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The Dissociation Constant of Hydrogen Sulphite Ion at High Ionic Strength

B. L. Wedzicha & S. J. Goddard

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

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ABSTRACT

The effect of ionic strength (0·08–4·6 M*), maintained by the addition of* $NaNO_3$*, on the pK of* HSO_3^- *measured using a combined glass and calomel electrode at 30°C, is reported. The data are corrected for the effect of ionic strength on the response of the electrode and the activity coefficients of* HSO_3^- *and* SO_3^{2-} *are found to obey the extended Debye Hückel theory to ionic strengths of at least 2·3* M.

INTRODUCTION

The preservative action of sulphur dioxide with respect to non-enzymic browning in food is due to the nucleophilicity of sulphite ion (Wedzicha, 1987). This species is derived by the ionisation of hydrogen sulphite ion and its concentration therefore depends on the pH of the food in question and the dissociation constant of the acid. The pK for the equilibrium:

$$HSO_3^- \rightleftharpoons SO_3^{2-} + H^+ \qquad (1)$$

is 7·18 at 25°C, extrapolated to zero ionic strength (Tartar & Garretson, 1941). It may be expected that, over the pH range of food, the predominating species is HSO_3^-. There are, however, no reliable data on the effects of ionic strength on this equilibrium and it is not possible to predict its behaviour in concentrated systems. It is likely, however, that the apparent pK of HSO_3^- falls with increasing salt concentration; Shapiro (1977) gives a value of 6·25 in ‘concentrated salt solution’. If this were the case the concentration of

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sulphite ion in foods at high ionic strength could be nearly an order of magnitude greater than estimated from the pK at infinite dilution. The purpose of this paper is, therefore, to explore the variation of pK with ionic strength.

EXPERIMENTAL

All reagents were of AnalaR grade and were obtained from BDH Chemicals Ltd., Poole. Solutions containing HSO_3^- (0·05M) were prepared by dissolving $Na_2S_2O_5$ in water containing ethanol (1% v/v) which inhibits autoxidation of sulphite ion, and ionic strength was adjusted by adding $NaNO_3$. pK values were determined by pH titration (Jenway PHM6 pH meter with combined glass–calomel electrode) with NaOH (0·1M) at 30°C and the ionic strength at half neutralisation calculated using the initial concentration and volume of the HSO_3^- solution, the volume of alkali added, the concentration of $NaNO_3$ and the fact that at half neutralisation equimolar concentrations of HSO_3^- and SO_3^{2-} are present. The pH meter was calibrated at pH 4 and 7 using phthalate and phosphate buffers.

The response of the electrode to a known concentration of H^+, as a function of ionic strength, was found by measuring the apparent pH of a solution of HCl (0·01M) whose ionic strength had been adjusted with $NaNO_3$.

RESULTS AND DISCUSSION

The principle of measurement of pH using the glass–calomel electrode assembly states that the emf, E, of the cell is related to the activity, a_{H^+}, of H^+ by:

$$E = E' - (RT/F) \ln a_{H^+} \tag{2}$$

where R is the gas constant, T is the absolute temperature, F is the Faraday constant and E' is a constant which is the sum of the standard electrode potential of the cell, the liquid junction potential and other contributions to the emf which do not arise from the cell reaction (e.g. the asymmetry potential of the glass electrode). The pH meter–electrode combination is calibrated using solutions of known H^+ activity at a given ionic strength and the pH of solutions to be measured may be read directly from the pH meter only if the value of E' is the same for the unknown as the calibrating solutions. Since the liquid junction and asymmetry potentials depend on ionic strength, the pH meter reading can only be used without correction if the ionic environments in the unknown and calibrating solutions are the same. This is clearly not the situation in the experiments described here.

It is impossible to measure reliably the variation in E' with ionic strength. Consider, however, two solutions containing the same H^+ concentration but at different ionic strengths. The activity coefficients of H^+, y_{H^+} (1) and y_{H^+} (2), in the two solutions will differ, as will the respective values of E', $E'(1)$ and $E'(2)$, when the apparent pH of these solutions is measured. Hence, the respective emf's $E(1)$ and $E(2)$ will be given by:

$$E(1) = E'(1) - (RT/F)\ln[H^+] - (RT/F)\ln y_{H^+}(1) \tag{3}$$

$$E(2) = E'(2) - (RT/F)\ln[H^+] - (RT/F)\ln y_{H^+}(2) \tag{4}$$

and the difference in potentials ΔE is:

$$\Delta E = \Delta E' - (RT/F)\ln\{y_{H^+}(1)/y_{H^+}(2)\} \tag{5}$$

The pH meter is calibrated as one pH unit per $2{\cdot}303RT/F$ volts and, therefore, the difference in apparent pH, ΔpH(app), is given by:

$$\Delta\text{pH(app)} = \Delta E'' - \log\{y_{H^+}(1)/y_{H^+}(2)\} \tag{6}$$

where E'' is the value of E' in the equivalent number of pH units. If solution 1 is 0·01 M HCl, the concentration of H^+ will be 0·01 M at all ionic strengths since the acid is completely dissociated. The value of $\log y_{H^+}(1)$ (actually $-0{\cdot}043$ (Robinson & Stokes, 1965)) remains constant as ionic strength is varied and if this is added to the ΔpH value, the effect of increasing ionic strength on $(\Delta E'' + \log y_{H^+})$ may be found from:

$$\Delta\text{pH(app)} - 0{\cdot}043 = \Delta E'' + \log y_{H^+} \tag{7}$$

The apparent pH of a half neutralised HSO_3^- solution at a given ionic strength will be lower than the value of $-\log a_{H^+}$ by an amount $\Delta E''$, or lower than $-\log[H^+]$ by $(\Delta E'' + \log y_{H^+})$. Equation (7) may, therefore, be used to obtain the true hydrogen ion *concentration* provided that E'' does not change with pH. This is a reasonable assumption. The value of this concentration at the half neutralisation point is the dissociation constant of HSO_3^- in terms of concentrations.

