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Vapour pressure of SO_2 above solutions of sulphur(IV) oxospecies: the effects of chloride ion and glycerol

B. L. Wedzicha* & P. P. Webb

Procter Department of Food Science, University of Leeds, Leeds LS2 9JT, UK

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A simple spectrophotometric technique to determine the headspace concentration of SO_2 above millimolar aqueous solutions of the gas is described. At a given concentration of SO_2 in the aqueous phase, the value of Henry's constant ($[S(IV)]_{aq}/p(SO_2)$, where $p(SO_2)$ is the pressure of the gas in the headspace above the solution, is increased by the addition of Cl^- but markedly decreased on adding 20–30 wt% glycerol. The data are used to obtain a value of 7.2 mol litre^{-1} for the dissociation constant of SO_2 Cl^- which has ϵ_{max} = 2000 mol litre^{-1} cm^{-1} at 280 nm. Copyright © 1996 Elsevier Science Ltd.

INTRODUCTION

There are two food-related reasons for a keen interest in the vapour pressure of SO_2 in the headspace above solutions of sulphur(IV) oxospecies, S(IV). First, the only known hazard associated with the use of S(IV) as a food additive stems from inhalation of gaseous SO_2 from the headspace of foods (Taylor *et al.*, 1986), or as a result of eructation following the consumption of S(IV)-treated foods. Secondly, the vapour pressure provides an unambiguous measure of the activity (in the chemical sense) of SO_2 in the medium in which it is dissolved and thereby leads to a fundamental approach to the study of interactions of S(IV) with food components.

When SO_2 is dissolved in water, its solution behaves as a dibasic acid, $pK_1 = 1.86$, $pK_2 = 7.18$ (Wedzicha, 1984), as follows:

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

$$HSO_3^- \rightleftharpoons SO_3^{2-} + H^+. \quad (2)$$

The species H_2SO_3, known as sulphurous acid, does not exist to any measurable extent (Falk & Giguere, 1958; Guthrie, 1979). The interaction between SO_2 and water is, in fact, very weak (Davis & Chatterjee, 1975) and is one reason why there is a significant pressure of the gas above solutions of it in water.

The relationship between the concentration of dissolved SO_2 and its pressure $p(SO_2)$ in the headspace above the solution is given by Henry's law,

$$K_H = [SO_2]/p(SO_2), \quad (3)$$

where K_H is Henry's constant. By plotting selected values of K_H, over the temperature range 7–122°C, Goldberg & Parker (1985) suggest the best overall value of K_H at 25°C to be 1.20 mol kg^{-1} bar^{-1}. This value is essentially independent of SO_2 concentration up to 7.5 wt%.

The molecule of SO_2 accepts electrons from nucleophiles and even halide ions can form complexes SO_2X^-. Thus, Br^- and I^- form weak complexes whose dissociation constants ($pK = -0.66$ and -0.41, respectively) have been measured spectrophotometrically (Salama & Wasif, 1975). Whilst there is evidence for SO_2Cl^- (Wedzicha & Goddard, 1991), this product is too unstable for its dissociation constant to be obtained in this way. The pressure of SO_2 above aqueous solutions is likely to be sensitive to the presence of many different solutes. In this investigation we describe the two contrasting effects of Cl^- and glycerol on SO_2 pressure above solutions of $SO_2.H_2O$; measured values of Henry's constant are used also to obtain the stability constant and molar extinction coefficient of SO_2Cl^-.

MATERIALS AND METHODS

With the exception of Ellman's reagent, chemicals were of AnalaR grade; all were obtained from BDH Chemicals Ltd, Poole, UK.

Solutions of S(IV) were prepared by dissolving solid sodium metabisulphite in water containing 1 vol% ethanol as an antioxidant and were standardised iodimetrically. In one series of experiments where it was desired not to add any cations, the solution was

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*To whom correspondence should be addressed.

prepared by dissolving SO_2 gas in water until an appropriate (11 mM) concentration of S(IV) had been reached, and the solution was standardized. The mixtures to be investigated (50 ml) were placed in 100 ml stoppered measuring cylinders which were immersed up to the neck in a water bath at 25.0 ± 0.05°C. The stopper had a clearance hole for a fine syringe needle, and was covered during equilibration of the headspace. The solution in the cylinder was shaken every 5 min over a period of at least 30 min.

