Influence of humic acid on ionisation constants of sulphurous acid: Calcium sulphite precipitation during clarification of cane juice

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Received 1 November 2001; revised received 27 November 2002; accepted 5 January 2003

The presence of humic acid seems to decrease the rate of CaSO₃ precipitation during clarification of cane juice in the sugar manufacturing. The first and second ionisation constants of H₂SO₃ were found to decrease by 8% and 13% at RT in presence of humic acid in solution, respectively. However, the first and second ionisation constants of the acid were affected in the range 19-16% respectively across the temperature range 50-90°C. In the presence of humic acid the activation energy was found to increase. The nature of positive slope of Arrhenius plot indicates the diffusion controlled reaction in the precipitation reaction which is consistent with low value of activation energy of ionisation of sulphurous acid.

The Indian sugar industry employs two processes for clarification of cane juice for the manufacture of crystal sugar. These are carbonation and sulphitation processes in which the cane juice is treated with lime, carbon dioxide and sulphur dioxide, respectively. The clarification of cane juice by either of the processes is primarily controlled by maintaining optimum pH. During the passage of SO₂ into limed cane juice, the most predominate chemical reaction other than decolourisation is the precipitation of CaSO₃. The stoichiometry of the reaction is as follows:

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\text{Ca(OH)_2} + \text{SO}_2 + \text{H}_2\text{O} \rightarrow \text{CaSO}_{3} \downarrow + 2\text{H}_2\text{O} \\
\text{SO}_3^{2-} + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_3 \rightarrow \text{H}_2\text{O} + \text{HSO}_3^- \\
\text{HSO}_3^- \rightarrow \text{H}^+ + \text{SO}_3^{2-} \\
\text{Ca}^{2+} + \text{SO}_3^{2-} \rightarrow \text{CaSO}_3 \downarrow
\]

The chemistry of cane juice clarification involves the removal of non-sugars. The removable could be organics, inorganics, precipitates, colourants or even colloids, etc. All of them are primarily governed by ionic reaction and/or an adsorption mechanism. In the present contribution, the influence of a cane juice colourant; humic acid on ionisation constants of sulphurous acid during precipitation of calcium sulphite is investigated.

Experimental Procedure

Humic acid was isolated from clarified cane juice by the method described elsewhere. Its isolation was confirmed by IR and UV absorption spectrum of the isolated product. The absorption peak at 3080 cm⁻¹ indicated the present of C-H groups. Other peaks at 1660 and 1590 cm⁻¹ suggested the presence of quinol and >C=C< groups respectively. In order to observe the effect of humic acid on ionisation constants of sulphurous acid a series of pH titrations of sulphurous acid with Ca(OH)₂ solution were performed. Fused CaO (15%) was used for liming of juice and limed juice was sulphited from SO₂ gas supplied by SPUN MAD ICCSE- 500 N 546. The supernatant solution of lime slurry was filtered through Whatman #1 filter paper. EDTA di-sodium salt (M/56) was prepared in deionised water. Eriochrome black T (Merc) and starch solution (1%) were used as indicators for the estimation of CaO and SO₂, respectively. The concentration of SO₂ and Ca²⁺ ion in solutions were determined iodimetrically and by EDTA titration, respectively.

Calibration of pH meter

The pH meter employed (CP-901-P) was calibrated with buffer solutions of known pH values of 4.0 and 7.0 respectively using 0.2 N 9.0 mL CH₃COONa + 0.2N 41.0 mL CH₃COOH (by standardisation) and 12.40 g H₃BO₃ + 0.93 g NaCl in one litre. Once the instrument is calibrated to give the known pH of the buffer solutions, pH of experimental solutions can be obtained directly without any calculation. This pH meter measures the pH in the range of 0-14 with an accuracy of ± 0.01 pH.
pH-metric titrations

In 20 mL sulphurous acid (SO₂ + H₂O solution) containing 10 kg/L SO₂ was titrated with Ca(OH)₂ solution by measuring the pH as function of Ca(OH)₂. In another four sets, 10 mL of sulphurous acid was diluted with 8, 6, 4, and 2 mL of deionised water and 2, 4, 6 and 8 mL of (0.1%) humic acid solution was added to each solution, respectively keeping volume equal to 20 mL in each case. Each solution was titrated with Ca(OH)₂ solution and change in pH was recorded as a function of volume of alkali using a digital pH meter.

