

Gas–Liquid Partition Coefficients and Henry's Law Constants of DMS in Aqueous Solutions of Fe(II) Chelate Complexes Using the Static Headspace Method

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Total reduced sulfurs quartet (H_2S , CH_3SH , CH_3SCH_3 [DMS], $\text{CH}_3\text{S}_2\text{CH}_3$ [DMDS]) is part of a spiny environmental problem afflicting the pulp mill industry exploiting the Kraft sulfate pulp process. Utilization of the ferric chelate complex of *trans*-1,2-cyclohexanediaminetetraacetic acid (CDTA) for the oxidative scrubbing of H_2S and CH_3SH in the Kraft mill atmospheric effluent streams is beneficial from the standpoints of iron protection against precipitation and oxygen-mediated regenerative oxidation of ferrous chelate CDTA. The remaining DMS and DMDS, considered non-oxidizable in CDTA–Fe(III) aqueous alkaline solutions, undergo physical absorption so their solubility is a crucial parameter for the design of the scrubbing–absorption process. The solubility of DMS in pure water, aqueous iron-free CDTA solutions, and CDTA–Fe(II) complex solutions was measured at atmospheric pressure between (288 and 308) K and for chelate concentrations between (38 and 300) $\text{mol}\cdot\text{m}^{-3}$. As experimental results revealed that DMS destabilized ferrous chelates at very large CDTA–Fe(II) concentrations, a maximum chelate concentration presenting practical interest was established. The static headspace method was used with an estimated uncertainty of $\pm 2\%$. It was shown that DMS solubility decreases with increasing temperature for all systems studied. CDTA concentration does not considerably affect DMS solubility; moreover, the concentration effect is negligible at 308 K. The solution pH was unimportant on DMS solubility over the covered concentration and temperature ranges. CDTA concentration less than 100 $\text{mol}\cdot\text{m}^{-3}$ is recommended for use in absorption scrubbing equipments.

Introduction

Total reduced sulfurs (TRS) quartet containing hydrogen sulfide (H_2S), methanethiol (CH_3SH), dimethyl sulfide (CH_3SCH_3), and dimethyl disulfide ($\text{CH}_3\text{S}_2\text{CH}_3$) is part of a well-known environmental problem afflicting pulp mills exploiting the Kraft mill sulfate pulp process. The origin of these odors is partly ascribable to pulp production equipment such as boilers, blow tanks, and washers, or to black liquor recovery equipment. Because of their toxic and corrosive character, they must be removed down to very low concentration levels. Since the early 1990s, several Canadian provincial governments and the United States promulgated a number of regulations upon the Kraft pulp manufacturers to collect and treat their total reduced sulfurs emitting vents. The olfactory threshold of TRS for human beings is 4 orders of magnitudes below the regulated emission level, which is approximately 10 ppm in Canada and the United States. This has ultimately given rise to strict regulations in order to reduce their emissions from specific sulfate pulp process equipments such as kilns, evaporators, washers, etc. Considering the progressive nature of legislations, it is anticipated that increasingly tighter regulations will be applicable soon especially in North America where about 15 % of the world Kraft mills are in operation.

Utilization of ferric chelate complex of *trans*-1,2-cyclohexanediaminetetraacetic acid (CDTA) for the oxidation of two of these sulfur compounds (H_2S and CH_3SH) is a favorable process from the standpoint of iron sequestration

and protection against precipitation in the alkaline environments characteristic of the Kraft mill streams.^{1–8} In two recent papers,^{9,10} we have studied the solubility of hydrogen sulfide and oxygen in chelate-containing solutions, which represent the key parameters needed for the design of absorption scrubbing equipments. Availability of oxygen along with hydrogen sulfide in the Kraft process atmospheric air emissions is propitious for the simultaneous Redox regeneration from ferrous to ferric chelate for perpetuating the scrubbing cycle.

