

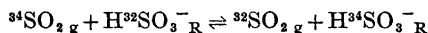
## Sulfur Isotope Effects

## IV. Sulfur Isotope Effects in Anion Exchange Systems

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Measurements of the isotopic exchange coefficient for the sulfur isotopes  $^{34}\text{S}$ – $^{32}\text{S}$  at  $25^\circ\text{C}$  in the ion exchange reaction  $\text{HSO}_3^-_{\text{aq}} = \text{HSO}_3^-_{\text{R}}$  have been carried out by means of adsorption experiments, and the isotope effect for the gross heterogeneous chemical exchange equilibrium



measured by displacement experiments in a "fluidized anion-exchanger bed". (g, aq and R relate to gaseous, aqueous, and resinous phase, respectively.)

The first investigations on the isotopic exchange of sulfur isotopes between an aqueous solution of sulfur dioxide and strongly basic anion exchangers saturated with hydrogen sulfite were carried out by Forberg *et al.*<sup>1-3</sup> The effect studied was, however, a gross effect due to the weighted averages of many sequential isotope exchange equilibria.

The aim of the present work has been to measure the isotope effects in the pure ion-exchange reaction  $\text{HSO}_3^-_{\text{aq}} = \text{HSO}_3^-_{\text{R}}$ , for the system  $\text{SO}_2_{\text{g}} - \text{HSO}_3^-_{\text{R}}$  and to relate the results obtained to the system  $\text{SO}_2_{\text{g}} - \text{HSO}_3^-_{\text{aq}}$ .

The isotope effect in the ion-exchange reaction  $\text{HSO}_3^-_{\text{aq}} \rightleftharpoons \text{HSO}_3^-_{\text{R}}$  can be measured by sorbing  $\text{HSO}_3^-$  ions from a large excess of hydrogen sulfite solution on a chloride saturated strongly basic anion exchanger and determining the  $^{34}\text{S}/^{32}\text{S}$  ratio in the solution and the ion-exchanger after adsorption. The exchange coefficient is then defined by

$$\alpha_{\text{sR}} = \frac{[^{34}\text{S}/^{32}\text{S}]_{\text{R}}}{[^{34}\text{S}/^{32}\text{S}]_{\text{aq}}} \quad (1)$$

where R and aq relates to resinous and aqueous phase, respectively.

The gross isotope effect in the heterogeneous system  $\text{SO}_{2\text{g}} - \text{HSO}_3^-_{\text{R}}$  can be measured by means of a desorption or displacement method as follows. A strongly basic anion exchanger is held dispersed in water by a stream of inert gas which also gives a continuous mixing of the exchanger beads (fluidized bed). Hydrochloric acid is continuously fed into the system, hydrogen sulfite ions in the resinous phase are displaced by chloride ions, and the  $\text{SO}_{2\text{aq}}$  formed is flushed out of the system by the stream of inert gas. If this process is carried out sufficiently slowly isotopic equilibrium exists at all time and the method is analogous to a Rayleigh distillation.

Thus the exchange coefficient, defined as

$$\alpha_{\text{SR}} = \frac{[^{34}\text{S}/^{32}\text{S}]_{\text{R}}}{[^{34}\text{S}/^{32}\text{S}]_{\text{aq}}} \quad (2)$$

can be calculated from the Rayleigh equation.<sup>4,5</sup>

$$\alpha_{\text{GR}} = \frac{\ln[S_1/S_2] + \ln[(1-x_1)/(1-x_2)]}{\ln[S_1/S_2] - \ln[(1-x_1)/(1-x_2)]} \quad (3)$$

where  $S_1$ ,  $x_1$  and  $S_2$ ,  $x_2$  denote the total amount of sulfur and the isotope fraction  $^{34}\text{S}/^{32}\text{S}$  in the resinous phase before and after displacement respectively.

