na$^+$ and SO$_3^{2-}$ has also been investigated (Wedzicha & Goddard, 1991). The equilibrium constant, $K$, for the formation of the ion-pair (eqn 5) was estimated to be of the order of 6 mol$^{-1}$ litre at 30°C and $I = 0$. This value was calculated from data at high ionic strengths, assuming that the equilibrium constant varies according to

$$K = K_o y$$

where $K_o$ is the formation constant at zero ionic strength and $y$ is the activity coefficient (molar concentration units) of SO$_3^{2-}$ at a given ionic strength. This equation was obtained by assuming that the activity coefficients of the singly charged species Na$^+$ and NaSO$_3^-$ change to the same extent with ionic strength. It is seen that if the total S(IV) concentration is increased from 0·01 to 1·0 M, the amount of NaSO$_3^-$ formed increases from 8 to 66 mol %. The formation of ion-pairs between metal ions and SO$_3^{2-}$ is, therefore, expected to be significant in concentrated systems, possibly leading to a reduction in the reactivity of SO$_3^{2-}$.

Ionic strength is predicted to have a significant effect on the formation constant of S$_2$O$_5^{2-}$ (eqn 6). By increasing the total HSO$_3^-$ concentration from 0·1 to 1·0 M, it
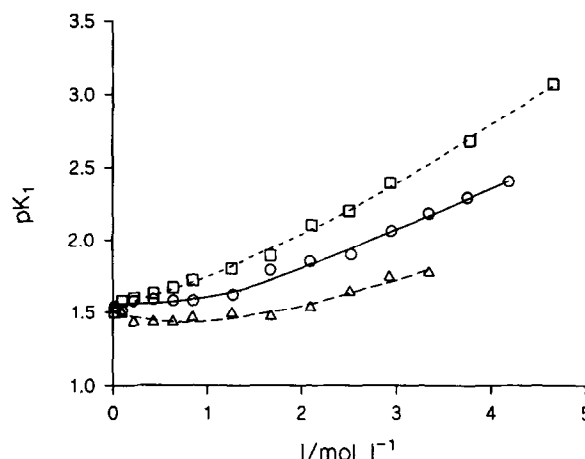


Fig. 1. Effect of ionic strength on pK$_1$ of SO$_2$.H$_2$O at 30°C for the addition of sodium halides at [S(IV)] = 50 mM. $\triangle$, NaCl; $\bigcirc$, NaBr; $\square$, NaI.

is predicted that the proportion of S$_2$O$_5^{2-}$ increases from 1 to 14 mol % (Wedzicha & Goddard, 1991). This prediction ignores the possibility of ion-pair formation between S$_2$O$_5^{2-}$ and metal ions (eqn 7). The formation of such an ion-pair has recently been inferred from the infrared and ultraviolet spectra of S(IV) in water–non-electrolyte mixtures (Wedzicha et al., 1992). Although S$_2$O$_5^{2-}$ and SO$_3^{2-}$ are each doubly charged ions, the formation of ion-pairs with metal ions will probably be weaker with S$_2$O$_5^{2-}$ as the charge on the ion is more delocalised. In the water–non-electrolyte mixtures the dielectric constant of the medium is lower than that of pure water, and the formation of singly charged species such as NaS$_2$O$_5^-$ and HSO$_3^-$ is thought to be favoured over the doubly charged S$_2$O$_5^{2-}$. The idea that singly charged ions are formed in preference to multiply charged ions on addition of non-electrolytes is evident from values of acid dissociation constants of dissolved sulphur dioxide in such mixtures. The addition of ethanol and polyethylene glycol, PEG-400, give rise to a large increase in pK$_1$ and pK$_2$. Glycerol causes a smaller increase at the same concentration but sucrose behaves differently giving a small decrease in pK values (Wedzicha & Goddard, 1991).