In a recent study,¹¹ dimethyl disulfide (DMDS) was found not to react with ferric chelates, which otherwise would have compromised the determination of the physical DMDS partition coefficients. Being only absorbed physically in the scrubbing solutions, its solubility, as an important parameter for designing the scrubbing–absorption process, was hence investigated.

As an extension, the solubility of dimethyl sulfide (DMS) in chelate solutions was also studied. It was observed that at all chelate–Fe(III) concentrations, parasitic destabilization of CDTA–Fe(III) solutions took place with faster destabilization occurring the larger the CDTA–Fe(III) concentration. CDTA–Fe(II) solutions behaved similarly but with an extent of parasitic destabilization that was incumbent upon the CDTA–Fe(II) concentration and temperature levels. Experiments were therefore preventively performed in aqueous CDTA–Fe(II) solutions at concentration and temperature levels exempting any parasitic phenomenon that would otherwise have impaired the accuracy of the solubility measurements.

The static headspace method is considered a very effective tool for analyzing volatile organic compounds present

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in contaminated condensed samples. Therefore, the method has found wide-ranging use in environmental analysis, and various techniques are available in order to determine the gas-liquid partition coefficients.¹²⁻¹⁸ The aim of this investigation was to determine the Henry's law constants of DMS in pure water, in iron-free CDTA solutions, and in CDTA-Fe(II) complex solutions using a static headspace method based on chromatography measurements of the equilibrium headspace peak areas of DMS. The method was successfully used in the case of DMDS.¹¹ New experimental solubility results over a chelate concentration ranging from (38 to 300) mol·m⁻³ are reported at different temperatures between (288 and 308) K. To the best of our knowledge, this study is the first of its kind that reports DMS solubility data in iron-free CDTA and CDTA-Fe(II) chelate aqueous solutions. Because of the importance of reliable pollutant aqueous solubility data for environmental processes as well as the impact of DMS on the earth's radiation balance and climate, new reliable DMS aqueous solubility experimental data obtained using this method contribute to widen the existing body of thermodynamic data on the topic.

Static Headspace Method

The headspace method is an appropriate method to analyze the volatile organic compounds (VOC) contained (absorbed) in a condensed sample. The headspace sample is prepared in a sealed vial by introducing a known volume of sample of initial concentration (C_S). Consider this system at equilibrium consisting of the liquid phase (L) with concentration (C_L) and the headspace gas phase (GH) with concentration (C_{GH}). A mole balance between the total moles of VOC in the sample, the moles of VOC in the liquid phase, and those in the headspace gas phase gives

$$C_S V_L = C_L V_L + C_{GH} V_{GH} \quad (1)$$

where V_L and V_{GH} represent the volumes of the liquid phase and the headspace gas phase, respectively.

After rearrangement, eq 1 yields

$$\frac{1}{C_{GH}} = \frac{K}{C_S} + \frac{1}{C_S} \frac{V_{GH}}{V_L} \quad (2)$$

where

$$K = \frac{C_L}{C_{GH}} \quad (3)$$

represents the partition coefficient (K).

Taking into account that the VOC concentration in the headspace gas phase is directly proportional to the peak area of the GC response (A_{GH}):

$$C_{GH} = a \cdot A_{GH} \quad (4)$$

eq 2 becomes:

$$\frac{1}{A_{GH}} = \frac{a}{C_S} K + \frac{a}{C_S} \frac{V_{GH}}{V_L} \quad (5)$$

According to eq 5, the partition coefficient K can be obtained through plotting $1/A_{GH}$ as a function of the V_{GH}/V_L ratio.

The six vials used for determining the partition coefficient at a given temperature represented different phase ratios V_{GH}/V_L between 2.33 and 19. The basic condition is

that all vials must contain the same sample initial concentration (C_S) without it being necessary to know its exact value.

