J. Chem. Eng. Data **2004,** *49,* 1691−1696

Solubility of Oxygen in Aqueous Solutions of Fe(III) Complexes of *trans*-1,2-Cyclohexanediaminetetraacetic Acid (CDTA) as a Function of Temperature and Chelate Concentration

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The utilization of ferric chelates for the oxidation of the total reduced sulfurs quartet (H_2S, CH_3SH, CH_3SCH_3, $CH_3S_2CH_3$) is one of the various approaches to mitigate the emission of these airborne pollutants from Kraft pulp-mills' effluents. Oxygen solubility in iron chelate solutions is one important parameter in designing and modeling the regeneration process from ferrous to ferric chelates. Because of the interfering oxidation occurring in Fe(II) chelate solutions, the solubility of oxygen in aqueous solutions in which the gas does not react (Fe(III) complexes of *trans*-1,2-cyclohexanediaminetetraacetic acid (CDTA)) was studied at pressures near atmospheric pressure and temperatures from (293 to 313) K. New experimental solubility results over a chelate concentration ranging from (38 to 124) $mol \cdot m^{-3}$ and pH values of 3 and 7.5 are reported. From the Henry's law constants and their variation with temperature, the standard thermodynamic solution properties of oxygen in these solutions were obtained.

Introduction

The utilization of ferric chelates for the oxidation of the total reduced sulfurs quartet (H_2S, CH_3SH, CH_3SCH_3, $CH_3S_2CH_3$) is one of the various approaches used to remove or at least reduce these airborne pollutants that afflict the Kraft pulp-mills' effluents.[1−8] These emissions in the pulp and paper air effluents can be easily perceived by humans through repulsive odors and create unpleasant life conditions in the neighborhood. The origin of these odors is partially ascribable to pulp production equipment such as boilers, blow tanks, and washers or to black liquor recovery equipment. 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 these sulfur compounds for human beings is 4 orders of magnitude below the regulated emission level, which is ca. 10 ppm in Canada and the U.S. Considering the progressive nature of legislation and the pressure due to public awareness, it is anticipated that increasingly tighter regulations will be applicable in the near future, especially in North America where about 15% of the world's Kraft mills are in operation.

Two fundamental reasons behind using ferric chelates are considered: (i) the protective hindrance of chelate toward sequestered iron to prevent its precipitation in alkaline solutions and (ii) the possibility to regenerate the ferrous chelate product into the active ferric chelate in the presence of dissolved oxygen. These processes proved to be economically advantageous over other options for throughputs between approximately (250 and 2.0 × 10^4) kg of sulfur/day.[9] The chemical absorption of hydrogen sulfide with trivalent iron chelates is usually represented by[10]

$$H_2S(g) \leftrightarrow H_2S(aq)$$

$$H_2S(aq) + 2Fe^{3+}chelat^{n-} \rightarrow S°\downarrow + 2H^+ + 2Fe^{2+}chelat^{n-}$$

in which n denotes the charge of the chelate anion, which can be a poly(aminocarboxylic acid) such as ethyenediaminetetraacetic acid (EDTA), (hydroxyethyl)ethylenediaminetriacetic acid (HEDTA), nitrilotriacetic acid (NTA), or *trans*-1,2-cyclohexanediaminetetraacetic acid (CDTA). Because the active ferric chelate is converted into inactive ferrous chelate, the latter component has to be regenerated into its ferric form by oxidation of the solution with oxygen. This reaction is usually represented by[10]

$$O_2(g) \leftrightarrow O_2(aq)$$

$$O_2(aq) + 4Fe^{2+}chelat^{n-} + 2H_2O \rightarrow 4Fe^{3+}chelat^{n-} + 4OH^-$$

In this way, the iron chelate can be regarded as a pseudocatalyst in the reaction of hydrogen sulfide with oxygen.[11]