## Effects of salt concentration on the acid dissociation constants of SO$_2$.H$_2$O

The consequences of interactions between SO$_2$ and nucleophiles in solution, to form species such as SO$_2$X$^-$, on the apparent pK of SO$_2$.H$_2$O were investigated by measuring the acid dissociation constants in the presence of simple electrolytes (alkali metal halides) which are known to form complexes with SO$_2$ of varying degrees of stability. The effects of the addition of NaCl, NaBr and NaI on pK$_1$ are illustrated in Fig. 1, where equilibrium constants are defined in terms of concentrations (i.e. not activities) 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 addition of the sodium halides has the
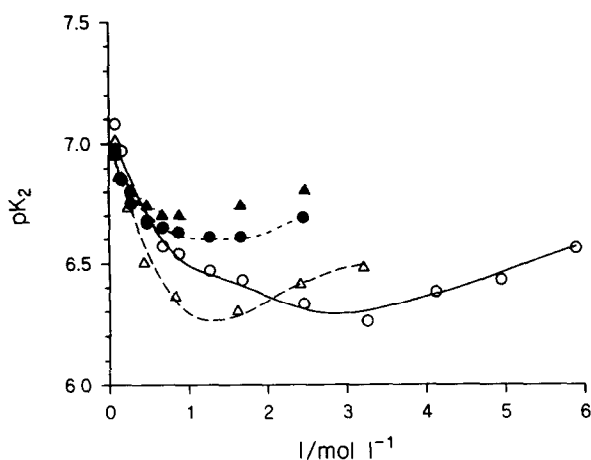
**Fig. 2.** Effect of ionic strength on $pK_2$ of $SO_2.H_2O$ at 30°C for the addition of the group 1 halides at [S(IV)] = 50 mM. ○, LiCl; △, NaCl; ●, KCl; ▲, CsCl.

effect of increasing $pK_1$, except in the case of NaCl, where there appears to be a slight initial decrease; the order of greatest effect is NaI>NaBr>NaCl. Whilst the behaviour of NaCl (and other salts such as $NaNO_3$ and $Na_2SO_4$) can be modelled using the extended Debye–Huckel theory (Wedzicha & Goddard, 1991), this does not apply to Br⁻ and I⁻. Instead, the behaviour is explained by considering the formation of the expected complex between $SO_2$ and halide ions (eqn 2). The increase in pK is in qualitative agreement with the formation of such complexes; the formation constants of $SO_2Br⁻$ and $SO_2I⁻$ are 0·21 and 0·39 mol⁻¹ litre, respectively (Salama & Wasif, 1975), whilst Cl⁻ forms a much weaker complex (Wedzicha & Goddard, 1991). Increasing the ionic strength by the addition of sodium halides favours the formation of complexes which 'stabilise' the dissolved sulphur dioxide and, hence, leads to an increase in $pK_1$.

The second dissociation of $SO_2.H_2O$ is subject to a specific effect of cations. This was studied by means of a series of alkali metal salts with common anions (Cl⁻, $NO_3⁻$ and $SO_4^{2-}$). Figure 2 shows the effects of LiCl, NaCl, KCl and CsCl, Fig. 3 the effects of the corre-
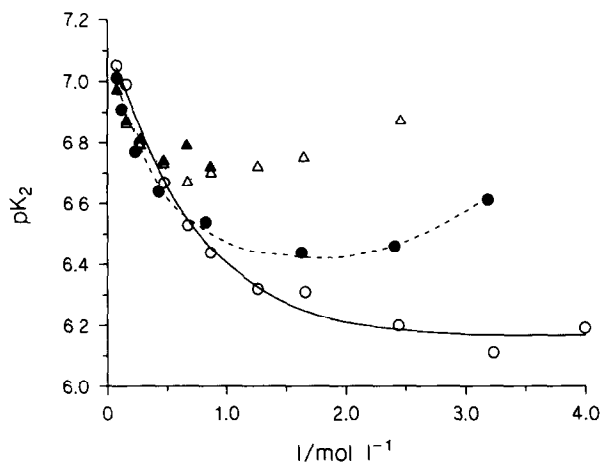


