Diffusion Coefficients in Cold Sulfuric Acid Solution

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The diffusion coefficients of dimethyl sulfoxide, dimethyl sulfone, ^{15}N-labeled DNO_3, and ^{17}O-labeled D_2O in solutions of 0.6−0.8 weight fraction D_2SO_4 in D_2O were studied at temperatures from 248 to 298 K by the pulsed gradient spin-echo NMR technique. Diffusion coefficients for these compounds are reported, and an empirical technique for extrapolating the results to sulfuric acid of stratospheric compositions and temperatures is discussed. The viscosity of 0.7 weight fraction D_2SO_4 in D_2O at temperatures from 248 to 298 K is also reported.

1. Introduction

Heterogeneous processing involving sulfuric acid aerosol particles is an important part of the complex stratospheric chemical system.[1] The rates of heterogeneous reactions and the reactive uptake coefficients are, in some cases, not easily obtained by direct measurements in the laboratory. However, they can be calculated from basic physical and chemical parameters,[2] one of which is the liquid-phase diffusion coefficient, D_l. Liquid-phase diffusion can limit the rate of reaction and can also limit the transport of reactants from an aerosol surface to the bulk and vice versa. These limitations arise because the diffusion coefficient decreases rapidly in sulfuric acid as the temperature is lowered to typical stratospheric temperatures (200−240 K).

Very few measurements of diffusion coefficients for molecular or ionic species in sulfuric acid have been reported.[3,4] In this paper, we present diffusion studies of sulfuric acid systems in the 248−298 K temperature range by the pulsed gradient spin-echo NMR technique. The systems studied include dimethyl sulfoxide (DMSO), dimethyl sulfone ($DMSO_2$), ^{15}N-labeled DNO_3, and ^{17}O-labeled D_2O in solutions of 0.6−0.8 weight fraction D_2SO_4 acid in D_2O. Although DMSO and $DMSO_2$ are not directly relevant to stratospheric chemistry, this set of results helps to improve the understanding and modeling of liquid-phase diffusion in sulfate aerosol particles.

2. Experimental Section

Diffusion Studies. Dimethyl sulfoxide, $(CH_3)_2SO$, and dimethyl sulfone, $(CH_3)_2SO_2$, were commercial samples from Merck (*pro analysi*) and from Fluka (*purum*), respectively, and were distilled before use. D_2SO_4 dissolved in D_2O (99.3 atom % D) was a commercial sample from ISOTEC. D_2O (99.99 atom % D) was from Cambridge Isotope Laboratory. ^{17}O-enriched D_2O was prepared by burning D_2 in an atmosphere of $^{17}O_2$ obtained from CAMPRO Scientific (98 atom % ^{17}O). $D^{15}NO_3$ (99.7 atom % ^{15}N in a 10 M solution) was also obtained from CAMPRO Scientific. For DMSO and $DMSO_2$, 0.2 molal solutions were used, and for $H^{15}NO_3$ and $D_2{}^{17}O$, 0.5 molal solutions were used.

The NMR spectra were obtained employing two NMR instruments with supercooled magnets: a Varian UNITY 400 in Copenhagen and a Bruker DSX500WB instrument at the Bruker application laboratory in Karlsruhe. The Varian instrument was equipped with a Performa I pulsed field gradient module providing 0.1 T m^{-1} and with a Varian PF6 probe. The probe allows cooling to about −25 °C. The Bruker instrument was equipped with a diff30 Diffusion Probe. Gradient pulses of 2 ms with a gradient strength from 0 to 12 T m^{-1} were used. The temperature range was between 0 and 25 °C. The strength of the gradient pulse was calibrated by measuring the line width of the water signal with the gradient applied to a sample of known geometry.

In the Pulsed Gradient Spin-Echo Nuclear Magnetic Resonance (PGSE-NMR) experiment, the sample undergoes two radio frequency (RF) and two magnetic gradient square wave pulses after which the signal (the echo) is measured.[5] (See ref 5 for a more thorough description of the experiment). The size of the detected signal depends on the extent to which the sample molecules (or ions) have diffused out of the excitation region, the geometry of which is determined by the length and the size of the gradient pulse. A longer gradient pulse duration and a larger gradient pulse defines a smaller volume. Therefore, small diffusion coefficients require either large or long gradient pulses, or both. Two echo signals are observed and compared: the signal without field gradient, *S(0)*, and the signal with the field gradient pulses present, *S(g)*. The ratio between the two echo signals, both taken at time 2τ (τ being the time between the two RF pulses) is given by

$$\frac{S(\mathrm{g})}{S(0)} = \exp\{-D_l\gamma^2\delta^2(\Delta - \delta/3)g^2\} \quad (1)$$

where γ is the magnetogyric ratio (γ = 26.8, −3.6, and -2.7×10^7 rad T^{-1} s^{-1} for ^{1}H, ^{17}O, and ^{15}N, respectively), δ (s) is the duration of the gradient pulse, Δ (s) is the time