In a recent paper,[12] we have studied the solubility of hydrogen sulfide in chelate-containing solutions, which is the key parameter needed for the design of absorption scrubbing equipment. As shown in the equation above, the availability of oxygen along with hydrogen sulfide in the Kraft process atmospheric air emissions is propitious for the simultaneous redox regeneration from the ferrous to the ferric chelate form for the perpetuation of the scrubbing cycle. Oxygen solubility in ferric chelate solutions is therefore an important parameter in modeling the regeneration process.[13] However, when the gas reacts within the aqueous solutions, as in the case of oxygen and Fe(II) chelates, the genuine oxygen physical solubility cannot be measured directly. This interfering oxidation is absent when oxygen is contacted with Fe(III) chelates. Therefore, the solubility of oxygen in aqueous solutions in which the

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10.1021/je049843m CCC: $27.50

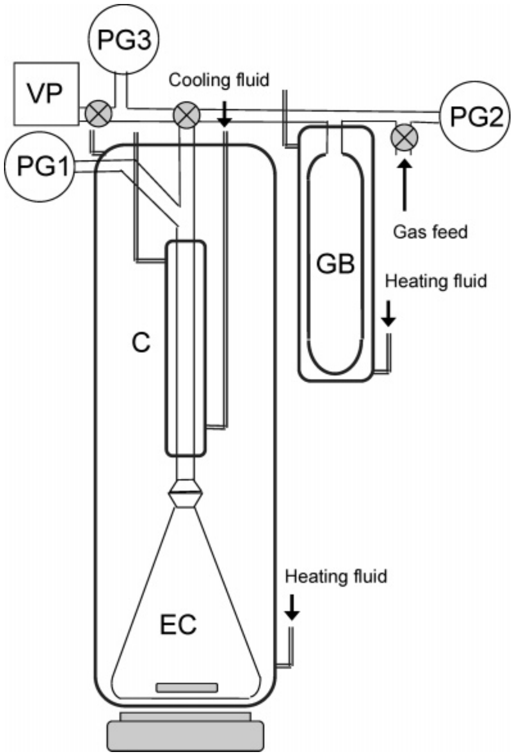

Figure 1. Solubility apparatus. EC, equilibrium cell; GB, gas buret; C, condenser; PG1 and PG2, precision pressure gauges; PG3, vacuum gauge; VP, vacuum pump.

gas does not react (Fe(III) complexes of *trans*-1,2-cyclohexanediaminetetraacetic acid (CDTA)) was studied at subatmospheric pressures and temperatures from (293 to 313) K. New experimental solubility results over a chelate concentration c range of (38 to 124) mol·m^{-3} are reported. To the best of our knowledge, this study is the first of its kind that reports oxygen solubility data in ferric CDTA chelate aqueous solutions within the context of pulp and paper sulfur-bearing compound scrubbing.

The experimental apparatus was based on the saturation method[12] because it is recognized to avoid the uncertainties introduced by analyzing the gas and liquid phases. The amount of gas absorbed in the liquid is determined from the pressure decrease in the equilibrium cell.

The work by Schumpe and collaborators[14−16] allows the estimation of gas solubilities in salt solutions. The model proposed by Schumpe et al.[14] for the solubility of oxygen in electrolyte solutions was chosen to compare the calculated values with the experimental data obtained at 298.15 K.

Experimental Section

trans-1,2-Cyclohexanediaminetetraacetic acid (CDTA) with a minimum purity of 99.3 mass %, iron (II) chloride tetrahydrate with a minimum purity of 99 mass %, 5.0 M sodium hydroxide solution, and HPLC distilled water were purchased from Aldrich Chemical Co. Purified oxygen (99.9%) was purchased from Praxair.

The solubility apparatus is shown in Figure 1. The complete description and procedure are presented in a previous publication;[12] therefore, only a few essentials are repeated here.