**Fig. 3.** Effect of ionic strength on $pK_2$ of $SO_2.H_2O$ at 30°C for the addition of the group 1 nitrates at [S(IV)] = 50 mM. ○, LiNO₃; ●, NaNO₃; △, KNO₃; ▲, CsNO₃.
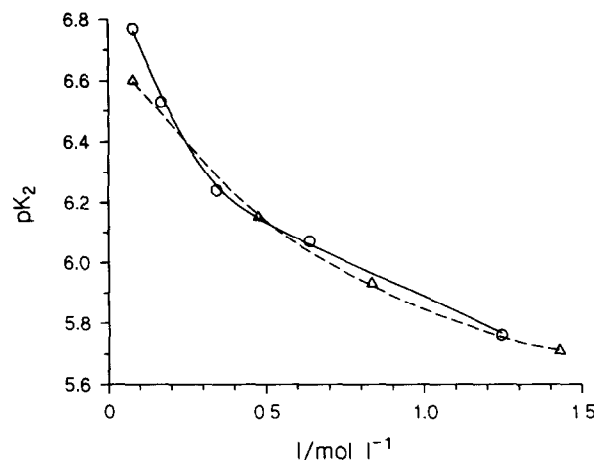


**Fig. 4.** Effect of ionic strength on $pK_2$ of $SO_2.H_2O$ at 30°C for the addition for sodium and potassium sulphate at [S(IV)] = 50 mM. ○, $Na_2SO_4$; △, $K_2SO_4$.

sponding nitrates, and Fig. 4 the effects of $Na_2SO_4$ and $K_2SO_4$ on $pK_2$ of $SO_2.H_2O$. In the case of the addition of the chlorides and nitrates, $pK_2$ is seen to initially decrease with increasing ionic strength, reach a minimum value and increase again. Considering the effect of the cations, $pK_2$ is decreased in the following order Li⁺>Na⁺>K⁺>Cs⁺, although at low ionic strength NaCl has a greater effect than LiCl. The magnitude of the effect decreases with increase in the size of the bare ions, i.e. without their hydration sphere; when water molecules surrounding these ions are taken into account, Li⁺ is, in fact, larger than Na⁺. The 2:1 electrolytes, $Na_2SO_4$ and $K_2SO_4$, have the greatest effects and show no minimum values. Using the extended Debye–Huckel equation to calculate the effect of ionic strength on the activity coefficients of $HSO_3⁻$ and $SO_3^{2-}$ (Wedzicha & Goddard, 1991), the value of $pK_2$ ($I = 0$) is determined as 7·41 ± 0·13, in reasonable agreement with the published value of 7·18 (Wedzicha, 1984). The application of the Debye–Huckel equation here merely serves to extrapolate $pK_2$ versus ionic strength data to zero ionic strength; the approach has little fundamental significance when one has the possibility of specific interactions, e.g. the formation of ion-pairs between the alkali metal ions and $SO_3^{2-}$.