## EXPERIMENTAL

The experiments were carried out with three different strongly basic anion exchangers

Dowex 1 × 8;	50–100 mesh	$\phi\text{-N}^+(\text{CH}_3)_3$
Dowex 2 × 8;	50–100 mesh	$\phi\text{-N}^+(\text{CH}_3)_2\text{C}_2\text{H}_5\text{OH}$
Dowex 21 K;	50–100 mesh	$\phi\text{-N}^+(\text{CH}_3)_3$
$(\phi = \text{C}_6\text{H}_5)$		

*Solutions.* The solutions were prepared and analyzed as described in Ref. 4.

*Sorption experiments.* Hydrogen sulfite ions were sorbed on 30 ml ion exchanger, in the chloride form, in a 13 mm i.d. column from a large excess of sodium hydrogen sulfite solution (0.5 M,  $\text{pH} \approx 4.5$ ) flowing through the column. At this pH and concentration all sulfur-containing species except hydrogen sulfite can be neglected.<sup>4,5</sup> The total amount of hydrogen sulfite was about tenfold excess of the nominal capacity of the resin.

The resin was then washed with deionized water and the isotopic ratio  $^{34}\text{S}/^{32}\text{S}$  in solution and ion exchanger determined as described below. The ion exchangers were found to take up  $\text{HSO}_3^-$  according to their nominal ( $\text{Cl}^-$ ) capacity.

*Displacement experiments.* The apparatus, consisting of a 14 mm i.d. laboratory column, a small pump which could be regulated to deliver from 0.03 to 30 ml  $\text{h}^{-1}$  and a supply of  $\text{N}_2$  gas, is sketched in Fig. 1.

The column was thermostated to  $T \pm 0.1^\circ\text{C}$ . 30 ml hydrogen sulfite saturated ion exchange resin was held dispersed in deionized water by a stream of fine  $\text{N}_2$  gas bubbles through a sintered glass filter at the base of the column which continuously mixed the resinous phase. Hydrochloric acid (5 M) was fed into the system near the base of the column at a rate of 0.3 ml  $\text{h}^{-1}$  until all but a few per cent of the hydrogen sulfite ions were estimated to be displaced by chloride ions.

Two 5 ml samples were then transferred to narrow columns, the remaining hydrogen sulfite ions displaced by a large excess of 0.3 M hydrochloric acid and the exchange-resin thoroughly washed with deionized water. The total amount of hydrogen sulfite displaced was determined by iodometry,<sup>7</sup> giving the fraction hydrogen sulfite ions left in the resinous phase.

The isotopic ratio  $^{34}\text{S}/^{32}\text{S}$  was determined as follows.

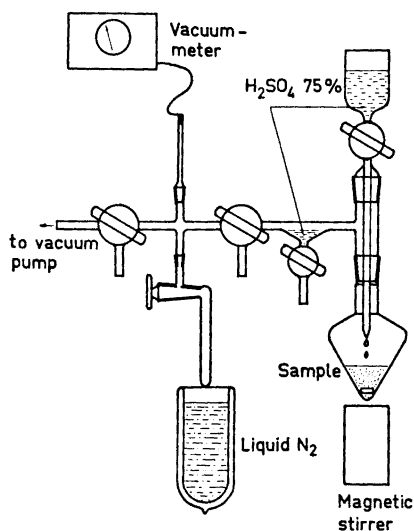


Fig. 1. Principle of distillation apparatus.

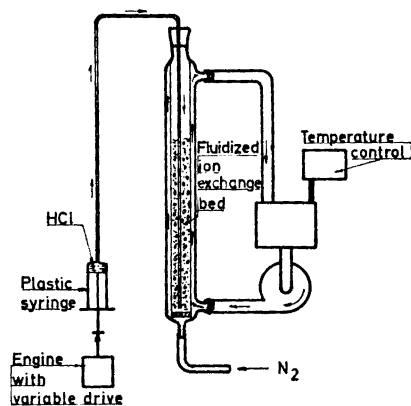


Fig. 2. Vacuum system for conversion of sulfurous species in ion-exchanger sample to sulfur dioxide.