The main parts of the apparatus consisted of an equilibrium cell (EC), a gas buret (GB), a condenser (C), and two precision pressure gauges (PG1 and PG2). The equilibrium cell consisted of a standard 250-mL Erlenmeyer flask that ensures, by means of good agitation, appropriate gas−liquid contact. The equilibrium cell is connected to the condenser that was made of stainless steel and optimized to avoid solvent loss during the degassing procedure. Because the precision of the solubility measurements depends strongly on accurate measurements of the total pressure inside the equilibrium cell, the gas pressure in the equilibrium cell was measured by means of a temperature-controlled MKS Baratron type 628B absolute pressure transducer (precision 0.25% full scale, measurement resolution 0.001% full scale), which provides high accuracy and operation that is extremely temperature-stable at operating pressure. Both the undissolved gas and the solvent vapor pressures in the gaseous mixture are determined. The temperature-controlled MKS Baratron 628B transducer used avoids vapor condensation during the measurements and allows very precise determinations of the total pressure. The pressure of the dry gas inside the thermostated gas buret GB (kept at a constant temperature using a thermostatic bath with a precision of ±0.01 °C) was measured using a NOSHOK 100-30/15-2127 transducer (precision 0.25% full scale) at constant temperature. The equilibrium cell together with the condenser and the connecting lines up to the Baratron transducer was kept at a constant temperature using a thermostated bath controlled to ±0.01 °C. The estimated experimental uncertainty in the measured solubility was thought to be about ±1%.

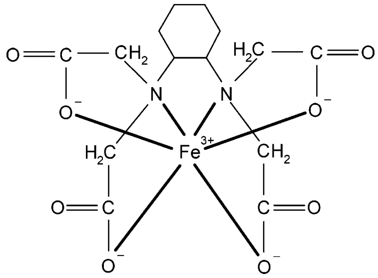

Figure 2. Structure of the Fe(III) complex of CDTA.

The solubility determination starts by preparing the solvent mixture. The concentrations of the iron-free chelate and the ferrous chelate were varied between 38 and 124 mol·m^{-3}. To prepare the CDTA solution, the CDTA was stoichiometrically added to a sodium hydroxide solutions to obtain a solution of pH 7. The pH was measured using an Oakton pH 1000 benchtop meter. For the preparation of the Fe(II) CDTA complexes, a corresponding quantity of iron (II) chloride tetrahydrate was added up to a ratio of chelant/Fe = 1 (pH 3). The Fe(II)−CDTA complex was then allowed to oxidize to the Fe(III)−CDTA complex (Figure 2) by oxygen bubbling under overnight continuous agitation. Complete oxidation was checked by using a Varian Cary 300 UV−vis spectrophotometer.[17] To determine the volume of the liquid in the equilibrium cell, the density of the solutions in the temperature range studied was necessary. The densities were measured using a calibrated pycnometer having a bulb volume of 10 cm^3.

It is important to note that the typical operation conditions of iron chelate-based procedures require a solution pH between 6 and 9.[10] Because of the decrease in the Fe(III) chelate stability at alkaline pH (conversion to Fe(OH)$_3$), solubility measurements were performed up to a solution of pH 7.5 to illustrate the pH influence on the oxygen solubility in these solutions. However, a numerical mass-transfer study of a packed-bed scrubbing process involving Fe(III)−EDTA chelates[13] showed that hydrogen sulfide conversion increases significantly with the increase in

EDTA–Fe(III) concentration, and this variation was more pronounced up to 50 mol·m^{-3}. This conversion exhibited a reduced sensitivity for chelate feed concentrations above 100 mol·m^{-3}. Taking into account that the regeneration process of ferrous chelate product into the active ferric chelate is performed in the same solution in the presence of dissolved oxygen, in this study the CDTA concentration did not exceed 124 mol·m^{-3}.

A weighed quantity of solution was injected into the equilibrium cell. The solution was then slowly degassed by stirring the liquid under vacuum until the base pressure of the vacuum pump was reached. After the solution degassing was completed, the vacuum pump was shut off, the equilibrium chamber was sealed, and the temperature in the water thermostated bath was raised to the value at which the solubility measurement was to be performed. The system kept at a constant temperature T reached the vapor–liquid equilibrium, and the vapor pressure of the degassed solution was measured (P_{VS}). The oxygen was added in the thermostated gas buret (kept at a constant temperature T_G), previously evacuated, and the pressure P_{G1} was read. The number of moles of gas in the buret of volume V_{GB} was then calculated at the gas temperature T_G:

$$n_{G1} = \frac{P_{G1}V_{GB}}{Z_{G1}RT_G} \tag{1}$$

After introducing a certain amount of gas into the equilibrium cell, a new pressure P_{G2} in the buret was read, and the number of moles of gas remaining in the gas buret was calculated:

$$n_{G2} = \frac{P_{G2}V_{GB}}{Z_{G2}RT_G} \tag{2}$$

The difference between n_{G1} and n_{G2} represents the number of moles of gas added to the equilibrium cell, $n_{G,in}$. Until reaching equilibrium, the solution was vigorously stirred to ensure good contact between gas and liquid. The constant pressure read at equilibrium represents the total pressure (gas + vapor). It was assumed that the vapor was exclusively contributed by water. The gas partial pressure was determined by subtracting the vapor pressure of the degassed solvent from the total pressure. The number of moles of gas absorbed in the equilibrium cell $n_{G,abs}$ was determined using relations similar to eqs 1 and 2:

$$n_{G,fin} = \left(\frac{P_{tot}}{Z_{mix}} - \frac{P_{VS}}{Z_{water}}\right)\frac{V_{G,EC}}{RT} \tag{3}$$

$$n_{G,abs} = n_{G,in} - n_{G,fin} \tag{4}$$

The volume of the gas phase in the equilibrium chamber $V_{G,EC}$ is given by the difference between the total volume V_{EC} and the volume occupied by the liquid. The Henry's law constant for the absorption of oxygen in a given solution (K_{O_2}) was then calculated. The compressibility factors for pure water (Z_{water}) and oxygen (Z_G) and their corresponding mixtures (Z_{mix}) were determined using the SRK equation of state as given by Reid et al.[18]

For each system, several runs were performed to check the reproducibility of the results. Measurements were performed in the temperature range of (293 to 313) K and near atmospheric pressure. The CDTA concentration was varied between (38 and 124) mol·m^{-3}. The reproducibility between the various experiments was within 1%.

Table 1. Solubility of Oxygen in CDTA–Fe(III) Solutions as a Function of Temperature *T*, Concentration *c*, and Solution pH

c/mol·m^{-3}	pH	T/K	P/kPa	$x_{O_2} \times 10^5$	K_{O_2}/MPa
38	3	293.15	104.02	2.459	4227
			92.17	2.160	4264
		298.15	106.08	2.355	4502
			87.62	1.959	4471
		303.15	105.58	2.185	4830
			89.34	1.865	4787
		308.15	107.52	2.086	5151
			90.50	1.739	5202
		313.15	106.70	1.944	5487
			89.70	1.651	5430
	7.5	293.15	105.16	2.502	4201
			92.40	2.183	4231
		298.15	112.82	2.518	4477
			93.30	2.099	4443
		303.15	114.99	2.390	4808
			95.20	2.001	4754
		308.15	108.57	2.117	5125
			90.70	1.790	5065
		313.15	109.88	2.014	5452
			93.20	1.726	5398
60	3	293.15	105.14	2.461	4270
			91.80	2.169	4229
		298.15	108.87	2.383	4566
			90.95	2.010	4522
		303.15	104.45	2.142	4873
			89.80	1.858	4832
		308.15	107.60	2.061	5219
			88.72	1.718	5162
		313.15	110.85	2.012	5507
			92.40	1.657	5574
	7.5	293.15	106.78	2.519	4236
			92.15	2.194	4198
		298.15	108.84	2.401	4531
			90.70	2.016	4496
		303.15	109.46	2.262	4837
			94.85	1.984	4778
		308.15	108.27	2.094	5169
			92.18	1.802	5114
		313.15	110.10	2.008	5481
			94.50	1.706	5536
124	3	293.15	105.11	2.358	4454
			91.92	2.080	4417
		298.15	107.38	2.241	4788
			90.57	1.906	4748
		303.15	109.48	2.157	5073
			88.70	1.764	5025
		308.15	109.70	2.045	5362
			89.55	1.650	5424
		313.15	110.57	1.904	5804
			94.65	1.611	5874
	7.5	293.15	103.24	2.331	4427
			94.92	2.165	4382
		298.15	103.88	2.187	4748
			97.12	2.060	4712
		303.15	106.70	2.121	5027
			91.58	1.841	4971
		308.15	110.72	2.074	5335
			94.75	1.796	5273
		313.15	117.54	2.041	5757
			93.30	1.637	5696

