

# Activity Coefficients of Sodium Sulfite in Aqueous Solution at 25° C.

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SODIUM SULFITE and bisulfite are active reagents in various processes for the separation of cellulose from wood and agricultural residues. In designing spent liquor recovery processes involving absorption with chemical reaction, it is most important to have a knowledge of the activity coefficients of the various salts present. Further, even rather empirical kinetic studies of the pulping reactions require an appreciation of the activities of the postulated reactants.

While the work of Johnstone, Read, and Blankmeyer (1) provides valuable information on the activity of sulfur dioxide in certain sodium sulfite-bisulfite solutions, data have been lacking on the activity coefficients of sodium sulfite itself. It was one purpose of the present investigation to provide data at 25° C.

## EXPERIMENTAL PROCEDURE

In the isopiestic vapor-pressure comparison technique, two solutions are isopiastically compared by being placed in separate dishes in a closed vessel at constant temperature. The solvent is the same in both solutions. Solvent from the solution which has the higher vapor pressure, or more strictly, the higher solvent activity, distills into the vapor space above the dishes and condenses into the other solution. At equilibrium, the two solutions have equal solvent activities. The concentrations of the solutions at equilibrium are calculated from the initial concentrations of the solutions and the mass of solvent gained or lost during the equilibration.

The apparatus and procedure used for the isopiestic measurements were essentially the same as those used by Sinclair (6) and Robinson and Sinclair (4). The closed vessel used for the equilibration was a vacuum desiccator. The solutions were weighed into small dishes made of fine silver, and the dishes were placed on a disk of high conductivity copper mounted inside the desiccator. The desiccator was evacuated to a pressure of about 20 mm. of mercury before being placed in the constant temperature bath controlled at  $25.000^\circ \pm 0.005^\circ$  C.

If the activity coefficients of the solute in one of the solutions are known, the coefficients in the other solution can be calculated from the isopiestic data. The solute for which the activity data are known is called the "reference" solute. In these measurements, aqueous sodium sulfite solutions were equilibrated isopiastically with aqueous sodium chloride solutions at 25° C.; the activity coefficient data for sodium chloride in aqueous solution are well established (5).

The sodium chloride reference solutions were prepared from Baker's reagent grade sodium chloride and deaerated conductivity water. A sodium chloride solution having a concentration of about 6 molal was prepared gravimetrically as a stock solution. A stock sodium sulfite solution having a concentration of about 2 molal was prepared gravimetrically by adding the stoichiometric amount of sulfur dioxide to a concentrated sodium hydroxide solution, so that the ratio of sulfur dioxide to sodium in the final solution was exactly 0.5. The sodium hydroxide solution was prepared from Baker's reagent grade 50% sodium hydroxide solution. Its concentration was determined gravimetrically by

converting the sodium hydroxide to sulfate with sulfuric acid. The sulfur dioxide used was Ansul's refrigeration grade having a manufacturer's assay of 99.98%. During the preparation and handling of these solutions, care was taken to keep oxygen exposure to a very minimum, as sulfite solutions are oxidized by exposure to air. The preparation of the sodium sulfite solutions and the various steps in the isopiestic procedure involving exposure of the solutions were carried out in a nitrogen chamber where the oxygen level was maintained below 2000 p.p.m.

## EXPERIMENTAL RESULTS

The results of the isopiestic measurements are given in Table I. The last column gives the isopiestic ratios of sodium sulfite and sodium chloride. The isopiestic ratio is defined as the product of the number of ions produced by the dissociation of one molecule of the reference electrolyte and the molality of that electrolyte divided by the product of the number of ions produced by the dissociation of one molecule of the other electrolyte and the molality of that electrolyte. In this case the isopiestic ratio is equal to  $2m_R/3m_1$ . With the exception of run 42, all values in Table I are the mean of three individual determinations—that is, the solutions in six dishes, three containing sodium sulfite solution and three containing sodium chloride solution, were equilibrated at the same time. The data for run 42 are based on two determinations. The number in parenthesis after each value is the standard deviation of the mean value expressed as a percentage of the mean value. A run was rejected on the basis of failure to reach equilibrium if the standard error of the isopiestic concentration of one of the solutions was greater than 0.1%. It was necessary to accept slightly greater standard errors when the concentrations were below 0.5 molal because of the magnification of errors at these low concentrations.