## Ion-pair interactions in sodium sulphate solutions

Changes in the UV absorbance spectra of sulphur oxospecies, such as thiosulphate, in the presence of cations, have been attributed to ion-pair interactions (Thomas & Monk, 1956) and have allowed ion-pair dissociation constants to be estimated. Thus, measurements of absorbance, at 255 nm, have proved useful for demonstrating the formation of the ion-pair $NaSO_3⁻$ (Wedzicha & Goddard, 1991). It is only possible to calculate the formation constant of this ion pair if the way in which the activity coefficient of $SO_3^{2-}$ changes with ionic strength is known. Unfortunately, only the mean ionic activity coefficients of $Na_2SO_3$ have been measured (Goldberg, 1981). For the other cations, it is only
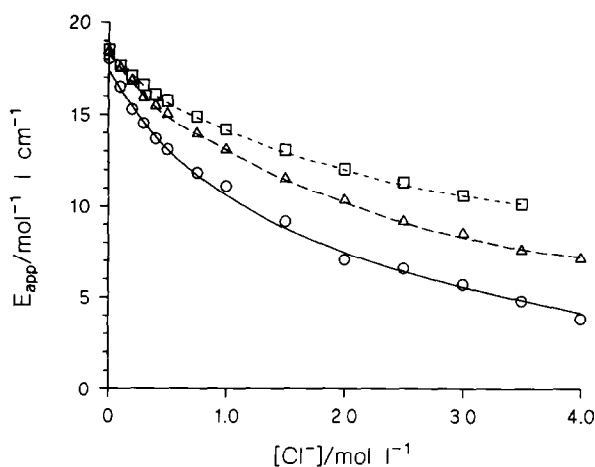
**Fig. 5.** The apparent extinction coefficient, $E_{app}$, at 255 nm, of a solution of $Na_2SO_3$ (60 mM) as a function of ionic strength for the addition of LiCl ($\bigcirc$), NaCl ($\triangle$), and KCl ($\square$).

possible to present values of the apparent extinction coefficient, $E_{app}$, versus ionic strength. The effect on $E_{app}$ of alkali metal chloride concentration is shown in Fig. 5 for the addition of LiCl, NaCl and KCl to solutions of $Na_2SO_3$ (60 mM) in order to demonstrate the effect of changing the cation. The addition of these salts has the effect of lowering $E_{app}$ which is consistent with the formation of ion-pairs; the order of greatest effect is LiCl>NaCl>KCl, i.e. increasing size of the bare ion as previously observed for the effect on the $pK_2$ value of $SO_2.H_2O$. At [LiCl] = 8·0 M, the sulphite salt precipitated. Assuming that, in all instances, the extinction coefficient of the ion-pair is smaller than that of the anion, it seems likely that the salts which lower $E_{app}$ to the greatest extent also form the most stable ion-pairs. However, values of the formation constants of other ion-pairs seem to contradict the trends reported here for sulphite ion. Davies (1962) reports the formation constants of $LiSO_4^-$, $NaSO_4^-$ and $KSO_4^-$ to be 3·98, 5·01 and 10·0 $mol^{-1}$ litre, respectively, and for $NaS_2O_3^-$ and $KS_2O_3^-$ as 3·98 and 7·94, respectively. Thiosulphate is considered to be a good model for sulphite ion
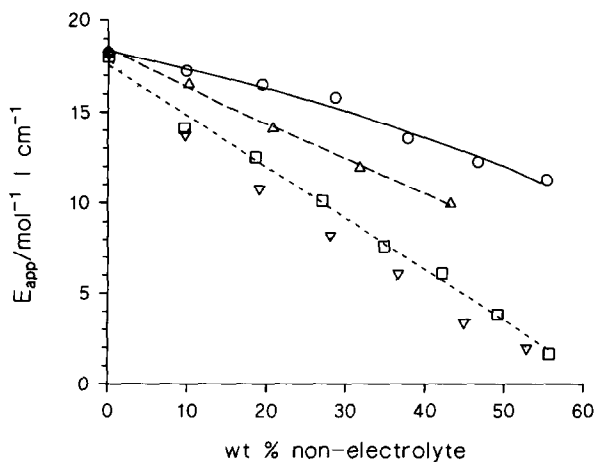


**Fig. 6.** The apparent extinction coefficient, $E_{app}$, at 255 nm, of a solution of $Na_2SO_3$ (50 mM) as a function of non-electrolyte concentration. $\bigcirc$, PEG-400; $\square$, sucrose; $\triangle$, ethanol; $\triangledown$, glycerol.