A 25 ml all-glass syringe was fitted into an assembly to provide end-stops such that successive preset volumes of 5.42 ± 0.05 and 10.09 ± 0.03 ml (determined from 15 measurements) could be drawn reproducibly.

The reagent for spectrophotometric analysis of SO_2 was 5,5′-dithiobis(2-nitrobenzoic acid), DTNB or Ellman's reagent (1 mM in 50 mM, pH 7, phosphate buffer). An aliquot (5.42 ml) of this reagent was drawn up into the syringe, followed by 10.09 ml of the headspace above the solution in the cylinder. After shaking the contents of the syringe, absorbance was measured at 412 nm. The concentration of S(IV) in this solution was calculated from calibration data obtained by mixing the reagent with iodimetrically standardized S(IV) solutions. pH measurements were carried out using a Jenway PHM6 digital pH meter and values were corrected by the method of Wedzicha & Goddard (1988).

RESULTS AND DISCUSSION

The headspace analysis technique involves absorbing the SO_2 present in 10 ml of headspace in 5 ml of DTNB reagent. This follows the well-established (Humphrey *et al.*, 1970; Wedzicha, 1984) procedure for the measurement of S(IV) by the cleavage of the disulphide bond in this reagent and the extinction coefficient of the resulting thiolate anion (13 000 mol^{-1} cm^{-1} at 412 nm) gives a detection limit of 12 μg SO_2 per litre of air for an absorbance (at 412 nm) in the final solution of 0.005. This sensitivity could easily be increased proportionately by analyzing a greater volume of the headspace; in the experiments reported here, absorbances were in the range 0.05–0.8 and the sensitivity was considered adequate for measuring the pressure of SO_2 above acidified solutions of the gas in the millimolar range. This applies also to S(IV) in beverages such as wines and fruit juices, and preliminary studies indicate sufficient sensitivity for measurements of the headspace SO_2-content above dehydrated fruit (apricot and pineapple). This technique therefore represents a simple method which does not require the use of gas chromatography and is relatively fast.

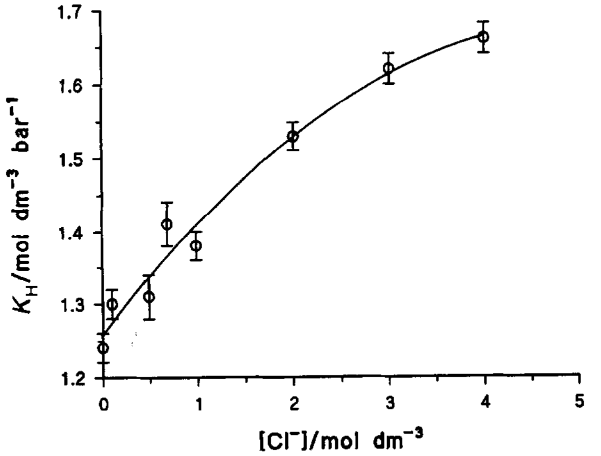

Fig. 1. Effect of [Cl^-] on the value of Henry's constant K_H for SO_2 in the headspace above a solution of the gas in water at 25°C. The error bars represent standard deviations obtained from 15 replicate experiments.