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lapse between the ramps of two consecutive gradient pulses, g (T m^{-1}) is the strength of the gradient, and D_l (m^2 s^{-1}) is the diffusion coefficient.

D_2SO_4 was used rather than protonated sulfuric acid because the NMR instruments use the deuterium nucleus as a field or frequency lock. These experiments required a large field gradient for two reasons. First, the smaller magnetogyric ratios (γ) for ^{15}N and ^{17}O require much larger gradients to produce the same effect as for ^{1}H (assuming equal diffusion coefficients). Second, short relaxation times for ^{15}N and ^{17}O require small values of Δ to produce a measurable echo. To counteract this, δ must be short and the field gradient, g, must be large.

Viscosity Studies. Absolute viscosities for 70 wt % D_2SO_4 in D_2O, 70 wt % H_2SO_4 in H_2O, D_2O, and H_2O were measured using a Brookfield viscometer (model DV−II). In this instrument, a cylindrical spindle is suspended in the liquid and rotated at a constant speed. A spring-mounted coupling between the spindle and the motor measures the drag of the liquid on the spindle, and this is converted to a viscosity. The measurement beaker containing the liquid and the spindle was submerged in a temperature-controlled ethanol bath (Neslab LT50). The temperature of the liquid was measured with a thermocouple to ±0.2 degrees. The viscometer was calibrated with a standard oil (Brookfield N35). The estimated experimental uncertainty in the viscosity measurements is ±5% based on previous measurements of H_2SO_4/H_2O solutions.[6]

The D_2SO_4/D_2O solution was made by diluting 96−98 wt % D_2SO_4 (Cambridge Isotope Laboratories) with D_2O (Aldrich). The concentration was measured by titration to be 69.9 ± 0.2 wt %. The sample was exposed to air during the viscosity measurement and could potentially have absorbed H_2O. We therefore titrated the sample after the viscosity measurement had been made and found the concentration had not changed. The H_2SO_4/H_2O solution was made by diluting 96.5 wt % H_2SO_4 (Aldrich) with distilled water. The concentration measured by titration was 69.9 ± 0.2 wt % before and after the viscosity measurement. We also compared the proton NMR signal for the two samples to estimate that the D_2SO_4/D_2O solution contained less than 2% H_2SO_4/H_2O.

3. Results and Discussion

When working with isotopically labeled samples, exchange must be taken into account. In the present case, we found that ^{17}O from $D_2{}^{17}O$ exchanged with O atoms in the sulfuric acid. This exchange must be brought to equilibrium before measurements can be carried out. Rate constants for this exchange were measured by the NMR technique.[7] Heating the samples for a few hours to 50 °C established isotopic equilibrium.

Examples of the experimental spin-echo decay data for ^{1}H in DMSO and for ^{15}N in DNO_3 dissolved in a solution of 0.6 weight fraction D_2SO_4 in D_2O are shown in Figures 1 and 2, respectively. The figures also include the least-squares fit of eq 1 to the PGSE data. The derived diffusion coefficients are collected in Table 1.

Two trends are apparent in the data in Table 1. First, the diffusion coefficient for a given species decreases as the temperature decreases, and second, the diffusion coefficient decreases as the sulfuric acid concentration increases. These trends are a result of the temperature and viscosity dependence of the liquid-phase diffusion coefficient, often described by the equation[8]