Henry's law constant expressed in Pa·m³·mol⁻¹, deriving from the partition coefficient, is then given by

$$K_H(T) = \frac{RT}{K} \quad (6)$$

Experimental Section

Materials. The chemicals used in this work, purchased from Aldrich Chemical Co, had the following stated minimum purities (in mass units): *trans*-1,2-cyclohexanediaminetetraacetic acid (CDTA), >99.3 %; DMS, >99 %; iron(II) chloride tetrahydrate, >99 %; sodium hydroxide solution 5.0 mol·L⁻¹; HPLC distilled water.

Sample Preparation. To prepare the standard CDTA solutions, the CDTA was stoichiometrically added to a sodium hydroxide aqueous solution to obtain a solution with pH 7. The pH was measured using an Oakton pH 1000 Benchtop Meter. For the preparation of the CDTA-Fe(II) complexes, a corresponding quantity of iron(II) chloride tetrahydrate was added up to a ratio of chelant/Fe = 1. The concentrations of iron-free chelate and ferrous chelate solutions were varied between (38 and 300) mol·m⁻³.

Fresh DMS/CDTA and DMS/CDTA-Fe(II) solutions of approximately 10 ppm by volume (DMS) were prepared for each experimental test performed at a constant temperature. CDTA-Fe(II) solutions were kept under an inert nitrogen atmosphere in order to prevent any contact with air because of rapid oxidation reaction into CDTA-Fe(III) in the presence of oxygen.

CDTA concentration range and solution pH were limited by the usual operation conditions on one hand and by the solution stability on the other hand. First, typical operation conditions of iron chelate based procedures require a solution pH between 6 and 9.¹⁹ Solubility measurements were therefore performed in the pH range between 2.4 and 8.5 in order to check the pH influence on DMS solubility in these solutions. Second, a numerical mass transfer study of a packed-bed scrubbing process involving EDTA-Fe(III) chelates²⁰ showed that a chelate feed concentration less than 100 mol·m⁻³ would be sufficient for scrubbing TRS-containing streams at the concentration levels typically encountered in industry. A concentration larger than 100 mol·m⁻³ was included to illustrate the influence of CDTA concentration on the DMS solubility, without exceeding 300 mol·m⁻³. However, due to the instability of the iron chelate complex observed in the presence of DMS, the experiments concerning the DMS solubility in CDTA-Fe(II) chelate were limited up to a CDTA concentration of 124 mol·m⁻³.

Static Headspace Method. DMS standard solutions of (1 to 6) mL of a given CDTA concentration and pH were introduced into six dry 20 mL headspace vials (Aldrich). The vials were then capped with silicone/PTFE faced septa (Aldrich) and holed screw caps (Aldrich). Each vial was kept at constant temperature for 60 min using a thermostated bath controlled to ±0.01 °C and shaken periodically. After equilibrating, 0.5 mL from the headspace was sampled for GC analysis using a valve-locking gastight syringe heated to a temperature comparable to the sample vial temperature to avoid pressure differences and condensation problems. The valve-lock assured proper transfer of gas samples by avoiding loss of volatile compound.

For the reasons outlined above, special attention was given to handle CDTA-Fe(II) solutions to prevent any contact with air. The preparation and transfer of these

Table 1. Gas–Liquid Partition Coefficient (K) and Henry's Law Constant (K_H) of DMS in Water and Comparison with Literature Data^a

T/K	K	R^2	SD	$K_H/\text{Pa}\cdot\text{m}^3\cdot\text{mol}^{-1}$	$K_H/\text{Pa}\cdot\text{m}^3\cdot\text{mol}^{-1}$ (literature data)
288.15	20.35	0.9991	0.43	117.7	na ^b
293.15	16.67	0.9995	0.33	146.2	164.6 ^c 160.9 ^d
298.15	13.61	0.9994	0.27	182.1	181.7 ^e 181.5 ^f 180.6 ^g
303.15	11.24	0.9999	0.24	224.3	224.7 ^g
308.15	9.38	0.9999	0.21	273.2	279.5 ^g

^a R^2 is the coefficient of determination, and SD is the standard deviation. ^b Not available. ^c Vitenberg et al.¹² ^d Brennan et al.²³ ^e Yaws et al.²⁴ ^f Dacey et al.²² ^g Przyjazny et al.¹⁴

solutions into the equilibrium headspace vials were performed using a glovebox under an inert nitrogen atmosphere.