It is believed that the small amount of impurities present in the sodium chloride and sodium sulfite solutions had no significant effect on the isopiestic data. The stock sodium chloride solution was compared isopiastically with a potassium chloride solution prepared from Baker's reagent grade potassium chloride. The results agreed with data in the literature to within 0.01%. The carbonate contamination of the sulfite solutions was minimized by starting with a 50% sodium hydroxide solution containing 0.02% carbonate and using deaerated water exposed only to nitrogen after deaeration. The effect of the presence of up to 2000 p.p.m. of oxygen in the nitrogen chamber was shown to be negligible. One particular run was exposed to the chamber atmosphere long enough to allow for about 80 times more oxygen diffusion into the solutions than would occur during the normal procedure. The results of this run agreed within 0.1% with the results of the other runs. A reddish brown precipitate resembling ferric hydroxide settled out of the stock sodium sulfite solutions. Spectrographic analysis showed that it was mostly iron. Because the precipitate settled out of solution and amounted to only 0.0008% of the total mass solution, it was concluded that its presence had no effect on the isopiestic data.

The reproducibility of the data was demonstrated for both the sodium chloride and the sodium sulfite solutions. Runs were made with different sodium chloride solutions

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and the same sodium sulfite solutions, and vice versa. There was no significant difference in the results.

The isopiestic data given in Table I were plotted on graph paper of sufficient size to allow interpolation of the data for even values of molality within the accuracy of the isopiestic measurements. The interpolated values were used for the activity coefficient calculations. It is believed that the standard error of the interpolated isopiestic data is about 0.1%.

#### CALCULATION OF ACTIVITY COEFFICIENTS

The activity coefficients of sodium sulfite were calculated from an integrated form of the Gibbs-Duhem equation (Equation 1) and an extended form of the Debye-Hückel equation (Equation 2):

$$\ln(\gamma_1/\gamma_{1,r}) = \ln(\gamma_R/\gamma_{R,r}) + \ln \frac{m_R/m_1}{(m_R/m_1)_r} + 2 \int_{a_{\pm R,r}}^{a_{\pm R}} \left( \frac{2m_R}{3m_1} - 1 \right) \frac{d(a_{\pm R})^{1/2}}{(a_{\pm R})^{1/2}} \quad (1)$$

and

$$\ln \gamma_1 = \frac{-1.0165(I)^{1/2}}{1 + A(I)^{1/2}} + Bm_1 \quad (2)$$

Equation 1 is equivalent to Equation 8.4 of Robinson and Stokes (5); it has been integrated using a finite, dilute concentration designated by subscript  $r$  as the lower limit of integration. Equation 2 has been shown to represent activity coefficient data up to 1 molal concentrations for many electrolytes and even up to 2 molal for some electrolytes. This equation was fitted to the activity coefficient ratio data calculated from Equation 1. Then  $\gamma_{1,r}$  was calculated from the fitted equation and used to calculate the activity coefficient data given in Table II from the activity coefficient ratio data. The activity coefficients shown in parenthesis in Table II were calculated from the fitted Debye-Hückel equation.

Because of the uncertainty of isopiestic data obtained on solutions of low concentration, the isopiestic data for sodium sulfite were plotted as the vapor pressure of water above the sodium sulfite solutions vs. the mole fraction of water in the solution. This plot became linear as the mole fraction of water approached unity and thus the extrapolation to infinite dilution was fairly certain. Comparison of the isopiestic data calculated from this plot with the measured isopiestic data indicated that the 0.2 molal data point was in error. The values of the isopiestic ratio calculated from such a plot are not sufficiently accurate for extending the experimental isopiestic data to more dilute concentrations; a very small error in the vapor pressure data produces a large error in the calculated isopiestic ratios.