Results and Discussion

Data Reduction. The solubility of oxygen in Fe(III)–CDTA solutions can be expressed in terms of the Henry's law coefficient:[19]

$$K_{O_2}(T) \equiv \lim_{x_{O_2} \to 0} \frac{f_{O_2}(T, P^{sat})}{x_{O_2}} \tag{5}$$

where $f_{O_2}(T, P^{sat})$ and x_{O_2} represent, respectively, the fugacity of oxygen and its concentration in the liquid phase

Table 2. Estimated Solubility of Oxygen in CDTA–Fe(III) Solutions at 101.325 kPa

c/mol·m^{-3}	pH	T/K	$x_{O_2} \times 10^5$	K'_{O_2}/MPa·m^3·kmol^{-1}
38	3	293.15	2.385	77.47
		298.15	2.257	81.89
		303.15	2.106	87.79
		308.15	1.956	94.54
		313.15	1.855	99.72
	7.5	293.15	2.402	76.93
		298.15	2.270	81.41
		303.15	2.118	87.29
		308.15	1.988	93.05
		313.15	1.867	99.10
60	3	293.15	2.383	78.18
		298.15	2.228	83.61
		303.15	2.087	89.29
		308.15	1.951	95.52
		313.15	1.828	101.99
	7.5	293.15	2.401	77.55
		298.15	2.243	83.02
		303.15	2.106	88.45
		308.15	1.970	94.61
		313.15	1.839	101.39
124	3	293.15	2.283	83.75
		298.15	2.124	90.09
		303.15	2.006	95.46
		308.15	1.878	102.02
		313.15	1.735	110.54
	7.5	293.15	2.299	83.02
		298.15	2.141	89.24
		303.15	2.026	94.43
		308.15	1.909	100.29
		313.15	1.769	108.37

expressed on a mole fraction basis. When the solute (O_2) concentration in the liquid phase is very low, eq 5 can be written as

$$K_{O_2}(T) = \frac{\varphi_{O_2}(T, P)\, P_{O_2}}{x_{O_2}} \tag{6}$$

in which $\varphi_{O_2}(T, P)$ and P_{O_2} represent the fugacity coefficient and the partial pressure of oxygen, respectively.

The fugacity coefficients were calculated using the SRK equation of state as given by Reid et al.[18]

Experimental Results. The proper operation of the apparatus and the accuracy of the measuring method have been demonstrated in our earlier study.[12] The solubility of oxygen in aqueous solutions of Fe(II)–CDTA complexes was measured at temperatures from (293 to 323) K and pressures near 1 atm, taking into account that this is the usual operating pressure in the industrial scrubbing processes. The solution concentrations were (38, 60, and 124) mol·m^{-3}, expressed on a CDTA basis. For the Fe(III)–CDTA solutions, the pH was varied between 3 and 7.5. A summary of the results is given in Table 1, and an estimation of the solubility at 101.325 kPa is presented in Table 2.

The chelate concentration has little effect on the oxygen solubility in the temperature range studied (Figure 3). The solubility decreases with increasing temperature (Figure 4), and it was observed that its influence was more important than the concentration effect (Figure 5). In addition, only a slight influence of pH can be observed at the same chelate concentration (Figures 3 and 4).

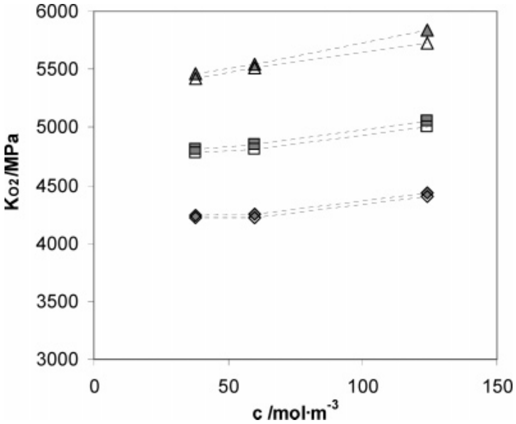

Figure 3. Influence of chelate concentration on the solubility of oxygen in CDTA–Fe(III) solutions at pH 3 and 7.5 and at different temperatures: 293.15 K (◆, pH 3; ◇, pH 7.5), 303.15 K (■, pH 3; □, pH 7.5), 313.15 K (▲, pH 3; △, pH 7.5).