For each system, several runs were performed in order to check the reproducibility of the results. Measurements involving all DMS containing systems were performed in the temperature range of (288 to 308) K. The CDTA concentration was varied between (38 and 300) mol·m⁻³.

Instrumental Conditions. The analysis was carried out using a Perkin-Elmer GC equipped with an FID and a capillary column of 0.32 mm i.d., 30 m in length with 5.0 μm film thickness of DB-1 (J&W Scientific). The split/splitless injector was used in a splitless mode. A GC oven temperature program between 40 and 130 °C was used. The injector and detector were held at 150 and 170 °C, respectively. Helium flow rate through the capillary column was about 2 mL/min. Silanized glass wool was packed into the glass injector port liner in order to prevent septum coring from entering the column.

Results and Discussion

The accuracy of the measuring method was already verified previously.¹¹ In addition, the solubility of DMS in distilled water at different temperatures between (288 and 308) K was studied in this work and compared with the data available in the literature. Unfortunately, the existing experimental data for this system are quite scarce on a larger temperature range. Vitenberg et al.¹² gave the value of the partition coefficient at 20 °C, 14.8 ± 1.4 , and compared it with the corresponding value of 17 at the same temperature derived graphically from Williams and Murrey.¹³ Wong and Wang²¹ reported the Henry's law constant at 18 °C. Przyjazny et al.¹⁴ presented the partition coefficient K value at 25 °C and the coefficients of the corresponding linear correlation $\log(K) - T$ (calculated "on the basis of the K values at (25, 35, 45, and 70) °C" without publishing, however, the raw solubility experimental data nor defining the temperature range for the DMS experiments. Dacey et al.²² reported the values of Henry's law constant between (-0.8 and 32.4) °C. In addition, theoretical work by Brennan et al.²³ and Yaws et al.²⁴ use in their correlative methods the values of Henry's law constants at (20 and 25) °C, respectively, taken from existing data banks, without however specifying the exact data source for a particular system.

Our results are summarized in Table 1 and compared with literature values. Figure 1 shows a much better depiction of the available databank for this system. Taking into consideration that the partition coefficient K was obtained graphically, R^2 represents the coefficient of determination of the plot $1/A_{GH}$ versus the V_{GH}/V_L ratio

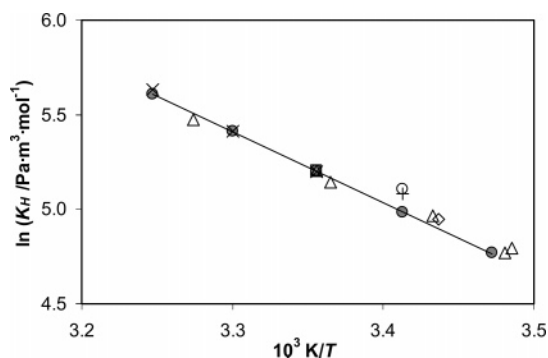


Figure 1. Henry's law constants of DMS in water at various temperatures. Comparison with literature data: ●, this work; ○, Vitenberg et al.;¹² ×, Przyjazny et al.;¹⁴ △, Dacey et al.;²² ◇, Wong and Wang;²¹ +, given in Brennan et al.;²³ □, given in Yaws et al.²⁴