The low pK of $SO_2.H_2O$ means that at any practical pH value there will be a significant proportion of the dissociated acid present. Thus, at a given pH value, the concentration of $SO_2.H_2O$ was obtained from (Wedzicha & Goddard, 1991):

$$[SO_2.H_2O] = [S(IV)]10^{-(pH-pK)}/(1 + 10^{-(pH-pK)}) \quad (4)$$

where the pK value is that which applies at the ionic strength of the medium and S(IV) represents the sum of concentrations of the relevant sulphur(IV) oxospecies in solution, i.e. $[SO_2.H_2O]$ + $[HSO_3^-]$ in this case. Wedzicha & Goddard (1991) investigated the relationship between the pK value of $SO_2.H_2O$ and ionic strength I. From their experiments in which I was adjusted with NaCl, an empirical relationship between pK and I/mol litre^{-1} can be given as a third-order polynomial,

$$pK = 1.86 - 0.322I + 0.200I^2 - 0.026I^3 \quad (5)$$

and used for purposes of calculating the pK value at any ionic strength in the range 0–4 mol litre^{-1}. The response of the pH-meter electrode was corrected by the method of Wedzicha & Goddard (1988) with a standard (10 mM) solution of HCl; the apparent pH of solutions was lower than $-\log_{10}a(H^+)$, where $a(H^+)$ is the activity of hydrogen ion, by $0.085I$, $0.124I$ and $0.084I$ for three electrodes used in the investigation. The appropriate corrections were applied to all NaCl- and HNO_3-containing mixtures.

The pressure of SO_2 in the headspace above solutions is given by,

$$p(SO_2)/\text{bar} = nRT/1.013 \times 10^5 V, \quad (6)$$

where n is the number of moles of SO_2 in the volume V (m^3) of headspace sample at a temperature T (K) and R is the gas constant. The value of n was obtained simply as the number of moles of SO_2 in the 5 ml of Ellman's reagent, i.e.

$$n = A/200\epsilon, \quad (7)$$

where A is the absorbance of the reagent + SO_2 in a 1 cm cell and ϵ is the molar extinction coefficient. The value of Henry's constant may thus be obtained from eqn (3).

Repeated measurement of the value of K_H at 25°C gave 1.24 ± 0.04 and 1.21 ± 0.02 mol litre^{-1} bar^{-1} ($n = 15$ in each case) when the pH of a solution of S(IV) (11 mM) was adjusted with 1 M HNO_3, or a solution of SO_2 in water (51 mM), respectively, was used. A *t*-test showed that there was no significant difference between these mean values (at the 1% level). The mean value of 1.23 mol litre^{-1} bar^{-1}, obtained from all the measurements ($n = 30$), was adopted. This is very close to the best overall value of 1.20 mol kg^{-1} bar^{-1} of Goldberg & Parker (1985); the difference between using molal and molar concentrations was estimated to be within the limits of experimental error.

The effect of increasing [Cl^-] on the value of K_H is illustrated in Fig. 1. As expected, this trend indicates a greater bias of SO_2 for the aqueous phase as [Cl^-] increases. The equilibrium for the interaction between SO_2 and Cl^- is

$$SO_2 + Cl^- \rightleftharpoons SO_2Cl^- \tag{8}$$

and the dissociation constant, *K*, of the product is given by

$$K \approx [Cl^-]([S(IV)] - [SO_2Cl^-])/[SO_2Cl^-], \tag{9}$$

where $[S(IV)] = [SO_2.H_2O] + [SO_2Cl^-]$ and $[Cl^-] \gg [S(IV)]$. The apparent value of Henry's constant K_H(app) is given by,

$$K_H(\text{app}) = ([SO_2.H_2O] + [SO_2Cl^-])/p(SO_2) \tag{10}$$

and is related to K_H by,

$$K_H(\text{app}) = K_H[C^-]/K + K_H. \tag{11}$$

Hence, a graph of K_H(app) vs [Cl^-] should be linear with a slope of K_H/K. According to the Brønsted formulation (Davies, 1962), the value of the dissociation constant for SO_2Cl^- should not depend on ionic strength, provided that the mean ionic activity coefficients of Na^+Cl^- and $Na^+SO_2Cl^-$ change to the same extent as the ionic strength is varied. The somewhat different ionic sizes of these two species means that this approximation is unlikely to apply, particularly at the high NaCl concentrations required to obtain a significant change in the value of K_H. Thus, to obtain the best value of *K*, the slope (0.17 bar^{-1}) of the graph in Fig. 1 was obtained at $[Cl^-] = 0$, to give $K = 7.2$ mol litre^{-1}, in agreement with the earlier suggestion that $K > 4$ mol litre^{-1} (Wedzicha & Goddard, 1991).