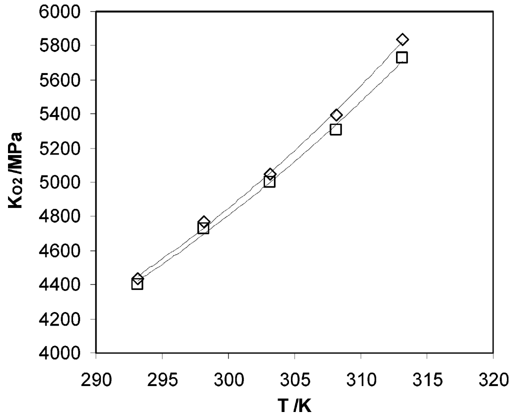

Figure 4. Influence of temperature on the solubility of oxygen in CDTA–Fe(III) solutions at a chelate concentration of 124 mol·m^{-3} at pH 3 (◇) and pH 7.5 (□).

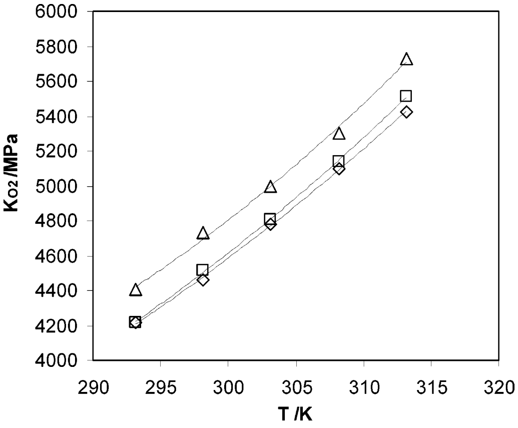

Figure 5. Influence of temperature on the solubility of oxygen in CDTA–Fe(III) solutions at pH 7.5 at different chelate concentrations c (mol·m^{-3}): ◇, 38; □, 60; △, 124.

On the basis of the model of Schumpe et al.,[14] it is possible to estimate the solubility of oxygen in CDTA–Fe(III) solutions. In this model, the solubility of oxygen in mixed-electrolyte solutions is given by

$$\log\left(\frac{C_0}{C}\right) = \log\left(\frac{K'_{O_2}}{K'_{O_2,0}}\right) = \frac{1}{2}\sum_i H_{O_2,i} C_{sp,i} z_i^2 \tag{7}$$

where C_0 and C are, respectively, the oxygen solubility in water and in the salt solution, $K'_{O_2,0}$ and K'_{O_2} are, respectively, the Henry's law constant in water and in the salt solution (MPa·m^3·kmol^{-1}), $H_{O_2,i}$ represents the ion-specific constants for salting-out oxygen corresponding to species i, $C_{sp,i}$ represents the concentration of species i in the solution, and z_i represents the ion charge. Using the values of the ion-specific constants for salting-out oxygen available at 298.15 K (expressed in m^3·kmol^{-1}), $H_{O_2,Na^+} = -0.55$, $H_{O_2,Cl^-} = 0.884$, and $H_{O_2,Fe^{3+}CDTA^{4-}} = 0.9$, and the experimental Henry's law constant in water at 298.15 K obtained in this work, $K'_{O_2,0} = 79.47$ MPa·m^3·kmol^{-1}, the Henry's law constants in the CDTA−Fe(III) solutions at this temperature were estimated with a mean absolute deviation of 1.55 % (maximum deviation of 2.1 %), mentioning that all predicted values were slightly overestimated through eq 7. However, it can be concluded that the predictions were in quite good agreement with the measured solubilities. It is important to note that the ion-specific constant for salting-out oxygen corresponding to the chelate complex, $Fe^{3+}CDTA^{4-}$, present in solution was estimated by assuming that $H_{O_2,i}z_i$ = constant.[20]

Standard Thermodynamic Properties of Solution. The standard thermodynamic properties of the solution are defined as the change in, respectively, the Gibbs energy, enthalpy, and entropy when the solute is transferred at constant temperature T from the pure perfect gas state at standard (unit) pressure to the infinitely dilute state of the solute in the solvent at pressure P.[21] The standard state of the solute is defined by the constraint that its activity coefficient is unity in a hypothetical solution of unit mole fraction (pure solute) extrapolated from the infinite dilution state (reference state).