Table 2. Gas–Liquid Partition Coefficient (K) and Henry's Law Constant (K_H) of DMS in CDTA Solutions of Concentration (c)^a

c mol·m ⁻³	T		K	R^2	SD	K_H Pa·m ³ ·mol ⁻¹
	K					
38	288.15	19.51	0.9993	0.43	122.8	
	293.15	15.93	0.9990	0.30	153.0	
	298.15	12.97	0.9998	0.26	191.1	
	303.15	10.59	0.9998	0.24	238.0	
	308.15	8.75	0.9997	0.24	292.8	
60	288.15	18.88	0.9993	0.41	126.9	
	293.15	15.22	0.9990	0.29	160.1	
	298.15	12.35	0.9994	0.25	200.7	
	303.15	10.10	0.9996	0.26	249.5	
	308.15	8.55	0.9996	0.23	299.6	
100	288.15	17.69	0.9990	0.34	135.4	
	293.15	14.38	0.9989	0.30	169.5	
	298.15	11.44	0.9995	0.24	216.7	
	303.15	9.57	0.9989	0.23	263.4	
	308.15	8.03	0.9992	0.23	319.0	
124	288.15	17.26	0.9988	0.37	138.8	
	293.15	14.01	0.9990	0.35	174.0	
	298.15	11.14	0.9988	0.22	222.5	
	303.15	9.43	0.9989	0.20	267.3	
	308.15	7.86	0.9990	0.23	326.0	
300	288.15	13.18	0.9986	0.27	181.7	
	293.15	10.84	0.9980	0.25	224.8	
	298.15	8.87	0.9995	0.21	279.4	
	303.15	7.27	0.9995	0.21	346.7	
	308.15	6.25	0.9990	0.19	409.7	

^a R^2 is the coefficient of determination, and SD is the standard deviation.

according to eq 5. Very good agreement was generally found between actual data and literature values. As seen in Figure 1, data from Vitenberg et al.¹² and those given in Brennan et al.²³ do not seem very plausible. Excluding these two data points, the absolute average deviation between actual data and literature values is 0.77 %. A very good reproducibility and a coefficient of determination of the linear regression curve $(\ln(K_H) - 1/T)$ approaching unity (0.9999) proved the high accuracy of our technique.

Results concerning DMS solubility in aqueous solutions of CDTA and CDTA–Fe(II) complexes at temperatures from (288 to 308) K, solution concentrations of (38, 60, 100, 124, and 300) mol·m⁻³ (expressed on CDTA basis), and pH of 2.4 and 8.5 are given in Tables 2 and 3. It is important to mention that each value given in Tables 1 to 3 represents a mean of 3 to 4 experimental data points.

As mentioned previously, the presence of DMS in the CDTA–Fe(II) solutions destabilized, under certain condi-

Table 3. Gas–Liquid Partition Coefficient (K) and Henry's Law Constant (K_H) of DMS in CDTA–Fe(II) Solutions of Concentration (c)^a

c mol·m ⁻³	pH	T				K_H Pa·m ³ ·mol ⁻¹
		K	K	R^2	SD	
38	2.4	288.15	18.69	0.9986	0.42	128.2
		293.15	15.20	0.9989	0.29	160.3
		298.15	12.53	0.9990	0.30	197.8
		303.15	10.30	0.9988	0.21	244.7
		308.15	8.63	0.9987	0.16	296.9
	8.5	288.15	18.55	0.9988	0.38	129.1
		293.15	15.00	0.9991	0.35	162.5
		298.15	12.47	0.9992	0.25	198.8
		303.15	10.17	0.9993	0.25	247.8
		308.15	8.57	0.9992	0.19	298.9
60	2.4	288.15	18.14	0.9987	0.44	132.1
		293.15	14.70	0.9985	0.29	165.8
		298.15	11.87	0.9990	0.25	208.8
		303.15	9.80	0.9996	0.17	257.2
		308.15	8.46	0.9993	0.15	302.8
	8.5	288.15	17.95	0.9985	0.35	133.5
		293.15	14.37	0.9990	0.29	169.6
		298.15	11.68	0.9991	0.32	212.2
		303.15	9.70	0.9989	0.21	259.8
		308.15	8.37	0.9988	0.22	306.1
100	2.4	288.15	16.87	0.9987	0.35	142.0
		293.15	13.60	0.9989	0.34	179.2
		298.15	11.03	0.9989	0.27	224.7
		303.15	9.30	0.9989	0.22	271.0
		308.15	7.81	0.9984	0.15	328.0
	8.5	288.15	16.57	0.9988	0.38	144.6
		293.15	13.44	0.9982	0.33	181.3
		298.15	10.82	0.9986	0.28	229.1
		303.15	9.10	0.9994	0.23	277.0
		308.15	7.78	0.9989	0.22	329.3