(Wedzicha, 1984) as the mean ionic activity coefficients of $Na_2SO_3$ and $Na_2S_2O_3$ change to a similar extent with concentration (Goldberg, 1981). The tendency towards ion-pair formation depends on competition between water and anions for positions within the critical distance of the cation. However, one possibility for the difference in trend of ion-pair stabilities between $SO_3^{2-}$ and other anions is that water molecules could be involved in bridging the species involved in the ion-pair when $MSO_3^-$ is formed.

## Effects of non-electrolytes

The effects of non-electrolyte–water mixtures on $E_{app}$ are shown in Fig. 6. For the non-electrolytes studied (ethanol, glycerol, PEG-400 and sucrose) it is seen that, in every case, $E_{app}$ is decreased with non-electrolyte concentration; the order of greatest effect being glycerol>sucrose>ethanol>PEG-400. Such a decrease in absorbance could, again, be explained by considering the formation of ion-pairs. The enhanced formation of ion-pairs in water–non-electrolyte mixtures is not unreasonable. Thomas & Monk (1956) have reported formation constants for $NaS_2O_3^-$ of 71·4 and 143 $mol^{-1}$ litre, and for $KS_2O_3^-$ of 83·3 and 217 $mol^{-1}$ litre in 44 and 50 wt % ethanol, respectively. Davies (1962) tabulates the pK values for a wide range of ion-pairs in ethanol–water mixtures; in all cases the extent of ion-pair formation increases with increasing ethanol content.

The dissociation of an acid, HA, in a solvent, SH, can be represented by

$$HA + SH \rightleftharpoons SH_2^+ + A^-  \qquad (8)$$
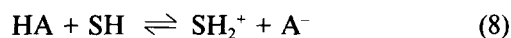
and the ratio of dissociation constants of the acid in water and in a different solvent, $s$, is

$$\log (K_w/K_s) = \log (y_{H^+}/y_A \cdot /y_{HA})  \qquad (9)$$

where $K_w$ and $K_s$ are the respective dissociation constants and $y$ represents activity coefficients. The relationship between the pK values of the acid in the two solvents is

$$pK_s - pK_w = a/\epsilon_s + b  \qquad (10)$$

where $a$ and $b$ are constants and $\epsilon_s$ is the dielectric constant of the solvent, $s$ (Davies, 1962). The value of pK should, therefore, be linearly related to $1/\epsilon_s$. It has been shown by Yasuda (1959) and Bates (1973) that lowering the dielectric constant by the addition of ethanol, methanol and dioxane gives rise to an increase in the pK of monoprotic acids such as acetic and benzoic, and an increase in both the pK values of diprotic acids such as adipic and succinic. The expected relationship between pK value and $1/\epsilon_s$ was observed although the gradients of the lines were dependent on the acid and the solvent used. Data published by Wooley et al. (1970) and Harned and Owen (1958) allowed the dielectric constants of the solutions of ethanol, glycerol and sucrose used in the present work to be obtained. A typical set of data, for $pK_1$ versus $1/\epsilon_s$ is plotted in
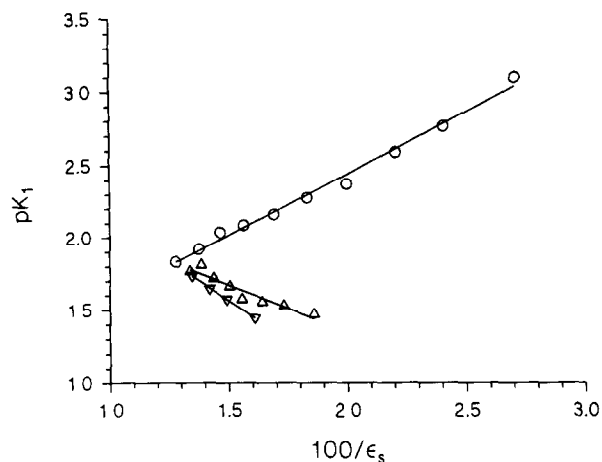
**Fig. 7.** Graph of $pK_1$ of $SO_2.H_2O$ versus the reciprocal of the dielectric constant $\epsilon$, for measurements in water–ethanol (O), water–glycerol ($\triangle$) and water–sucrose ($\triangledown$) mixtures at 30°C.