$$D_{l,x} = C_x \frac{T}{\eta} \qquad (2)$$

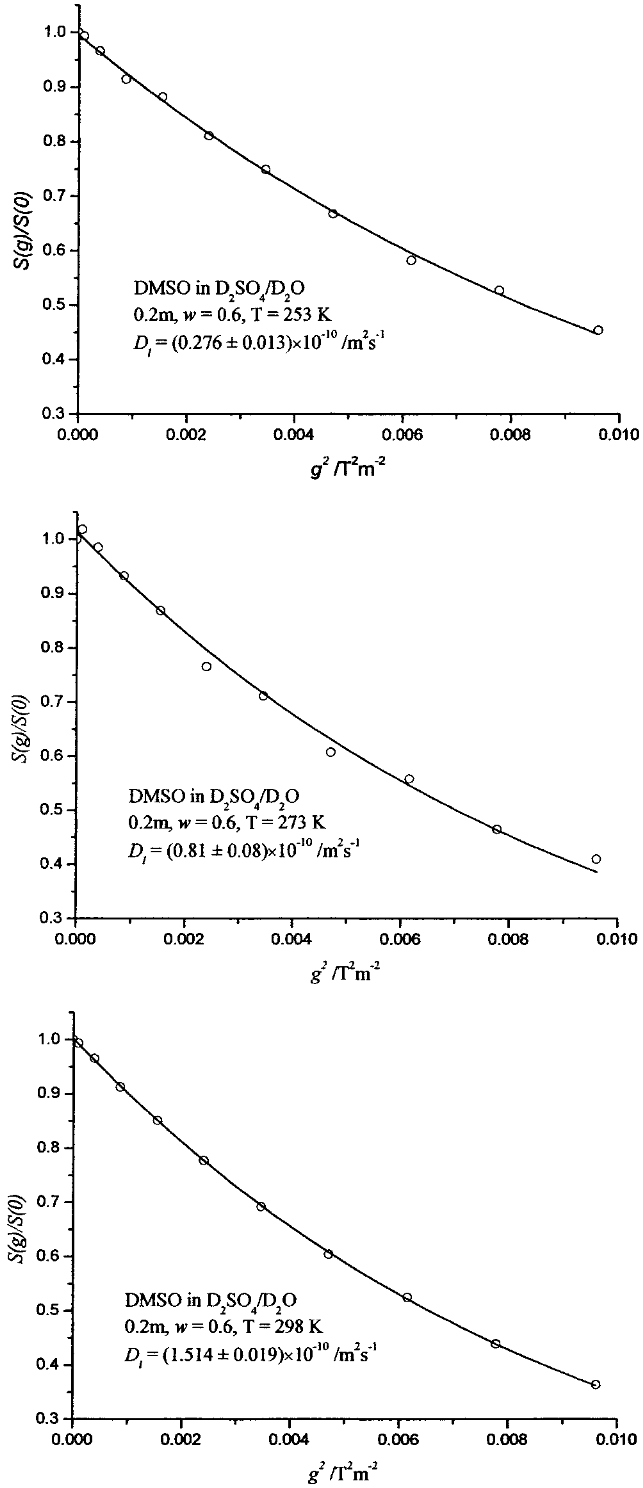

Figure 1. Pulsed gradient spin-echo signals at 253, 273, and 298 K for ^{1}H in DMSO dissolved in 0.6 weight fraction D_2SO_4 in D_2O and the derived diffusivities, D_l, with 3σ statistical errors. The data were fitted to an exponential decay (see text).

where $D_{l,x}$ (m^2 s^{-1}) is the liquid-phase diffusion coefficient of substance x, C_x (kg m s^{-2} K^{-1}) is a coefficient, T (K) is the temperature, and η (Pa s) is the viscosity.

Determining the coefficient C_x in eq 2 from the diffusion coefficient measurements is useful for two reasons. First, the diffusion coefficients can be calculated for temperatures and concentrations of sulfuric acid other than the conditions of the measurements. Second, the C_x determined from the measurements can be compared to those predicted from empirical