The standard thermodynamic properties of solution can be calculated from the correlation of the Henry's law constant by applying the following thermodynamic relations:

$$\Delta_{sol}G^\circ = RT\ln\left(\frac{K_{O_2}(T)}{P^\circ}\right) \quad (8)$$

$$\Delta_{sol}H^\circ = -T^2\left(\frac{\partial(\Delta_{sol}G^\circ(T, P)/T)}{\partial T}\right)_P = R\left(\frac{\partial \ln(K_{O_2}(T)/P^\circ)}{\partial(1/T)}\right)_P \quad (9)$$

$$\Delta_{sol}S^\circ = \frac{\Delta_{sol}H^\circ - \Delta_{sol}G^\circ}{T} \quad (10)$$

$$\Delta_{sol}C_p^\circ = \left(\frac{\partial\Delta_{sol}H^\circ}{\partial T}\right)_P \quad (11)$$

The function $K_{O_2}(T)$ was obtained from the experimental data considering that the Henry's law constants are pressure-independent over the explored range, using a correlation of the type

$$\ln K = A + B(T/\mathrm{K}) + C/(T/\mathrm{K}) \quad (12)$$

All experimental data for CDTA−Fe(III) (pH 3 and 7.5) solutions were fit with a global average deviation of 0.55%. Figure 6 shows the good agreement between experimental and calculated Henry's law constants over the whole range of temperature and concentration used in this work. The fitted coefficients A, B, and C of eq 12 are given in Table 3. From the dependence of Henry's law constants on temperature, the thermodynamic properties of a solution at standard pressure (P° = 0.1 MPa) were calculated, and the values at 298.15 K are presented in Table 4.

For all of the systems studied, the standard Gibbs energy increases with temperature over the entire temperature range. This behavior can be observed in Table 5, for example, in the case of the two extreme concentrations used, namely, 38 and 124 mol·m^{-3}, at both pH 3 and 7.5. This indicates negative values for the standard entropy. As shown in Figure 7 for two chelate concentrations, 60 and 124 mol·m^{-3}, the logarithms of Henry's law constants decrease with increasing reciprocal temperature. This variation is in agreement with the negative standard enthalpy of solution, which is proportional to the partial derivative of the logarithms of Henry's law constants with respect to inverse temperature at constant pressure.

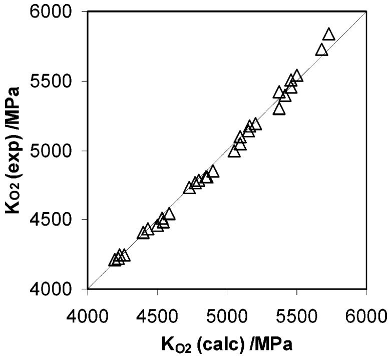

Figure 6. Comparison between experimental and calculated oxygen solubility using eq 12.

Table 3. Coefficients of Equation 12

c/mol·m^{-3}	pH	A	B	C
38	3	24.416	−0.019900	−2999.9
	7.5	24.532	−0.020280	−3003.5
60	3	24.425	−0.019900	−3000.0
	7.5	24.390	−0.019818	−3000.1
124	3	24.446	−0.019847	−2999.2
	7.5	24.457	−0.019900	−3000.0

Table 4. Thermodynamic Properties of Solution for Oxygen in CDTA−Fe(III) Solutions at 298.15 K

c		$\Delta_{sol}G^\circ$	$\Delta_{sol}H^\circ$	$\Delta_{sol}S^\circ$	$\Delta_{sol}C_p^\circ$
mol·m^{-3}	pH	kJ·mol^{-1}	kJ·mol^{-1}	J·mol^{-1}·K^{-1}	J·mol^{-1}·K^{-1}
38	3	26.6	−10	−123	99
	7.5	26.6	−10	−123	101
60	3	26.6	−10	−124	99
	7.5	26.6	−10	−124	98
124	3	26.7	−10	−124	98
	7.5	26.7	−10	−124	99