The relationship between the thermodynamic pK value, in terms of activities, pK(a), and that in terms of concentration is given by:

$$\text{pK} = \text{pK}(a) + \log y_{2-} - \log y_{-} + \log y_{H^+} \tag{8}$$

where y_{2-} and y_{-} represent the activity coefficients of SO_3^{2-} and HSO_3^-, respectively. At 30°C the activity coefficient of an ion at high ionic strength may be calculated from empirical extensions of the Debye Hückel theory as (Robinson & Stokes, 1965):

$$-\log y = 0{\cdot}52z^2I^{1/2}/(1 + BaI^{1/2}) - bI \tag{9}$$

where z is the charge on the ion, I is the ionic strength, $B = 3{\cdot}3 \times 10^9\,\mathrm{m}^{-1}\,\mathrm{M}^{-1/2}$, a is an ion size parameter and b an empirical constant. It is, however, not possible to predict reliably the activity coefficient of H^+ in this way and one solution is to consider measured values of the mean ionic activity coefficients of acids such as HCl or HNO_3. The value of y_{H^+} in 0·1 M HCl is 0·818 whilst the mean ionic activity coefficients of 0·1 M HCl and 0·1 M HNO_3 are, respectively, 0·796 and 0·791. These are, therefore, within 2–3% of the value of y_{H^+} at $I = 0{\cdot}1$ M and it is reasonable to use tabulated mean ionic activity coefficients of HNO_3 at the appropriate concentration as an estimate of y_{H^+} at the corresponding value of ionic strength, maintained by $NaNO_3$.

Table 1 gives the measured value of pH at half neutralisation for pH titrations at $I = 0{\cdot}08$–$4{\cdot}6$ M, the corresponding values of $(\Delta E'' + \log y_{H^+})$ and hence the pK of HSO_3^- in terms of concentration, the value of y_{H^+} interpolated from data for HNO_3 given by Robinson & Stokes (1965) and the calculated pK(a) using eqns (8) and (9) with $Ba \approx 1$ and a difference of 0·1 M^{-1} in the values of b for SO_3^{2-} and HSO_3^-. When taken simply as the pH at half neutralisation, the pK of HSO_3^- is seen to decrease with increase in ionic strength and the lowest value attained, pK 6·25, is the same as given by Shapiro (1977) for the pK in concentrated salt solution. The pH of 0·01 M HCl was found to be 2·02, in good agreement with the expected value of

TABLE 1

Effect of Ionic Strength, I on the pK of HSO_3^- at 30°C in the Presence of $NaNO_3$

I (M)	*Measured pH at half neutralisation*	$\Delta E'' + \log y_{H^+}$	*pK*	$\log y_{H^+}$	*pK(a)*
0·081	7·00	−0·163	7·16	−0·097	7·60
0·109	7·00	−0·188	7·19	−0·105	7·67
0·231	6·80	−0·218	7·02	−0·127	7·63
0·570	6·65	−0·266	6·92	−0·144	7·68
1·16	6·45	−0·333	6·78	−0·135	7·61
2·31	6·35	−0·461	6·81	−0·084	7·60
3·47	6·25	−0·590	6·84	−0·012[a]	7·52
4·58	6·25	−0·713	6·96	—	—

[a] Extrapolated value.

[b] y_{H^+} and $\Delta E''$ are, respectively, the activity of H^+ and the difference in the sum of the liquid junction and asymmetry potentials when pH is measured at $I = 0{\cdot}01$ M and the value shown. pK and pK(a) are, respectively, the pK values in terms of concentrations and activities. The value of $\Delta E'' + \log y_{H^+}$ was calculated from the pH of 0·01 M HCl at the ionic strengths shown. Each value of $\log y_{H^+}$ is equal to the mean ionic activity coefficient of HNO_3 at the ionic strength shown and was found from data tabulated by Robinson & Stokes (1965).

pH 2·04 (Robinson & Stokes, 1965). The corrected pK value in terms of concentration is seen to fall to a minimum value of approximately pK 6·8 ($I = 1$–2M). When the activity of H^+ is taken into account it is found that the activity coefficients of HSO_3^- and SO_3^{-2} follow the extended Debye Huckel expression from the relatively constant calculated value of pK(a). This is somewhat greater than pK 7·18 obtained previously from measurements on dilute solutions ($I = 0{\cdot}001$–$0{\cdot}01$M) at 25°C (Tartar & Garretson, 1941), but is, nevertheless, encouraging when the extent of the extrapolation to zero ionic strength, implied in the calculation of pK(a), and the approximations involved are taken into account.

The data given here also provide an insight into the effect of ionic strength on the significance of apparent pH measurements. It can be seen from Table 1 that the relationship between $\Delta E''$ and ionic strength is linear with a slope of 0·15M^{-1} for the electrode used for this work. Particular care is required in interpreting the measured pH value of foods and particularly when concentrated systems are studied.

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