The UV absorbance maximum for $SO_2.H_2O$ and SO_2Cl^- is at 280 nm. At this wavelength, the apparent extinction coefficient ϵ_{app} of $SO_2.H_2O$ in the NaCl solution is given by

$$\epsilon_{app} = A_{obs}/([SO_2.H_2O] + [SO_2Cl^-]), \tag{12}$$

where A_{obs} is the measured absorbance of the mixture of species. Thus, introducing the extinction coefficients for the individual species, $\epsilon(SO_2)$ and $\epsilon(SO_2Cl^-)$, eqn (12) becomes,

$$\epsilon_{app} = \epsilon(SO_2) + \frac{\{\epsilon(SO_2Cl^-) - \epsilon(SO_2)\}}{[SO_2] + [SO_2Cl^-]}[SO_2Cl^-]. \tag{13}$$

Applying this equation to the tabulated values of ϵ_{app} at various concentrations of NaCl published by Wedzicha & Goddard (1991) gives $\epsilon(SO_2Cl^-) = 2000$ mol^{-1} cm^{-1}, which is four times greater than $\epsilon(SO_2)$ [500 mol^{-1} cm^{-1}, Huss & Eckert (1977); Scoggins (1970)] and is the reason why the absorbance of aqueous solutions of SO_2 increases when NaCl is added.

Of the non-electrolytes (ethanol, glycerol, polyethylene glycol, sucrose) used in previous studies of the dissociation of $SO_2.H_2O$ (Wedzicha & Goddard, 1991), glycerol was found to have the smallest effect on the p*K* of $SO_2.H_2O$; indeed this was of similar magnitude to its effect on the response of the pH measuring electrode.

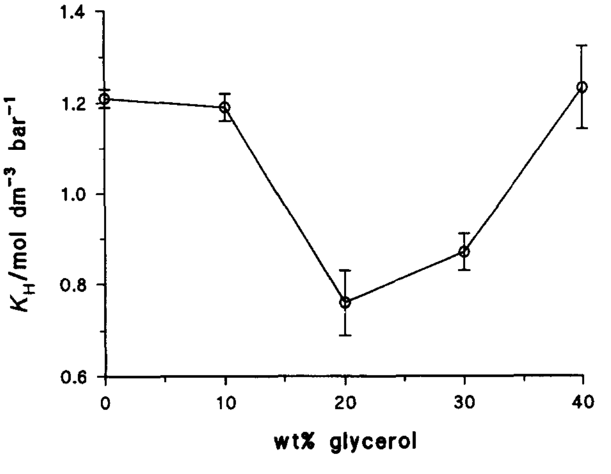

Fig. 2. Effect of glycerol content on the value of Henry's constant K_H for SO_2 in the headspace above a solution of the gas in water at 25°C. The error bars represent standard deviations obtained from five replicate experiments.

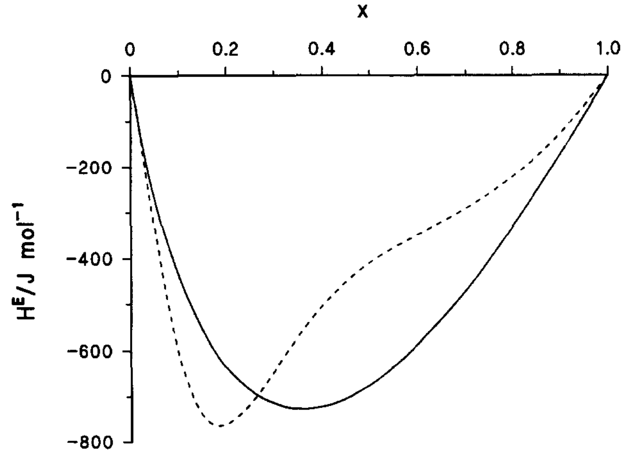

Fig. 3. Excess enthalpy of mixing H^E at 25°C as a function of the composition of water–ethanol (- - -) and water–glycerol (———) mixtures. Data for water–ethanol are taken from Larkin (1975) and those for water–glycerol have been recalculated from the equation given by Bennani *et al.* (1989).