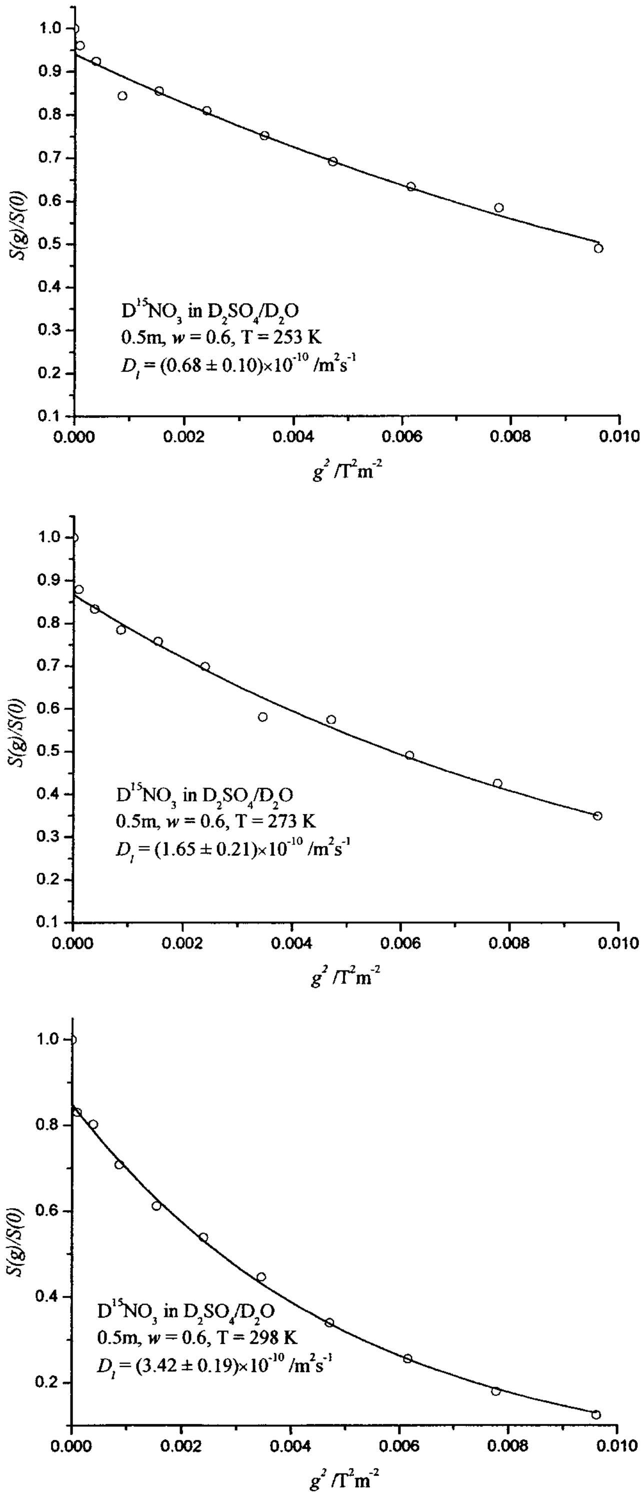

Figure 2. Pulsed gradient spin-echo signals at 253, 273, and 298 K for ^{15}N in $D^{15}NO_3$ dissolved in 0.6 weight fraction D_2SO_4 in D_2O and the derived diffusivities, D_l, with 3σ statistical errors. The data were fitted to an exponential decay (see text).

estimation methods that were generally developed for solutes in water or organic solvents. Demonstrating that an empirical estimation method also works when sulfuric acid is the solvent will allow the estimation of diffusion coefficients for species for which measurements are not easily made.

To calculate C_x using eq 2, one requires values of the viscosity of the D_2SO_4/D_2O solutions at the temperatures of the diffusion measurements. The measured viscosity for solutions of 0.7 weight fraction D_2SO_4 in D_2O are shown in Part I of Table 2 as a function of temperature. The viscosity of 0.7 weight fraction H_2SO_4 in H_2O (not shown) was also measured and was in good agreement (±4%) with previous measurements.[6] For the diffusion coefficients measured in the 0.7 weight fraction D_2SO_4 in D_2O solutions, the measured viscosity was used to calculate C_x, and the resulting values are shown in Table 3.

For the 0.6 and 0.8 weight fraction D_2SO_4/D_2O solutions, the viscosity was calculated from the viscosity of the mole fraction equivalent H_2SO_4/H_2O solutions. Because of the difference in molecular mass, D_2SO_4 and H_2SO_4 solutions need to be compared on a mole fraction rather than a weight fraction basis for a property such as viscosity that likely depends on intermolecular forces. A 0.7 weight fraction D_2SO_4/D_2O solution (mole fraction = 0.32) is thus equivalent in chemical composition to a 0.72 weight fraction H_2SO_4/H_2O solution. The viscosity of 0.72 weight fraction H_2SO_4/H_2O calculated from the equations in Williams and Long[6] is shown in the third column of Table 2, and the ratio of D_2SO_4 to H_2SO_4 viscosity is shown in the fourth column. The D_2SO_4 solution is on average 10% more viscous than the H_2SO_4 solution and appears to have a slightly different temperature dependence. Although the ratio has a large uncertainty (±20% due to the uncertainty in the viscosity calculated from the equations in Williams and Long[6]), we believe that the increase in viscosity is statistically significant. An increase is not surprising given that the viscosity of D_2O is about 35% higher than the viscosity of H_2O (see Part II of Table 2). Presumably, the increase in viscosity is due to an isotope effect on the "hydrogen" bonding in the liquid that increases the resistance to a shear force. The measurements of H_2O and D_2O viscosity are in good agreement with literature values.[9,10]

