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SOLUBILITIES OF OXYGEN IN SELECTED ALKANE SOLVENTS AND IN AQUEOUS COPPER ELECTROREFINING SOLUTIONS

by

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Ottawa, Ontario

A thesis submitted to the school of Graduate Studies and Research in partial fulfillment of
the requirements for the degree of

MASTER OF APPLIED SCIENCE

in the Department of Chemical Engineering

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ABSTRACT

The equilibrium solubilities of oxygen were determined in aqueous solutions which were made to simulate solutions typically found in electrorefining processes to obtain ultra pure copper. The electrorefining solutions were composed of 30 g/L Cu^{+2} / 150 g/L H_2SO_4 and 60 g/L Cu^{+2} / 150 g/L H_2SO_4. The solubilities of oxygen were also determined in aqueous solutions containing 30 g/L Cu^{+2}, 60 g/L Cu^{+2}, 75 g/L H_2SO_4, and 150 g/L H_2SO_4. The solubilities of oxygen were determined in these solutions at a temperature of 333.15 K and at atmospheric pressure. In addition, the densities of the aqueous solvent solutions were measured in the temperature range between 313.15 K and 413.15 K. Further, the vapor pressures of the copper sulphate-sulphuric acid solutions were determined at a temperature of 333.15 K.

Oxygen solubilities in straight chain alkanes were also measured. The hydrocarbons investigated include: hexane, octane, decane, dodecane and hexadecane at temperatures of 273.15 K, 298.15 K, and 323.15 K and at atmospheric pressure.

The solubilities were determined volumetrically in a two stage process. The first stage ensured adequate deareation of the solvents, while the second stage allowed the solvent to be completely saturated with oxygen gas. The aqueous densities were measured by means of Pyrex glass dilatometer tubes. Further, since the vapor pressures and the densities of the aqueous solutions were experimentally determined, the solubilities found in this work are believed to be more accurate than those solubility values found in the literature.

The solubilities of oxygen in the aqueous solutions were found to be very low, on the order of 10^{-5} mole fraction, for an oxygen partial pressure of 101.325 kPa. Addition of electrolytes to water, such as the sulphuric acid and the copper sulfate salt, salted out the oxygen. The solution containing 60 g/L Cu^{+2} and 150 g/L H_2SO_4 exhibited a

decrease in oxygen solubility of approximately 53% as compared with the solubility of oxygen in pure water.

The solubilities of oxygen in the hydrocarbons were approximately ten times larger than the solubilities of oxygen in the aqueous solutions. The solubilities of oxygen in the normal alkanes were found to increase as the carbon number of the alkane was increased. Further, the temperature coefficient of solubility for the normal alkanes studied was found to be very small; that is, temperature had little effect on the solubility of oxygen in the alkanes.

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NOMENCLATURE

a_i	Activity of species i
C_i	Nonelectrolyte solute gas concentration, mole/m^3 (mole/L)
C_s	Electrolyte concentration, mole/m^3 (mole/L)
f, f_i	Fugacity, fugacity in species *i*
f_g	Gas phase fugacity
$\hat{f}_l$	Fugacity of pure liquid at a specified temperature and pressure
K_i	Solute-solute gas interaction parameter, m^3/mole (L/mole)
K_H	Henry's law constant, kPa/mole fraction
K_s	ion-nonelectrolyte interaction parameter, salt effect parameter, m^3/mole (L/mole)
K_{scL}	Setschenow salt effect parameter based on the Bunsen coefficient, m^3/mole (L/mole)
$K_{sc\alpha}$	Setschenow salt effect parameter based on the Ostwald coefficient, m^3/mole (L/mole)
L_{actual}	Actual length of solution dilation, m (cm)
$L_{measured}$	Measured length of solution dilation, m (cm)
L_l	Ostwald coefficient for the solution
L_l°	Ostwald coefficient for the pure solvent
L_v	Ostwald coefficient based on the solution volume
M_s	Solvent molecular weight
n_g	Number of moles of gas
n_s	Number of moles of solvent
P	Vapor pressure of a solution, kPa (psi, mmHg)
P°	Vapor pressure of pure solvent, kPa (psi, mmHg)

P_g	Partial pressure of gas, kPa (mmHg)
r	Correction factor
R	Gas constant
S_i	Gas solubility in solution, mole/m^3 (mole/L)
$S_i^{\bullet}$	Gas solubility in pure solvent, mole/m^3 (mole/L)
T	Temperature, K (°C)
V_1	Volume of solution at temperature T1, m^3 (cm^3)
V_2	Volume of solution at temperature T2, m^3 (cm^3)
$V_i^{\bullet}$	Molar volume of gas at 0 °C, m^3/mole (cm^3/mole)
V_g	Volume of gas absorbed at specified temperature and pressure, m^3 (cm^3)
V_L	Volume of solution absorbing gas at specified temperature and pressure, m^3 (cm^3)
x_g, x_L	Mole fraction gas absorbed