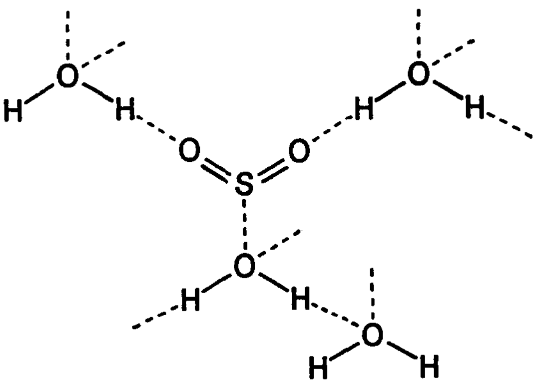

Fig. 4. Suggested interactions between SO_2 and water molecules, based loosely on the structures suggested by Gerrard (1976).

Thus, it was decided to use glycerol as a solute to investigate the effect of a non-electrolyte (and humectant in this case) on the value of $p(SO_2)$ above solutions of $SO_2.H_2O$, without introducing complications and uncertainty associated with the variation of pK value. This variation can be large, as seen for ethanol and polyethylene glycol.

Figure 2 illustrates the effect of glycerol content, up to 40 wt%, on the value of K_H. Since this result is independent of the effect of glycerol on the ionization of $SO_2.H_2O$, it represents the differences in solvent properties between water and water–glycerol mixtures. It is striking that the addition of 20 wt% glycerol to a solution of $SO_2.H_2O$ at a given concentration, nearly doubles the amount of SO_2 in the headspace above the solution.

The structure of water can be regarded as clusters of molecules, hydrogen bonded as in ice, in equilibrium with less strongly bonded molecules in between the clusters and in regions (cavities) within the clusters. The excess enthalpy of mixing of ethanol (Larkin, 1975), or glycerol (Bennani *et al.*, 1989), with water is exothermic and is attributed to the formation of additional structure, probably dominated by water–water bonds (Larkin, 1975). In the case of ethanol–water mixtures, the relationship between the excess enthalpy of mixing and mole fraction, x, of ethanol, at 25°C is highly skewed showing that much of the structure-making behaviour of the ethanol takes place at $x < 0.2$. Larkin (1975) considers that ethanol molecules occupy the spaces in between the clusters of water molecules, displacing the weakly bound water molecules and increasing their tendency to become involved in strong water–water bonds within clusters. The data (Larkin, 1975) for ethanol–water mixtures are shown in Fig. 3, superimposed on results for the excess enthalpy of mixing of water and glycerol, recalculated here from a correlation reported by Bennani *et al.* (1989). Whereas the water–glycerol mixtures give rise to a more symmetrical plot, it is still skewed in the same direction as for ethanol, indicating the exothermic effect particularly of small amounts of glycerol ($x < 0.3$). The similar magnitudes of the maximum (negative) enthalpy of mixing supports the view expressed by Larkin (1975) that the structural change which occurs as non-electrolyte is added to water occurs within the structure of water rather than as a result of specific non-electrolyte–water interactions.

The value of $K_H = 1.23$ mol litre^{-1} bar^{-1} implies that there are approximately 30 times more SO_2 molecules in a given volume of aqueous phase than the same volume of the gas phase with which it is in equilibrium. Although the interaction between SO_2 and water is very weak, it is envisaged that the molecules are held in the water structure by specific interactions, for example as shown in Fig. 4 based on the ideas put forward by Gerrard, (1976). It is not clear whether or not such interactions can be accommodated within the ordered regions of water molecule clusters. However, a simple hypothesis is to assume that SO_2 molecules are solvated in the less well-ordered regions between the clusters and the addition of glycerol serves to break the SO_2–water interactions as water molecules move to form more ordered structures. Such behaviour would be evident at low values of glycerol mole fraction; 20–30 wt% glycerol in water, the range in which the value of K_H is a minimum (Fig. 2), corresponds to $x = 0.04$–0.07. This is on the steepest part of the graph of excess enthalpy vs x shown for glycerol in Fig. 3.