*Isotopic analysis.* The vacuum system used for converting the hydrogen sulfite ions adsorbed on the ion exchanger to  $\text{SO}_2$  gas is sketched in Fig. 2. Small dried samples of the ion exchanger resin (estimated to give  $\sim 10$  ml  $\text{SO}_2$  gas) was placed in the retort which was then evacuated. A small volume of 14 M sulfuric acid was then fed into the retort and the ion exchange resin held dispersed in the acid by means of a magnetic stirrer. The  $\text{SO}_2$  gas evolved was transferred to a gas analysis ampoule by cooling the ampoule with liquid nitrogen. The gas samples were analyzed mass-spectrometrically w.r.t. the masses 64 + 65 and 66.<sup>4</sup> Three parallel samples were analyzed for each experiment.

## RESULTS

The results obtained are tabulated in Tables 1 and 2.

Table 1. The isotope exchange coefficient  $\alpha_{\text{SR}}$  for the sulfur isotopes  $^{34}\text{S} - ^{32}\text{S}$  in the ion exchange reaction  $\text{HSO}_3^-_{\text{aq}} \rightleftharpoons \text{HSO}_3^-_{\text{R}}$  at 25°C.

	Dowex 1 × 8 50 – 100 mesh	Dowex 2 × 8 50 – 100 mesh	Dowex 21 K 50 – 100 mesh
	1.0053	1.0066	1.0069
	1.0040	1.0066	1.0063
	1.0038	1.0065	1.0036
		1.0077	1.0039
		1.0076	
		1.0076	
$\bar{\alpha}_{\text{SR}}$	$1.0044 \pm 0.0005$	$1.0071 \pm 0.0003$	$1.0052 \pm 0.0009$

Table 2. The isotope separation coefficients  $\alpha_{gR}$  for the sulfur isotopes  $^{34}\text{S}$ – $^{32}\text{S}$  in the heterogeneous system  $\text{SO}_{2g}$ – $\text{HSO}_3^-_{R}$  at 25°C.

	Dowex 1 × 8 50–100 mesh	Dowex 2 × 8 50–100 mesh	Dowex 21 K 50–100 mesh
	1.0156	1.0178	1.0149
	1.0123	1.0180	1.0159
	1.0196	1.0131	1.0143
	1.0167	1.0155	
$\bar{\alpha}_{gR}$	$1.0161 \pm 0.0015$	$1.0161 \pm 0.0012$	$1.0150 \pm 0.0005$

## DISCUSSION

The isotope effect found in the pure ion exchange reaction  $\text{HSO}_3^-_{aq} \rightleftharpoons \text{HSO}_3^-_R$  is about half as large as the effect due to the protolytic reaction  $\text{SO}_{2aq} \rightleftharpoons \text{HSO}_3^-_{aq}/^{4-6}$  and has the same direction as the gross heterogeneous reaction.

The concentration in the resinous phase is very high and the ionic species adsorbed on the ion exchange resin might therefore be a mixture of  $\text{HSO}_3^-$  and  $\text{S}_2\text{O}_5^{2-}$ .

The isotope effect might be considered to be due to the rupture of the  $\text{R}-\text{HSO}_3^-$  (or  $2\text{R}-\text{S}_2\text{O}_5^{2-}$ ) bonds and the difference in ionic strength in resinous and aqueous phase. Dowex 21 K is a strongly basic type resin with exchange groups identical to those of Dowex 1 [ $\phi\text{-N}^+(\text{CH}_3)_3$ ]. However, due to different crosslinking some of its properties such as permeability and rate of equilibration are comparable to that of a less cross-linked resin ( $\times 4$ ) while its volume changes and capacity are comparable to an 8 % cross-linked resin.

A t-test<sup>9</sup> on the experimental results tabulated in Table 1 shows that the difference is not significant compared with the experimental error on 5 % level. (Critical value  $t=2.57$ , calculated value 0.75.)