The viscosity of the 0.6 weight fraction D_2SO_4 in D_2O solution was estimated by calculating the viscosity of a 0.62 weight fraction H_2SO_4/H_2O from the equations in Williams and Long[6] and multiplying by 1.1. Similarly, for 0.8 weight fraction D_2SO_4 in D_2O, the viscosity of 0.81 weight fraction H_2SO_4/H_2O was calculated and multiplied by 1.1. The resulting values for C_x calculated from the diffusion coefficients are presented in Table 3.

For a given species, the values of C_x showed no obvious dependence on temperature or on the D_2SO_4 weight fraction. The averaged value over temperature is presented in Table 3 for each weight fraction. The average over weight fraction is also shown for each solute species. Two uncertainties are shown. The first is the statistical uncertainty in the measured values, and the second is an estimated uncertainty (±21%) based on the uncertainties in the viscosity (±20% when using the equations in Williams and Long[6]), the diffusion coefficient (±5%), and the temperature (±0.5%). With the exception of $D_2{}^{17}O$, the statistical uncertainty in the measurements is smaller than the estimated uncertainty.

Various empirical equations have been developed for estimating diffusion coefficients in liquids when the solvent is an organic liquid or water.[8] One such equation is a modification of the Wilke-Chang equation:[11]

$$C_x = 7.4 \times 10^{-15} \kappa_{solvent}^{0.5} V_x^{-0.6} \tag{3}$$

where $\kappa_{solvent}$ is a solvent dependent empirical factor, and V_x (cm^3/mol) is the molar volume of solute X at its normal boiling temperature. The quantity V_x can be estimated using the additivity rules of Le Bas given in Reid et al.[8] Klassen et al.[3] determined that $\kappa_{solvent} = 64$ for sulfuric acid by fitting a set of diffusion coefficient measurements that included their measurements of HCl and HBr and the measurements presented here for DMSO, $DMSO_2$, and $D^{15}NO_3$ in 0.7 weight fraction D_2SO_4

TABLE 1: Diffusion Coefficients/10^{-10} m^2 s^{-1} (3σ Statistical Error) as a Function of D_2SO_4 (in D_2O) Acid Weight Fraction, *w*, and Temperature, *T*/K, Obtained from PGSE-NMR Experiments

		T/K						
compd	w	248	253	273	278	283	288	298
DMSO	0.6		0.276 (13)	0.81 (8)				1.514 (19)
	0.7	0.101 (3)		0.440 (8)				1.02 (6)
	0.8	0.019 (1)		0.133 (5)				0.50 (6)
$DMSO_2$	0.6		0.42 (8)	0.95 (17)				2.05 (17)
	0.7	0.112 (1)		0.460 (9)				1.07 (5)
	0.8			0.18 (2)				0.52 (1)
$D^{15}NO_3$	0.6		0.68 (10)	1.65 (21)		2.28 (11)		3.42 (19)
	0.7		0.22 (7)	0.80 (7)				2.13 (7)
$D_2{}^{17}O$	0.6			1.2 (3)	2.2 (4)		3.1 (5)	3.7 (5)
	0.7						3.1 (5)	3.6 (5)

TABLE 2: Viscosity, η/Pa s, as a Function of Temperature, *T*/K, of (I) 0.7 Weight Fraction D_2SO_4/D_2O (Measured, 2σ Experimental Error ± 5%) and 0.72 Weight Fraction H_2SO_4/H_2O (Calculated, 2σ Estimated Error ± 20%, from Williams and Long[a]) and (II) D_2O and H_2O

(I) 0.7 Weight Fraction D_2SO_4/D_2O and 0.72 Weight Fraction H_2SO_4/H_2O

	η/Pa s		
T/K	0.7 weight fraction D_2SO_4/D_2O	0.72 weight fraction H_2SO_4/H_2O	ratio D_2SO_4/H_2SO
248	0.084	0.081	1.0
253	0.060	0.060	1.0
258	0.047	0.046	1.0
263	0.039	0.036	1.1
268	0.030	0.028	1.1
273	0.026	0.023	1.1
278	0.022	0.019	1.2
283	0.019	0.016	1.2
288	0.016	0.013	1.2
293	0.014	0.012	1.2
298	0.012	0.010	1.2
		average:	1.1

(II) D_2O and H_2O

	η/Pa s		
T/K	D_2O/Pa s	H_2O/Pa s	ratio D_2O/H_2O
274	0.0023	0.0017	1.35
283	0.0018	0.0013	1.38

[a] Reference 6.