Table 5. Temperature Dependence of the Standard Gibbs Energy, Enthalpy, and Entropy of Solution for Oxygen in CDTA−Fe(III) (pH 3 and 7.5) Solutions of Concentration 38 and 124 mol·m^{-3}

c		T	$\Delta_{sol}G^\circ$	$\Delta_{sol}H^\circ$	$\Delta_{sol}S^\circ$	$\Delta_{sol}C_p^\circ$
mol·m^{-3}	pH	K	kJ·mol^{-1}	kJ·mol^{-1}	J·mol^{-1}·K^{-1}	J·mol^{-1}·K^{-1}
38	3	293.15	26.0	−11	−125	97
		298.15	26.6	−10	−123	99
		303.15	27.2	−10	−122	100
		308.15	27.8	−9	−120	102
		313.15	28.4	−9	−119	104
	7.5	293.15	25.9	−10	−124	99
		298.15	26.6	−10	−123	101
		303.15	27.2	−9	−121	102
		308.15	27.8	−9	−119	104
		313.15	28.4	−8	−117	106
124	3	293.15	26.1	−11	−126	97
		298.15	26.7	−10	−124	98
		303.15	27.3	−10	−122	100
		308.15	27.9	−9	−121	102
		313.15	28.5	−9	−119	103
	7.5	293.15	26.1	−11	−125	97
		298.15	26.7	−10	−124	99
		303.15	27.3	−10	−122	100
		308.15	27.9	−9	−121	102
		313.15	28.5	−9	−119	104

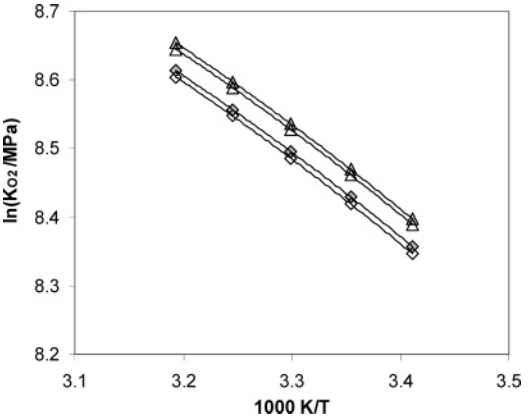

Figure 7. Logarithms of Henry's law coefficients as a function of inverse temperature for various O_2−CDTA/Fe(III) systems: c = 60 mol·m^{-3}, pH 3 (◆); c = 60 mol·m^{-3}, pH 7.5 (◇); c = 124 mol·m^{-3}, pH 3 (▲); c = 124 mol·m^{-3}, pH 7.5 (△).

Moreover, as expected, the increase in the Henry's law constants with temperature corresponds to a decrease in oxygen solubility with temperature in CDTA−Fe(III) solutions.

Conclusions

New experimental results for the solubility of oxygen in the ferric CDTA complex in the temperature range of (293 to 323) K and pressures near atmospheric for a chelate concentration varying between (38 and 124) mol·m^{-3} and a pH of 3 and 7.5 were obtained using an experimental apparatus based on the saturation method with an accuracy estimated to about 1%. It was shown that the solubility of oxygen decreases with increasing temperature. The effect of temperature on oxygen solubility in these solutions was found to be more important than the concentration effect. Moreover, the observed influence of solution pH was quite slight. Bearing in mind the inception of the degradation of the organometallic complex in alkaline solutions, the pH range used in this work extended from acidic to slightly alkaline solutions. For a constant solution pH, it was observed that the decrease in oxygen solubility is more pronounced at the highest chelate concentrations. Because solubility data on similar systems are not available in the literature, this work may generate an incentive in the literature to gather additional results for more exhaustive comparisons.

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Received for review April 22, 2004. Accepted July 26, 2004. Financial support from the Natural Sciences and Engineering Research Council of Canada (NSERC) Strategic Grant Program Environment & Sustainable Development is gratefully acknowledged.

JE049843M