**Fig. 8.** Comparison of the apparent extinction coefficients, $E_{app}$, a 255 nm, of solutions of $Na_2SO_3$ (O) and $(C_2H_5)_4N)_2SO_3$ ($\triangle$) as a function of ethanol content.

Fig. 7. Whereas the expected relationship is obeyed for a given water–non-electrolyte system, the dielectric constant is not the independent variable, which consolidates the results in the presence of different non-electrolytes. This is probably due to specific solute–solvent and solute–non-electrolyte interactions or it implies that another property of the solvent is affecting the dissociation constants.

Davies (1962) tabulated the pK values for a wide range of ion-pairs in ethanol–water mixtures; in all cases, ion-pair formation increases with increasing ethanol content. Graphs of pK values of ion-pairs versus $1/\epsilon_s$ plotted by Davies give rise to straight lines as illustrated above for the acid dissociation equilibria. Again, the slopes differ for different solvent mixtures and the order of strength of ion association in a solvent mixture is not necessarily the same as in water. If the dielectric constant were a determining factor in the formation of ion-pairs, then it would be expected that the apparent extinction coefficient of $SO_3^{2-}$ would be lower in solutions of ethanol–water than in glycerol–water, as ethanol reduces the dielectric constant more than does glycerol.

In a further experiment, $Na^+$ was replaced by the large cation $(C_2H_5)_4N^+$ which, due to its large size, may be expected to shield the charge on the nitrogen atom, and ion-pair formation is less likely. Figure 8 shows how $E_{app}$ changes with ethanol content for solutions containing either $Na_2SO_3$ or $(C_2H_5)_4N)_2SO_3$. Although $E_{app}$ is higher for solutions containing the latter compound, the extinction coefficient is lowered to a similar extent for both sulphites. The value of 23·5 mol⁻¹ litre cm⁻¹ for the true extinction coefficient of $SO_3^{2-}$ at 255 nm (Wedzicha & Goddard, 1991) is similar to the value of 25 mol⁻¹ litre cm⁻¹ for a solution of $(C_2H_5)_4N)_2SO_3$ (50 mM) which suggests that ion-pairs are not formed at this concentration.

The data for the $pK_2$ value of $SO_2.H_2O$, as a function of the concentrations of different cations are consistent with the spectrophotometric data, because they imply that the smaller cations stabilise the $SO_3^{2-}$ ion (thereby
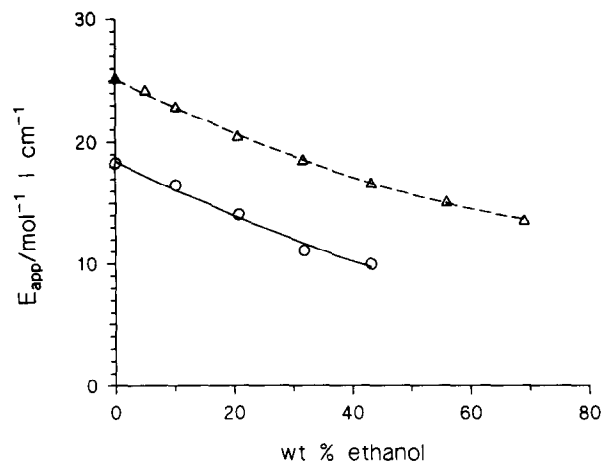
reducing the pK value), and give rise to the largest changes in extinction coefficient.