Greek Symbols

α	Bunsen coefficient
γ_b	Activity coefficient of electrolyte
γ_i, γ_2	Activity coefficient of the gas in solution
$\gamma_i^{\bullet}$	Activity coefficient of the gas in the pure solvent
ρ_1	Density of solution at temperature T1, kg/m^3 (g/cm^3)
ρ_2	Density of solution at temperature T2, kg/m^3 (g/cm^3)
ρ_{actual}	Actual density of water, kg/m^3 (g/cm^3)
$\rho_{measured}$	Measured density of water kg/m^3 (g/cm^3)
ρ_s	Solution density, kg/m^3 (g/cm^3)

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1. INTRODUCTION

A knowledge of the solubilities of gases in liquids is of considerable importance to Chemical Engineers. For example, for many reactions which involve gases and liquids, solute solubilities must be known for an analysis of the process (Hildebrand and Scott, 1964). Quite often, however, the solubility of a gas in a solvent is not known, especially for solvent solutions involving binary mixtures. In certain instances, the solubility may be known but for a limited range of temperature, pressure or composition. Furthermore, in some situations a lack of agreement amongst researchers renders available solubility data questionable.

The main objective of the present thesis was to provide accurate and reliable gas solubility data. The solubility of oxygen in a number of liquids and solvent solutions was determined. Equilibrium solubilities of oxygen were determined in linear, saturated hydrocarbons such as hexane, octane, decane, dodecane, and hexadecane. Furthermore, oxygen solubility in aqueous sulphuric acid solutions as well as solutions containing copper sulphate salt were measured. The aqueous solutions were made to simulate solutions typically found in the electrorefining of copper. In addition, the densities and vapor pressures of the aqueous solutions were also measured.

1.1 OXYGEN SOLUBILITY IN HYDROCARBONS

Oxygen solubilities were measured in the following straight chain alkanes: hexane, octane, decane, dodecane, and hexadecane. Solubility of oxygen in these solvents has been critically evaluated by Battino et al. (1981). Battino has noted a lack of agreement, amongst researchers, in the solubility of oxygen as a function of the chain length of the alkane. Most notably, the results of Makranczy et al. (Battino et al., 1981), showed a decrease in the solubility of oxygen as the chain length, or the carbon number of the alkane was increased. However, the work of Blanc and Batiste (Battino et al., 1981) indicated an increase in oxygen solubility with increasing carbon number. Therefore, further investigation of oxygen solubility in n-alkanes was undertaken to contribute towards the resolution of the discrepancy cited above.

1.2 OXYGEN SOLUBILITY IN AQUEOUS SOLUTIONS

The study of oxygen solubility in the aqueous solutions consisted of solubility determinations in pure water, in sulphuric acid solutions, in copper sulphate solutions and in solutions containing both sulphuric acid and copper sulphate. The acidic copper sulphate solutions were made to simulate solutions typically found in electrorefining processes to purify copper.

The solubility of oxygen in water is known precisely. The work of Benson et al. (1979) is considered to be the most precise measurement of gas solubility to date. They have proposed an equation to predict the amount of oxygen dissolved in water, in the temperature range from 273.15 K to 373.15 K, with a standard deviation of ±0.017%. For that reason, the solubility of oxygen in water can serve as a reference to ensure the reliability of the solubility apparatus, and more importantly, the experimental technique of the investigator. After examination of the water reference system, gas solubilities in sulphuric acid and copper sulphate solutions were measured.

A compilation of oxygen solubilities in various aqueous solutions was produced in 1981 by Battino et al. Surprisingly, only six reports concerning the solubility of oxygen in aqueous sulphuric acid solutions were found. Most of the initial work was performed near the turn of the century. Additional data were made available by Bruhn et al. (Battino et al., 1981), who studied oxygen solubility in 0.5, 1.0 and 1.5 mole/L H_2SO_4 solutions at five temperatures ranging between 323 and 523 K. Paucity of solubility data was even more apparent with binary solutions of acid and metal salts. At the time of the compilation by Battino, there was only one study which dealt with binary mixtures. Klyueva (Battino et al., 1981), measured oxygen solubilities in sulphuric acid solutions saturated with either Ni_3S_2, Cu_2S or Co_4S_3. The most recent work of Hayduk and Kimweri (1990), reported the solubility of oxygen in aqueous sulphuric acid containing varying amounts of zinc and iron sulphate salts (Kimweri, 1990).

