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Diffusion Coefficient of Aqueous Sulfur Dioxide at 25 °C

Derek G. Leaist

Department of Chemistry, University of Western Ontario, London, Ontario, Canada N6A 5B7

The diffusion coefficient of aqueous sulfur dioxide has been measured at 25 °C over the concentration range 0.003–0.1 mol dm^{-3} by the Harned conductimetric technique. At concentrations less than about 0.02 mol dm^{-3}, extensive hydrolysis to bisulfite and hydrogen ions produces a sharp increase in the rate of diffusion of the sulfur dioxide component. The observed concentration dependence of the diffusion coefficient is consistent with theory for diffusion with simultaneous hydrolysis.

Introduction

Absorption and diffusion of sulfur dioxide into water are processes of importance to the chemical industry and to pollution studies. The transport properties of this system are complicated by the fact that aqueous sulfur dioxide diffuses as molecular species together with bisulfite and hydrogen ions produced by hydrolysis. In dilute solutions where most of the dissolved gas is hydrolyzed, a sharp increase in the rate of diffusion of the sulfur dioxide component may be anticipated as a consequence of the aqueous hydrogen ion's exceptional mobility.

The diffusivity of aqueous sulfur dioxide has been estimated in previous studies from rate of uptake of the gas by water (*1–4*). However, the concentration dependence of the diffusivity was neglected in those studies. Furthermore, the reported data vary by up to 25%. Accurate values of the diffusion coefficient of aqueous sulfur dioxide reported here were determined as a function of concentration by a conductimetric technique. The present data are compared with behavior predicted by theory (*5*) for diffusion with simultaneous hydrolysis.

Experimental Section

Procedure. Diffusion coefficients were determined by Harned's conductimetric technique (*6*, *7*). This method was chosen because it can provide accurate data at low concentrations where hydrolysis is extensive. In the conductimetric experiment, electrolyte is diffused in a vertical column of solution. The rate of diffusion is followed by measuring the electrical conductivity near the top and bottom of the column. Because the concentration gradient along the column is very small, the measured diffusion coefficient corresponds to the differential diffusion coefficient at the final cell concentration (*6*, *7*). (Integral diffusion coefficients, such as those obtained from rates of gas absorption or by diaphragm cell techniques, are determined over a range of concentration. Consequently, integral data are more difficult to interpret, especially in cases such as the present one where the rate of diffusion is sensitive to concentration.)

The conductimetric cells (*6*, *7*) used in this study were constructed with cylindrical diffusion channels (height 5.334 cm, bore 1.270 cm) machined from high-density polyethylene. Circular platinum electrodes (diameter 1 mm) were cemented with epoxy into holes drilled at one-sixth of the distance from the top and bottom of the chambers. At the start of a run, the diffusion chambers were filled with conductivity water and then sealed at the top with glass slides lubricated with Apiezon M grease. Following thermal equilibration at 25 ± 0.01 °C, concentration gradients were formed by carefully introducing the appropriate volume of approximately 1 mol dm^{-3} aqueous sulfur dioxide into the bottom of each chamber via syringe (*8*). Conductances were measured with a Leeds and Northrup Jones bridge 1–2 days after injection of electrolyte for an additional 3–4 days. Details of the data analysis procedure have been described (*9*, *10*).

Table I. Diffusion Coefficient of Aqueous Sulfur Dioxide at 25 °C

$c/10^{-3}$, mol dm^{-3}	α	$y_\pm$	f	$D/10^{-9}$, m^2 s^{-1}
0.0	1.00	1.000	2.000	2.316[a]
2.8	0.86	0.948	1.718	2.130
5.4	0.78	0.934	1.608	2.076
9.5	0.70	0.920	1.506	2.021
20.5	0.58	0.898	1.379	1.950
29.7	0.52	0.888	1.326	1.924
52.1	0.43	0.870	1.256	1.891
70.3	0.39	0.861	1.225	1.876
84.4	0.36	0.855	1.207	1.868
97.2	0.35	0.851	1.194	1.862

[a] From eq 1.