### Effect of concentration on the formation of disulphite ion

The $S_2O_5^{2-}$ ion has the useful property of absorbing much more strongly at 255 nm than $HSO_3^-$, which is the principal species with which it is in equilibrium. The effect of ionic strength on the absorbance at 255 nm of a solution of S(IV) (30 mM) at pH 5 is shown in Fig. 9, for various concentrations of LiCl, NaCl, KCl, and CsCl. Experimental and theoretical studies (Bourne *et al.*, 1974; Connick *et al.*, 1982) indicate that the $HSO_3^-/S_2O_5^{2-}$ equilibrium is displaced in favour of $S_2O_5^{2-}$ with ionic strength, which should lead to an increase in absorbance. This characteristic increase in absorbance with ionic strength is illustrated in Fig. 9, but the magnitude of the effect depends also on the salt added. At any salt concentration, the increase in absorbance is in the order $Cs^+>K^+>Na^+>Li^+$ and it is suggested here that the smaller cations suppress the
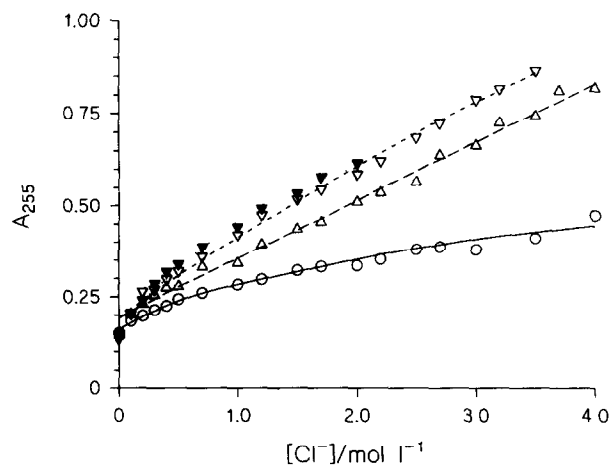


**Fig. 9.** The absorbance, at 255 nm, of a solution of S(IV) (30 mM) at pH 5, as a function of the concentration of alkali metal chloride. O, LiCl; $\triangle$, NaCl; $\triangledown$, KCl; $\blacktriangledown$, CsCl.

increase, by also forming ion-pairs, i.e. $MS_2O_5^-$. On this supposition, the order of stability of the ion-pairs is, therefore, the same as that inferred for $MSO_3^-$ above. Previous workers (Bourne et al., 1974; Connick et al., 1982) have determined values for the formation constant of $S_2O_5^{2-}$ by fitting values of the extinction coefficient of $S_2O_5^{2-}$, and the equilibrium constant, to experimental data. Both workers used only $Na^+$ salts and constant values for the extinction coefficient of $S_2O_5^{2-}$ over the entire ionic strength range used; the possibility of ion-pairing between metal ions and $S_2O_5^{2-}$ has not been considered. Such ion-pairing would lead to a variation of values of extinction coefficient as a function of ionic strength. Refinement of these data may be required.

## CONCLUSION

The distribution of S(IV) in concentrated systems depends on the composition of the medium but it is not possible to attribute this to any one physical or chemical property of the solution. As a general rule, a reduction in the dielectric constant of the medium, by the addition of non-electrolytes, favours the formation of uncharged and singly charged species either by increasing the acid dissociation constants or by the formation of ion-pairs. Whereas an increase in ionic strength generally favours the formation of the doubly charged species by increasing the acid dissociation constants and by increasing the tendency for formation of $S_2O_5^{2-}$, an increase in the concentration of these species is also accompanied by a decrease in total charge due to the increased tendency to form ion-pairs with metal ions.

Although the mechanisms of many of the reactions of S(IV) with food components and additives are well understood, the only work involving concentrated systems has been to elucidate the rate of reaction of S(IV) as a whole. With the knowledge of the effects of composition on the distribution of the S(IV) oxospecies, it becomes possible to resolve the effect that each species has on the reaction kinetics in model systems. The present investigation outlines the important considerations which need to be taken into account when modelling food systems.

## ACKNOWLEDGEMENT

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