Dowex 2 is slightly more basic than Dowex 1 and 21 K, the primary difference being in the quaternary ammonium group ( $\phi\text{-N}^+(\text{CH}_3)_2\text{C}_2\text{H}_5\text{OH}$ ) as compared to  $\phi\text{-N}^+(\text{CH}_3)_3$ .

A t-test on the experimental results obtained with Dowex 2 × 8 compared to the pooled experimental results obtained with Dowex 1 and 21 K gives  $t=3.9$ . Critical value 5 % level is 2.201, (DF=11). Thus, Dowex 2 with the active group  $\phi\text{-N}^+(\text{CH}_3)_2\text{C}_2\text{H}_5\text{OH}$  gives a higher isotope effect than Dowex 1 and 21 K with the active group  $\phi\text{-N}^+(\text{CH}_3)_3$ .

The 95 % confidence limits for the average increase are 0.001 and 0.0036.

The isotope separation factor obtained in the displacement experiments (Table 2) can be considered as consisting of three parts: the isotope effect caused by the pure physical transfer between the gas and liquid phase and hydration, further reaction in the solution, and the ion exchange discussed above. The overall coefficient  $\alpha_{gR}$  can thus be written  $\alpha_{gR} = \alpha_{gl} \alpha_s \alpha_{sR}^{3-5}$  where  $gl$ ,  $s$ , and  $sR$  related to transfer and hydration, solution, and the ionic exchange, respectively.

Table 3. A comparison of the isotope exchange coefficients  $\alpha_t$  for the system  $\text{SO}_{2g} - \text{HSO}_3^-_{\text{aq}}$  obtained by anion exchange, Rayleigh distillation, and chemical exchange experiments at 25°C.

$\bar{\alpha}_t = \bar{\alpha}_{gR}/\bar{\alpha}_{sR}$	$\bar{\alpha}_t^a$ Rayleigh dist.	$\bar{\alpha}_t^b$ Chemical exchange
Dowex 1 × 8 1.0116 ± 0.0016		
Dowex 2 × 8 1.0089 ± 0.0012	1.0109 ± 0.0006	1.0099 ± 0.0010
Dowex 21 K 1.0097 ± 0.0010		

<sup>a</sup> From Paper I in this series, Ref. 4.

<sup>b</sup> From Paper III in this series, Ref. 6.

On the basis of the experimental results obtained in this work the isotopic exchange coefficient  $\alpha_t$  for the system  $\text{SO}_{2g} - \text{HSO}_3^-_{\text{aq}}$  has been calculated. A comparison of the calculated exchange coefficients and data previously obtained by Rayleigh distillation and exchange experiments <sup>4-6</sup> shows very good agreement (Table 3).

Anion exchangers in the  $\text{HSO}_3^-$  form have been shown to take up an extra amount of sulfurous species if placed in contact with hydrogen sulfite solutions containing  $\text{SO}_{2\text{aq}}$ .<sup>3</sup> As no chemical binding is involved<sup>8</sup> this might be expected to decrease the gross isotope effect in an ion exchange column where  $\text{HSO}_3^-$  ions are displaced by  $\text{Cl}^-$  ions from hydrochloric acid. The highest  $\epsilon$  value obtained by Forberg<sup>3</sup> for the exchange system  $\text{SO}_{2\text{aq}} = \text{HSO}_3^-_{\text{R}}$  is valid for an excess of 20–25 %  $\text{SO}_{2\text{aq}}$  adsorbed by the resinous phase.

If the isotope effect in the exchange reaction  $\text{SO}_{2\text{aq}} = \text{SO}_{2\text{R}}$  is assumed to be small as compared to the effect in the ion exchange reaction  $\text{HSO}_3^-_{\text{aq}} = \text{HSO}_3^-_{\text{R}}$  Forberg's data should give an isotope exchange coefficient for the system  $\text{SO}_{2g} - \text{HSO}_3^-_{\text{R}}$  equal to (1.014–1.016) which is in good agreement with the results obtained in this work.

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