Final cell concentrations were determined in situ from the measured conductances and published specific conductivity data (*11*). This procedure avoids possible errors caused by volatilization of sulfur dioxide. Cell constants were determined by calibration with potassium chloride solutions.

Materials. Linde anhydrous sulfur dioxide was distilled once and used without further purification. Sulfur dioxide solutions were freshly prepared prior to each run by bubbling the gas through deaerated water that had been deionized and twice distilled. Reagent-grade potassium chloride was dried at 130 °C.

Results and Discussion

Diffusion coefficients of aqueous sulfur dioxide are listed in Table I. The accuracy of the data is 0.5–1%. At concentrations below about 0.02 mol dm^{-3}, the diffusion coefficient rises sharply as the concentration drops. In this region an appreciable fraction of the sulfur dioxide component is converted by hydrolysis into more-rapidly diffusing bisulfite and hydrogen ions:

$$SO_2 + H_2O \rightleftharpoons HSO_3^- + H^+ \qquad \text{(I)}$$

The limiting value of the diffusion coefficient at zero concentration for completely hydrolyzed sulfur dioxide was determined from limiting ionic conductivities (*11*, *12*)

$$\lambda^\circ_{H^+} = 0.03498 \text{ m}^2\ \Omega^{-1}\ \text{equiv}^{-1}$$

$$\lambda^\circ_{HSO_3^-} = 0.00497 \text{ m}^2\ \Omega^{-1}\ \text{equiv}^{-1}$$

with the Nernst equation

$$D_\pm^\circ = 2RT\lambda^\circ_{H^+}\lambda^\circ_{HSO_3^-}/F^2(\lambda^\circ_{H^+} + \lambda^\circ_{HSO_3^-}) \qquad (1)$$

For purposes of comparison, Table I includes values of α, the apparent degree of hydrolysis

$$\alpha = [HSO_3^-]/([HSO_3^-] + [SO_2]) \qquad (2)$$

calculated from the equilibrium condition of reaction I

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$$K = \alpha^2 c y_\pm^2/(1 - \alpha) \qquad (3)$$

with hydrolysis constant $K = 0.013$ mol dm^{-3} at 25 °C (*13*). The mean ionic activity coefficient on the molar concentration scale, $y_\pm$, was estimated (*13*) from values of the mean molal activity coefficient of aqueous hydrochloric acid (*14*, *15*) at the same ionic strength. Molal activity coefficients were converted to the molar scale by using published density data (*14*). Because the solutions were dilute, the activity coefficient of the molecular species was set equal to unity (*13*).

Hydrolysis influences the diffusion coefficient in two important ways (*5*). First, for a given concentration gradient, hydrolysis increases the gradient in chemical potential, $\nabla\mu$ (the "driving force" for diffusion). On the other hand, because transport of hydrolysis products H^+ and HSO_3^- is subject to more frictional resistance than transport of a single molecular species, hydrolysis tends to reduce the effective mobility of the sulfur dioxide component. Compared to the duration of a typical conductimetric experiment (~400 000 s), the rate of hydrolysis (*16*) is virtually instantaneous. Thus, chemical equilibrium may be assumed at each point along the diffusion path. Under these conditions diffusion of the solute component is described by a single diffusion coefficient, regardless of the number of solute species present. Further, the diffusion coefficient of the solute component can be estimated from the concentrations and diffusion coefficients of the various solute species. The following expression has been obtained (*5*) for the diffusion coefficient of aqueous sulfur dioxide

$$D = [(1 - \alpha)D_m + (\alpha D_\pm^\circ/2)]f \qquad (4)$$

f is the dimensionless thermodynamic factor evaluated from

$$f = \frac{c}{RT}\frac{\partial\mu}{\partial c} = \frac{2}{2-\alpha}\left(1 + \alpha\frac{\partial \ln y_\pm}{\partial \ln c}\right) \qquad (5)$$

The diffusion coefficient D_m appearing in eq 4 is the number-weighted average of the diffusion coefficients of the neutral solute species: unhydrated molecular SO_2; and the free acid, H_2SO_3. Because the activity of water in dilute solutions is effectively constant, the equilibrium $SO_2 + H_2O \rightleftharpoons H_2SO_3$ ensures that the SO_2 and H_2SO_3 species are present in constant proportion. Therefore, separate values of their diffusivities are not required to describe diffusion of the sulfur dioxide component at the various concentrations studied here. Also, changes in the viscosity of the solutions are small and have negligible effect on the rate of diffusion.