Because of this uncertainty in the 0.2 molal data point, the activity coefficient ratios were calculated using both

Table I. Molalities of Isopiestic Sodium Sulfite and Sodium Chloride Solutions at 25° C.

Molality of NaCl, $m_R$	Molality of Na <sub>2</sub> SO <sub>3</sub> , $m_1$	Isopiestic Ratio, $2m_R/3m_1$
0.2595 (0.11%) <sup>a</sup>	0.2071 (0.06%)	0.8354 (0.12%)
0.4920 (0.16%)	0.4095 (0.08%)	0.8010 (0.18%)
0.8982 (0.04%)	0.7844 (0.05%)	0.7633 (0.07%)
1.195 (0.02%)	1.073 (0.04%)	0.7425 (0.05%)
1.233 (0.09%)	1.110 (0.08%)	0.7409 (0.12%)
1.304 (0.06%)	1.178 (0.01%)	0.7381 (0.06%)
1.571 (0.06%)	1.436 (0.07%)	0.7294 (0.10%)
1.892 (0.07%)	1.742 (0.09%)	0.7240 (0.12%)
2.028 (0.02%)	1.865 (0.05%)	0.7251 (0.05%)
2.239 (0.07%)	2.058 (0.07%)	0.7252 (0.10%)

<sup>a</sup> Number in parenthesis after each value is the standard error of the value expressed as a percentage of the value.

Table II. Activity Coefficients of Sodium Sulfite at 25° C.

Molality	Activity Coefficients
0.0333	(0.5710) <sup>a</sup>
0.0667	(0.4863)
0.1	(0.4378)
0.2	(0.3600)
0.3	(0.3189)
0.4	(0.2920)
0.5	0.2724
0.6	0.2572
0.7	0.2448
0.8	0.2345
0.9	0.2257
1.0	0.2179
1.2	0.2055
1.4	0.1962
1.6	0.1895
1.8	0.1844
2.0	0.1806

<sup>a</sup> Values in parentheses calculated from fitted Debye-Hückel equation.

0.2 and 0.4 molal solutions as the solutions designated by subscript  $r$  in Equation 1. It is estimated that the calculated ratios have a standard deviation of about 0.2%. Also, the extended form of the Debye-Hückel equation (Equation 2) was fitted to both sets of calculated activity coefficient ratio data using the method of Jones and Dole (2). The equation was fitted to the activity coefficient ratio data for even values of the molality up to 1.0. In the case of the 0.2 molal solution, it was not possible to fit the equation within the accuracy of the activity coefficient ratio data. However, the equation was readily fitted within the accuracy of the activity coefficient ratio data in the case of the 0.4 molal solution. On the basis of the results of these two cases and the previous indication of the unreliability of the 0.2 molal data point, this point was discarded.

An unsuccessful attempt was made to fit the Debye-Hückel equation to the activity coefficient ratio data from 0.4 to 1.4 molal. It was concluded that this equation could not represent the activity coefficient data for sodium sulfite much above a concentration of 1.0 molal. The values of  $A$  and  $B$  obtained for the fitted Debye-Hückel equation were 1.0310 and  $-0.0295$ , respectively. The value of  $\gamma_{1,r}$  was calculated from this equation and used to calculate the values of the activity coefficients from the ratio data.

The degree of hydrolysis was estimated by a method similar to that used by Taylor (7), except that actual activity coefficient data for sodium bisulfite (3) were used. The equation used is

$$K_H = \frac{K_w}{K_2} = \frac{m_1 x^2}{(1-x)} \left( \frac{\gamma_{\text{HSO}_3^-} \gamma_{\text{OH}^-}}{\gamma_{\text{SO}_3^{2-}}} \right) \quad (3)$$

which is analogous to Equation 6 of Taylor. Equation 3 is strictly valid only at infinite dilution; it is not known how well this relationship holds as the concentration is increased. The degree of hydrolysis in a 0.4 molal sodium sulfite solution was calculated from this equation to be 0.00024. Thus, it is evident that the hydrolysis of sodium sulfite has a negligible effect on the value of the activity coefficients calculated by the above procedure. The degree of hydrolysis varies with concentration: At 0.1 molal, it is 0.001; at 2.0 molal, it is 0.00007.