^a R^2 is the coefficient of determination, and SD is the standard deviation.

tions, the ferrous chelate complex. This process was clearly observed at CDTA–Fe(II) concentrations larger than 124 mol·m⁻³. At a concentration of 124 mol·m⁻³, it was quite slow at (15 and 25) °C and became faster at larger temperatures; at 300 mol·m⁻³, it was so fast that it precluded the preparation of any stable chelate solutions at room temperature. Although it was possible to determine the partition coefficient of DMS in a 124 mol·m⁻³ CDTA–Fe(II) solution up to 20 °C, we restricted ourselves with presenting the complete experimental data series up to a chelate concentration of 100 mol·m⁻³ because of very good data reproducibility and actual practical interest for low CDTA–Fe(II) concentration solutions.

With increasingly temperatures, DMS partition coefficient (and DMS solubility) exhibited increasingly attenuated dependence to CDTA (Figure 2a) and CDTA–Fe(II) (Figure 2b) concentrations. In addition, as seen in Figure 3 at 298.15 K, the presence of CDTA-iron complex led only to a slight decrease of DMS solubility with respect to the iron-free CDTA solutions. The same behavior was observed over the whole temperature range under study.

For industrial purposes, a larger value of DMS solubility at low chelate concentrations is favorable, allowing good absorption capacity at lower cost of DMS-containing Kraft mill atmospheric air effluents. On the other hand, numerical mass transfer simulations of EDTA–Fe(III) based packed-bed scrubbing revealed that chelate feed concentration less than 100 mol·m⁻³ would be sufficient for scrubbing TRS-containing streams at the concentration levels typically encountered in industry.²⁰ The fact that DMS absorption was improved at lower CDTA concentrations (Figure 2) is therefore industrially favorable. Moreover, current

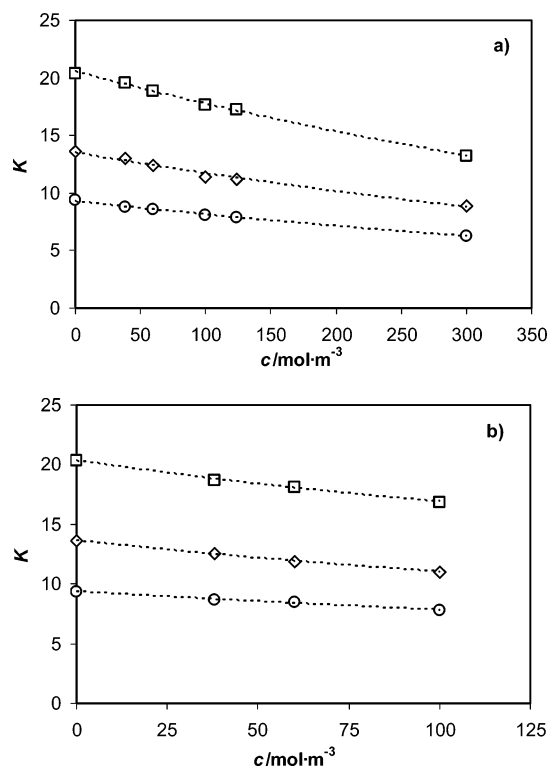


Figure 2. Influence of temperature and chelate concentration on (a) gas/CDTA and (b) gas/CDTA–Fe(II) pH 2.4 solution partition coefficient of DMS: □, 288.15 K; ◇, 298.15 K; ○, 308.15 K.