Results and Discussion

All pH titration curves are shown in Fig. 1 in which curve I refers to the pure sulphurous acid titration whereas curves II, III, IV and V correspond to the titration of H₂SO₄ in presence of 100, 200, 300 and 400 ppm humic acids, respectively. At a glance it could be noticed from Fig. 1 that the presence of humic acid in (SO₂+H₂O) solution has marked influence on the titration curve showing increase in consumption of Ca(OH)₂ for neutralization and its consumption appears to be proportional to the concentration of humic acid. It is observed further that pH increases slightly in the range 1.5-3.0. However, beyond pH 3.0, the value increases abruptly to 6.0 on addition of only 0.044 millimole Ca(OH)₂ solution showing the first inflection in the titration curve. The second inflection was observed when lime just exceeds 0.325 millimole.

Since in the above observations the effect of humic acid on both the ionisation constants of sulphurous acid was fairly established. It was, therefore, decided to observe the effect of temperature on the ionisation constants of pure H₂SO₄ in presence of humic acid. In order to observe the effect of temperature of sulphurous acid with Ca(OH)₂ solution were also performed at higher temperatures viz. 50, 70 and 90°C in absence and presence of 250 ppm humic acid in sulphurous acid. The data are shown in Figs 2 and 3. In Figs 2 and 3 curves A, B, C and D correspond to the titrations data at 25, 50, 70 and 90°C, respectively. Fig. 2 demonstrates that the temperature has marked effect on the titration curves. These titration curves were utilized to determine the ionisation constant of sulphurous acid in each case by the half equivalence method.

Half equivalence method

Let the ionisation and neutralisation of H₂SO₄ be considered.

![Fig. 1—pH metric titration of H₂SO₄ and H₂SO₃ containing humic acids with Ca(OH)₂ at room temperature.](image1)

![Fig. 2—pH metric titration of sulphurous acid with Ca(OH)₂ in absence of humic acid at different temperatures.](image2)

![Fig. 3—pH metric titration of sulphurous acid with Ca(OH)₂ in presence of humic acid at different temperatures.](image3)
The first and second ionisation constants of sulphurous acid are decreased by 8% and 13% in presence of 100 ppm of humic acid in solution, respectively.

Ionisation constants of sulphurous acid at different temperatures in absence of humic acid are given in Table 2. The first and second ionisation constants of sulphurous acid at 25°C are reported to be $1.47 \times 10^{-2}$ and $2.88 \times 10^{-7}$ respectively. These values differ only by 4.05% and 5.73% respectively from literature value. At 25°C both ionisation constants of the acid in presence of humic acid are $1.20 \times 10^{-2}$ and $2.51 \times 10^{-7}$ respectively which differ by 10 and 13% from that of pure sulphurous acid. Both the values of ionisation constants in absence and presence of humic acid at 50, 70, and 90°C differ by 19, 17, 19, and 20% respectively. Therefore, on an average it is approximated that at all temperatures the first and second ionisation constants of acid in absence and presence of humic acid are affected by 19% and 16%, respectively. Ionisation constants of sulphurous acid at different temperatures either in pure form or in presence of humic acid solution employed for Arrhenius plot in both cases gave positive slopes. Activation energy of first and second ionisation of the acid in presence and in absence of humic acid were calculated by the slopes equal to $-E_A/2.303 R$ form the Arrhenius plots shown in Figs 4 & 5. The energy of activation of first and second ionisation of sulphurous acid in absence of humic acid were 3.51 and 2.01 kcal mole$^{-1}$, respectively while in presence of 250 ppm of humic acid...
these values increased to 3.66 and 2.28 kcal mol$^{-1}$, respectively.

In the present case the Arrhenius plots demonstrate a positive slope. However, the precipitation of CaSO$_3$ in water and in sugar solution in the absence of humic acid$^7$ is governed by a mechanism which is different from that in the presence of humic acid. The slope of the Arrhenius plot was found negative indicating that precipitation reaction is controlled by an activation process. The nature of positive slopes of Arrhenius plots (Figs 4 & 5) indicate the diffusion controlled reaction in the precipitation reaction which is consistent with low value of activation energy of ionisation of sulphurous acid. Thus, in general the presence of humic acid seems to decrease the rate of precipitation reaction.

References