There is no way to determine the accuracy with which the Debye-Hückel equation represents the activity coefficient data below the concentrations for which experimental data have been reliably measured. It was estimated that the calculated activity coefficient ratios have a standard error of about 0.2%. On the basis of past success in using the Debye-Hückel equation, the closeness of fit in this application, and the accuracy of the activity coefficient data, it is believed that the standard error of the activity coefficient data for sodium sulfite does not exceed 0.5%.

## NOMENCLATURE

- $a_{\pm}$  = mean ionic activity  
 $A$  = constant in Debye-Hückel equation  
 $B$  = constant in Debye-Hückel equation  
 $I$  = total ionic strength of Lewis and Randall  
 $K_H$  = hydrolysis constant  
 $K_w$  = ionization constant of water  
 $K_2$  = second ionization constant of sulfurous acid  
 $\ln$  = natural logarithm  
 $m$  = molality, moles/1000 grams of solvent  
 $x$  = degree of hydrolysis—the fraction of the sodium sulfite that is hydrolyzed  
 $\gamma$  = mean ionic molal activity coefficient

## Subscripts

- 1 = refers to sodium sulfite  
 $r$  = refers to dilute solution used for lower limit of integration in Equation 1  
 $R$  = refers to sodium chloride reference solution

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# Explosion Limits of Liquid Systems Containing Hydrogen Peroxide, Water, and Oxygenated Organic Compounds

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**STUDIES** on the explosive limits at room temperature of hydrogen peroxide-water systems containing methanol (4), ethanol (4), or glycerol (4, 8) show that the regions of unstable compositions are well defined. In this investigation, an attempt has been made to assess the effect of such factors as temperature and type of initiation on mixtures of hydrogen peroxide and water with various organic compounds such as 2-propanol, all of which are soluble in hydrogen peroxide. As yet the effect of temperature has not been described in the literature.

Several types of initiation are described—impact, blasting cap, and a high velocity shock wave.

For some compositions, the over-all reaction between the organic materials and hydrogen peroxide can proceed at a rate such that a stable detonation wave is propagated through the liquid. Near the limits determined by impact or blasting cap, however, the reactions are more nearly characteristic of rapid deflagration or explosion than of sustained detonations. In all of these instances, the force of the reaction is sufficient to lead to the destruction of containers and considerable damage to the surroundings. A knowledge of the explosion boundaries will thus define the limits of safe operation or safe handling of mixtures of hydrogen peroxide and organic compounds. These bound-

aries have been well defined for many systems and may be easily determined by a simple impact test for others.

## METHODS OF MEASUREMENT

**Impact Tests.** Two types of impact testers have been used during the investigation. The simpler of these is a modification of the test apparatus described by Bellinger (1).

The piston and cylinder ( $1\frac{3}{8}$  and 1 inch long, respectively, and  $0.3 \pm 0.0002$  inch in diameter, lapped to fit) were of hardened tool steel for greater reproducibility of the impact shock. Straight pins without enlarged heads were less susceptible to breakage but required a guide pipe to center the striking blow delivered by a 360-gram weight falling from a height of 180 cm.

The more complicated apparatus shown in Figure 1 was designed to study the effect of higher temperatures on the explosion limits. A 500-gram weight falling 200 cm. drives the piston into the chamber containing the test solution with approximately 50% greater energy than the first tester. The steam jacket around the cavity allows the attainment of elevated temperatures (within 20 to 30 seconds) just prior to the moment of impact. The packing gland prevents evaporation from the hot sample.

Both instruments were designed with a small cavity or