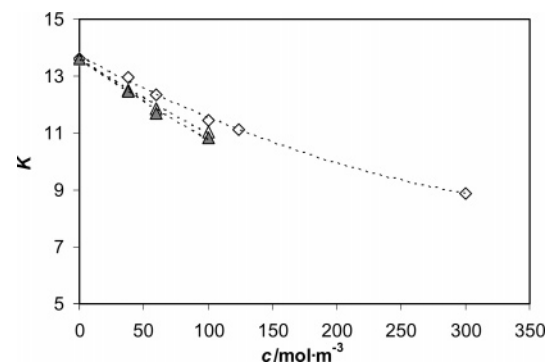


Figure 3. Influence of pH and chelate concentration on gas/CDTA–Fe(II) solution partition coefficient of DMS at 298.15 K: ◇, CDTA; △, CDTA–Fe(II) pH 2.4; ▲, CDTA–Fe(II) pH 8.5.

results showed that CDTA concentration less than 100 mol·m⁻³ is mostly recommended for use in absorption scrubbing equipments, due to likely instability of chelate solutions at larger concentrations.

Experimental data were obtained over a broad pH range between (2.4 and 8.5). It was observed that the pH had practically no effect on DMS solubility over the whole temperature and chelate concentration ranges of this study. This is shown in Figure 3 for a selected temperature of 298.15 K. Taking into account that typical operation conditions of iron chelate based procedures require pH between 6 and 9,¹⁹ even an important change within this pH range will practically not influence DMS solubility in the chelate solutions.

Temperature Dependence of Henry's Law Constant.

A quite important influence of temperature was observed on DMS solubility in both CDTA and CDTA–Fe(II) solutions at constant concentration (Figure 4).

At constant pressure, the temperature dependence of Henry's law constant can be considered a linear relation-

Table 4. Temperature Dependence of Henry's Law Constants of DMS in Water, CDTA, and CDTA-Fe(II) Solutions According to Equation 7^a

system	$c/\text{mol}\cdot\text{m}^{-3}$	pH	A	B	R^2	SD	$\Delta_{\text{GL}}H/\text{kJ}\cdot\text{mol}^{-1}$
water			17.783	-3750.7	0.9999	0.0028	-31.2
CDTA	38		18.239	-3870.9	0.9999	0.0045	-32.2
	60		18.182	-3842.2	0.9993	0.0104	-31.9
	100		18.198	-3828.2	0.9988	0.0138	-31.8
	124		18.119	-3797.9	0.9985	0.0152	-31.6
	300		17.899	-3658.2	0.9989	0.0124	-30.4
CDTA-Fe(II)	38	2.4	17.816	-3735.1	0.9999	0.0032	-31.1
	60		17.840	-3730.9	0.9978	0.0180	-31.0
	100		17.845	-3711.1	0.9989	0.0126	-30.9
	38	8.5	17.815	-3731.9	0.9996	0.0073	-31.0
	60		17.784	-3710.1	0.9973	0.0197	-30.8
	100		17.753	-3679.5	0.9979	0.0173	-30.6

^a A and B represent the corresponding coefficients. R^2 is the coefficient of determination. SD is the standard deviation. $\Delta_{\text{GL}}H$ is the enthalpy of gas-liquid phase transfer.