TABLE 3: Coefficients $C_x/10^{-15}$ kg m s^{-2} K^{-1} (number samples averaged) for Compounds in Deuterated Sulfuric Acid from Measured Diffusion Coefficients[a]

compd	w	$C_x/10^{-15}$ kg m s^{-2} K^{-1}, from data, statistical uncertainty (2σ)	$Cx/10^{-15}$ kg m s^{-2} K^{-1}, average, statistical uncertainty (2σ)	estimated uncertainty (2σ), see text	$C_x/10^{-15}$ kg m s^{-2} K^{-1}, predicted
DMSO	0.6	3.4 ± 0.4 (3)			
	0.7	3.9 ± 0.4 (3)	3.5 ± 0.5 (9)	±0.7	4.1
	0.8	3.1 ± 0.5 (3)			
$DMSO_2$	0.6	4.6 ± 0.2 (3)			
	0.7	4.2 ± 0.3 (3)	4.3 ± 0.3 (8)	±0.9	3.9
	0.8	3.9 ± 0.2 (2)			
$D^{15}NO_3$	0.6	7.6 ± 0.2 (4)	7.4 ± 1.0 (7)	±1.6	6.2
	0.7	7.1 ± 1.7 (3)			
$D_2{}^{17}O$	0.6	7.8 ± 1.5 (4)	10.5 ± 4.4 (6)	±2.2	10
	0.7	15.9 ± 1.9 (2)			

[a] The predicted values are from eq 3 using $\kappa_{solvent} = 64$ and V_A = 85.7, 94, 42.8, and 19 cm^3/mol for DMSO, $DMSO_2$, $D^{15}NO_3$, and $D_2{}^{17}O$, respectively.[8]

in D_2O. Table 3 shows the values of C_x calculated from Equation 3. For the one datapoint not used in determining $\kappa_{solvent}$ (i.e., $D_2{}^{17}O$), the agreement between the measured and calculated values of C_x is good. This supports the suggestion in Klassen et al.[3] that the Wilke-Chang equation may be useful for estimating diffusion coefficients in sulfuric acid systems. This is particularly important for species of atmospheric interest for which direct measurements of diffusion coefficients may be precluded by lack of detection techniques or by fast hydrolysis reactions.

One other measurement of diffusion coefficients in sulfuric acid has appeared in the literature and does not agree with the estimation method in Equation 3. Langenberg et al.[4] reported measurements of diffusion coefficients for SO_2 in sulfuric acid thin films using a capillary gas chromatography technique. The liquid-phase diffusion coefficient is derived from the peak broadening of an SO_2 gas sample injected into a capillary coated with sulfuric acid. The Langenberg et al.[4] measurements give much smaller values of C_x than eq 3. For example, using the Langenberg et al.[4] data point at 41 wt % sulfuric acid and 243 K ($D_l = 8 \times 10^{-12}$ m^2/s) gives $C_x = 4.7 \times 10^{-16}$ kg m s^{-2} K^{-1}, while eq 3 gives $C_x = 6.1 \times 10^{-15}$ kg m s^{-2} K^{-1} (V_x = 43.8 cm^3/mol for SO_2). However, Langenberg et al.[4] suggest that their data should be considered lower limits to the diffusion coefficient because of other potential sources of peak broadening in their experiments. Thus, until more experimental data becomes available, we still propose the use of Equation 3 to estimate diffusion coefficients in sulfuric acid solutions.

The PGSE-NMR method used in these experiments requires fairly high solute concentrations, on the order of 0.1 to 0.5 molal. A dependence of the diffusion coefficient on solute concentration has been observed in water[12] but was not observed in previous work on sulfuric acid solutions.[3] We assume that the diffusion coefficients measured here are also independent of solute concentration and can therefore be used to parametrize eq 3 for calculating the diffusion coefficients of trace species.

4. Conclusion

We have presented direct measurements of the liquid-phase diffusion coefficient for DMSO, $DMSO_2$, ^{15}N-labeled DNO_3, and ^{17}O-labeled D_2O in solutions of 0.6−0.8 weight fraction D_2SO_4 in D_2O. These measurements are important as scaling values for empirical estimation methods, such as the Wilke-Chang equation discussed in this paper,[11] and for other methods reviewed in the literature.[13]

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