In previous studies of weak electrolyte transport (*17–19*), diffusion coefficients of the neutral species were estimated by extrapolation to zero concentration of precise diffusion coefficients measured at concentrations where the degree of ionization is negligible. Unfortunately, ionization is too extensive for this procedure to be feasible for sulfur dioxide solutions. Instead eq 4 was fitted to the data listed in Table I with D_m as the adjustable least-squares parameter. Allowance was made for experimental error by assigning weights $(1 - \alpha)^2 f^2$ to each data point. The value of D_m obtained by this procedure is 1.77×10^{-9} m^2 s^{-1}. The data and fitted curve are compared in Figure 1. Agreement between the two is very good.

Infrared studies (*20*) provide convincing evidence that aqueous sulfur dioxide solutions do not contain significant amounts of the H_2SO_3 species. The value of D_m quoted above is thus a close approximation to the diffusion coefficient of molecular SO_2. The diffusion coefficient of the bisulfite ion is considerably smaller: 1.32×10^{-9} m^2 s^{-1}. This may be explained, qualitatively, by the smaller Stokes-law radius of the unhydrated SO_2 species. At extremely low sulfur dioxide concentrations ($\lesssim 10^{-5}$ mol dm^{-3}) the equations presented here would have to be elaborated to allow for dissociation of bisulfite to sulfite and hydrogen ions: $HSO_3^- \rightleftharpoons SO_3^{2-} + H^+$.

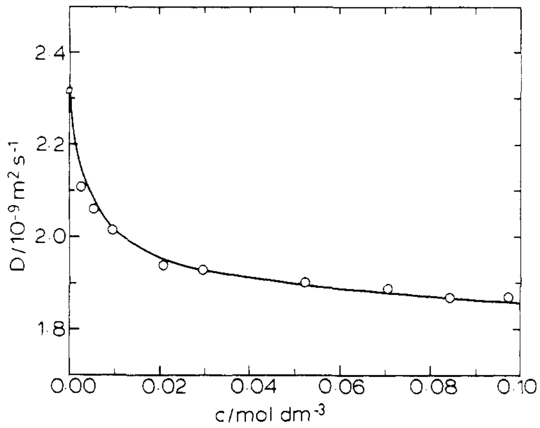

Figure 1. Comparison of observed diffusion coefficients with eq 4.

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Glossary

[A]	concentration of species A, mol dm^{-3}
c	$[HSO_3^-] + [SO_2]$ = total concentration of sulfur dioxide, mol dm^{-3}
D	diffusion coefficient, m^2 s^{-1}
$D_\pm^\circ$	limiting ionic diffusion coefficient defined by eq 1, m^2 s^{-1}
D_m	number-average diffusion coefficient of molecular species, m^2 s^{-1}
f	thermodynamic factor defined by eq 5, dimensionless
F	the Faraday, C mol^{-1}
K	equilibrium constant for hydrolysis, mol dm^{-3}
R	gas constant, J K^{-1} mol^{-1}
T	temperature, K
$y_\pm$	mean molar ionic activity coefficient, dimensionless
α	degree of hydrolysis defined by eq 2, dimensionless
∇	gradient operator, m^{-1}
λ°_i	limiting ionic equivalent conductance of ion, m^2 Ω^{-1} equiv $^{-1}$
μ	solute chemical potential, J mol^{-1}

Registry No. SO_2, 7446-09-5.

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