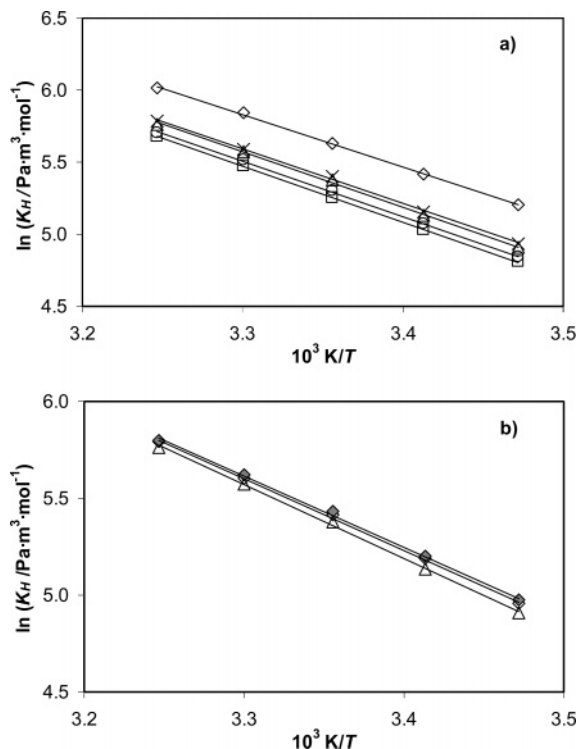


Figure 4. Logarithms of Henry's law coefficients as a function of temperature reciprocal. (a) CDTA solutions: \square , $38 \text{ mol}\cdot\text{m}^{-3}$; \circ , $60 \text{ mol}\cdot\text{m}^{-3}$; \triangle , $100 \text{ mol}\cdot\text{m}^{-3}$; \times , $124 \text{ mol}\cdot\text{m}^{-3}$; \diamond , $300 \text{ mol}\cdot\text{m}^{-3}$. (b) CDTA and CDTA-Fe(II) solutions of concentration $100 \text{ mol}\cdot\text{m}^{-3}$: \triangle , CDTA; \diamond , CDTA-Fe(II) pH 2.4; \blacklozenge , CDTA-Fe(II) pH 8.5.

ship over the explored temperature range, assuming that in the actual experimental conditions the enthalpy of solution is temperature independent. The Henry's law constant is usually expressed as

$$\ln(K_{\text{H}}) = A + B/T \quad (7)$$

where the constant B is a function of the enthalpy of solution. Only two adjustable parameters are considered sufficient in representing experimental data on a quite limited temperature range, (288 to 308) K.

All experimental data for DMS in water, CDTA, and CDTA-Fe(III) (pH 2.4 and 8.5) solutions were fitted using eq 7 with a global average percent absolute deviation (AAD) of 0.21 % (water), 0.71 % (CDTA), 0.90 % (CDTA-Fe(II)) and a maximum deviation of 0.31 % (water), 1.98 % (CDTA), and 2.16 % (CDTA-Fe(II)). AAD was calculated as

$$\text{AAD} = \frac{100}{n} \sum \left| \frac{X_{\text{exp}} - X_{\text{calc}}}{X_{\text{exp}}} \right| \quad (8)$$

where X_{exp} and X_{calc} represent the experimental and calculated values, respectively, and n is the number of experimental data points.

Equation 7 fitted coefficients A and B are given in Table 4. The validity of eq 7 represents additional post facto verification of the correctness of experimental data. The logarithms of Henry's law constants decrease with increasing temperature reciprocal, this variation being in agreement with the negative solution enthalpy. The increase of the Henry's law constants with temperature corresponds to a decrease of DMS solubility with temperature in water, CDTA, and CDTA-Fe(II) solutions.

Conclusions

Using the static headspace method with uncertainty estimated to about 2 %, new experimental results for the solubility of DMS in water, CDTA, and ferrous CDTA complex solutions in the temperature range of (288 to 308) K and atmospheric pressure are presented. The chelate concentration was varied between (38 and 300) $\text{mol}\cdot\text{m}^{-3}$. DMS solubility decreases with increasing temperature for all systems studied. CDTA concentration does not affect considerably DMS solubility, and this concentration effect is minor at the largest temperature studied. The solution pH, varied between (2.4 and 8.5), has practically no influence on DMS solubility over the whole concentration and temperature range. The recommended CDTA concentration in the absorption scrubbing equipments should be less than $100 \text{ mol}\cdot\text{m}^{-3}$. As solubility data on similar systems containing DMS/CDTA are not available in the literature, this work is hoped to be an incentive to generate additional results for more exhaustive comparisons.

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