Unlike the thermochemical data, the shape of the graph of K_H vs composition shown in Fig. 2, should include contributions from the solubility of SO_2 in glycerol. Sulphur dioxide is, in fact, more soluble in glycerol than in water (Gerrard, 1976), and this could explain why the minimum value of K_H appears at a much lower value of x than the minimum value of the excess enthalpy of mixing. We suggest, therefore, that the effect of glycerol on the value of K_H is due to the water structure-making behaviour of glycerol at low non-electrolyte concentration and its solvent behaviour as concentration is increased.

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REFERENCES

Bennani, P., Coronas, A. & Prevost, M. (1989). Mélange eau–glycérol données thermodynamiques en vue de la simulation de cycles a absorption. *J. Chim. Phys.*, **86**, 2125–48.

Davies, C. W. (1962). *Ion Association*. Butterworth, London.

Davis, A. R. & Chatterjee, R. M. (1975). A vibrational spectroscopic study of the SO_2–H_2O system, *J. Solution Chem.*, **4** 399–412.

Falk, M. & Giguere, P. A. (1958). On the nature of sulphurous acid. *Can. J. Chem.*, **36**, 1121-5.

Gerrard, W. (1976). *Solubility of Gases and Liquids*. Plenum Press, New York, pp. 103–13.

Goldberg, R. N. & Parker, V. B. (1985). Thermodynamics of solution of SO_2(g) in water and of aqueous sulfur dioxide solutions. *J. Res. Natl. Bur. Stand.*, **90,** 341–58.

Guthrie, P. J. (1979). Tautomeric equilibria and pK_a values for 'sulfurous acid' in aqueous solution. A thermodynamic analysis, *Can. J. Chem.*, **57,** 454–7.

Humphrey, R. E., Ward, M. H. & Hinze, W. (1970). Spectrophotometric determination of sulfite with 4,4′-dithiodipyridine and 5,5′-dithiobis(2-nitrobenzoic acid). *Analyt. Chem.*, **42,** 698–702.

Huss, A. Jr. & Eckert, C. A. (1977). Equilibria and ion activities in aqueous sulfur dioxide solutions. *J. Phys. Chem.*, **81,** 2268–70.

Larkin, J. A. (1975). Thermodynamic properties of aqueous nonelectrolyte mixtures. I. Excess enthalpy for water + ethanol at 298.15 to 383.15 K. *J. Chem. Thermodyn.*, **7,** 137–48.

Salama, S. B. & Wasif, S. (1975). Weak complexes of sulphur and selenium. Part III. Effect of solvent on the stability of 1:1 complexes of sulphur dioxide, sulphinyl dichloride and sulphonyl dichloride with halogen ions. *J. Chem. Soc. Dalton Trans.*, 151–3.

Scoggins, M. W. (1970). Ultraviolet spectrophotometric determination of sulfur dioxide. *Analyt. Chem.*, **42,** 1091–3.

Taylor, S. L., Higley, N. A. & Bush, R. K. (1986). Sulfites in foods: uses, analytical methods, residues, fate, exposure assessment, metabolism, toxicity and hypersensitivity, *Adv. Food Res.*, **30,** 1–76.

Wedzicha, B. L. (1984). *Chemistry of Sulphur Dioxide in Foods*. Elsevier Applied Science, London.

Wedzicha, B. L. & Goddard, S. J. (1988). The dissociation constant of hydrogen sulphite ion at high ionic strength. *Food Chem.*, **30,** 67–71.

Wedzicha, B. L. & Goddard, S. J. (1991). The state of sulphur dioxide at high concentration and low water activity. *Food Chem.*, **40,** 119–36.