The above historical review served to demonstrate the need for additional data. Solubility data in sulphuric acid is available for narrow ranges of temperature, pressure and composition so that interpolation or extrapolation for purposes of comparisons is extremely difficult and unreliable. Similar difficulties arise with solubilities of binary mixtures. As mentioned previously, these binary solutions are used in the electrorefining of copper ores. The process of electrorefining of copper metal from aqueous electrolytes is used along with the pyrometallurgical processes for the recovery and purification of copper metal.

Chalcopyrite ($CuFeS_2$) is the most abundant copper bearing ore. The main constituents of chalcopyrite are: copper, iron, and sulphur in approximately equal proportions. In addition, copper ores also contain impurities such as nickel, silver and gold as well as trace quantities of zinc, selenium, arsenic, antimony, tellurium, cobalt, tin and lead among others. Fine particles of chalcopyrite can be separated from other sulphide minerals and gangue materials present in the ore through flotation. Separation by flotation yields a product which typically contains about 90% copper (Habashi, 1978). The copper mineral from the flotation unit is roasted, smelted and fire refined to yield crude copper. In these pyrometallurgical steps, the chalcopyrite loses most of the iron and sulphur, leaving mainly copper, some sulphur and other trace impurities (Moore, 1981). Recovery of trace impurities, such as the precious metals, represents a significant economic gain. These impurities are separated and collected in the electrorefining process.

The blister copper containing the precious metals is oxidized with air and cast on horizontal casting wheels to produce copper anodes. The anodes at this stage are approximately 98% pure (Bertocci and Turner, 1974). The copper anodes are electrorefined further to yield pure copper cathodes with a purity of 99.99% or better. The associated impurities, namely the precious metals, form insoluble anode slimes which collect on the faces of the corroded anodes or at the bottom of the electrorefining tanks. The anode slimes are further treated to recover the precious metals present (Chen, 1989).

Copper anodes are typically electrorefined in a $CuSO_4$ - H_2SO_4 electrolytic solution. The electrolytic solutions generally consists of 30 to 60 g/L Cu^{2+} and 130 to 210 g/L H_2SO_4 (Schloen, 1987). In the present work, two electrolyte solutions were investigated. The first solution contained 30 g/L Cu^{2+} and 150 g/L H_2SO_4 and the second solution contained 60 g/L Cu^{2+} and 150 g/L H_2SO_4. The determination of oxygen solubilities in these electrolytes was considered to provide useful information about the maximum rate of copper dissolution (Bertocci and Turner, 1974). Consider, for example, the role of oxygen on the recovery of silver during electrorefining.

Analytical data for the copper anodes from the three copper refineries in Canada (Noranda, Inco and Kidd Creek Mines) showed that the major constituent of the anodes was copper, in excess of 99%. Anodic impurities will vary depending upon ore origin as well as efficiency and type of subsequent processing. Typical concentrations of impurities range from approximately 0.67% down to trace quantities. A particularly important impurity that must be recovered is silver. The silver concentration in the copper anodes ranges from approximately 0.035 to 0.21% (Dutrizac and Chen, 1988). Thus silver recovery from the copper anodes represents a major economic gain for copper refineries. The chemical changes of silver during electrorefining is still uncertain. Determination of equilibrium oxygen solubilities may provide insight into the reactions occurring between silver and oxygen. It should be noted that since silver and other impurities are present in such small quantities, their affect on oxygen solubility may be considered to be negligible and beyond the precision of the experimental method.

The process of anodic copper dissolution during electrorefining may be written as:

$$Cu^{\circ} \; - \; 2e \; \rightarrow \; Cu^{2+}. \tag{1}$$

The anodic dissolution process can also produce the cuprous ion, hence reaction [1] represents a simplification of the dissolution process. The standard electrode potential for the reduction of copper to produce the cupric ion was 0.337 V, while the standard electrode potential for the generation of the cuprous ion was 0.518 V (Harris, 1982). Therefore, for the dissolution process, an electrode potential equivalent to the reduction potential must be applied. As the anode was made progressively more positive, the predominant electrode reaction observed would be the one with the least positive electrode potential; that is, preferential production of the cupric ion would occur (Moore, 1981). Furthermore, Jardy et al. (1992) have reported that the dissolution mechanism of copper was dependent on the current density. Jardy et al. (1992) found that the copper metal dissolved through the monovalent state at low current densities. On the other hand, the divalent form was favored at higher current densities. The copper dissolution valency changed from one to two at a current density of about 100 A/m^2. Typical current densities found in industry are on the order of 200 A/m^2. Even though the dissolution of the copper anode during electrorefining strongly favors the production of the cupric ion, the cuprous ion could still be produced. The cuprous ions can undergo further reaction with dissolved oxygen or with other cuprous ions to form the cupric ions:

$$2Cu^{+} \; + \; \frac{1}{2}O_2 \; + \; 2H^{+} \; \rightarrow \; 2Cu^{2+} \; + \; H_2O, \tag{2}$$

$$2Cu^{+} \rightarrow Cu^{2+} + Cu^{\circ}. \tag{3}$$

Dissolution of the copper anode exposes the silver to the acidic electrolyte. Approximately 99% of the silver is present as a solid solution in the copper anode. Thus dissolution of copper results in the concomitant dissolution of silver at the anode - electrolyte interface. Silver dissolution may occur electrochemically or by dissolved oxygen

$$Ag_{solid\ solution} - e \rightarrow Ag^{+}, \tag{4}$$

$$2Ag_{solid\ solution} + \frac{1}{2}O_2 + 2H^{+} \rightarrow 2Ag^{+} + H_2O\ . \tag{5}$$

Once in solution, the silver ion is precipitated to metallic silver and incorporated in the slimes layer. Thus the slimes layer must be further processed to recover the silver.

The role of oxygen in silver recovery is quite evident from reaction [5]. Oxidation of 1 mg of silver would require approximately 0.07 mg of oxygen. Furthermore, oxygen is also consumed in the oxidation of cuprous ion to cupric ion. Most of the impurities in the copper anode exist as a solid solution in the copper matrix or as discrete inclusions of Cu_2O, $Cu_2(Se, Te)$ etc. Dissolved oxygen also serves to oxidize the cuprous ion in these inclusions to cupric ions. Consider, for example, the oxidation of cuprous selenide to cupric selenide and cupric sulphate,

$$Cu_2Se + \frac{x}{2}O_2 + xH_2SO_4 \rightarrow Cu_{2-x}Se + xCuSO_4 + xH_2O, \tag{6}$$

$$2Cu_{2-x}Se + \left(\frac{1-2x}{2}\right)O_2 + (1-2x)H_2SO_4 \rightarrow Cu_3Se_2 + (1-2x)CuSO_4 + (1-2x)H_2O, \tag{7}$$

$$\frac{1}{2}Cu_3Se_2+\left(\frac{05-x}{2}\right)O_2+(0.5-x)H_2SO_4 \rightarrow Cu_{1-x}Se+(0.5-x)CuSO_4+(0.5-x)H_20, [8]$$

$$Cu_{1-x}Se \quad + \quad \frac{x}{2}O_2 \quad + \quad xH_2SO_4 \quad \rightarrow \quad CuSe \quad + \quad xCuSO_4 \quad + \quad xH_2O. \qquad [9]$$

The degree to which selenide oxidation proceeds is influenced by the contact time of the slime with the oxygenated electrolyte as well as the quantity of silver present (Chen and Dutrizac, 1989).

1.2.1 FACTORS INFLUENCING PRECISION OF GAS SOLUBILITY MEASUREMENTS

Gas solubilities were measured using the solubility apparatus described by Hayduk et al. (1972) and is similar to the apparatus first used by Morrison and Billet. The gas solubility measurement method consisted of contacting degassed solvent with dry gas, which was confined at atmospheric pressure in a burette over mercury. It was possible to volumetrically determine the rate of gas absorption and to measure the volume of accumulated solution. Repeated readings of the volume of gas absorbed per unit volume of accumulated solution allowed for the determination of the gas solubility.

Gas solubility measurements are influenced by the following factors (Clever and Battino, 1975):

- Purity of materials (96 - 99%)
- Temperature measurement and control (±0.1 °C)
- Pressure measurement and control (±1 mmHg)
- Weighings (±0.01 mg)

- Volume determinations (±0.1 cm^3)
- Saturation of solvent with gas; that is, attainment of equilibrium
- Solvent deareation
- Determination of true volume of gas dissolved and
- Occurrence of any contamination during the transferring procedure.

Control of the variables above to the close tolerances as indicated in parenthesis in the above list would lead to an overall precision in the gas solubility measurements of 2% or better. Factors such as the purity of materials, and the determination of experimental variables such as temperature, pressure, volume, and mass are usually adequate so as to contribute negligibly to the final experimental error. The control of temperature and pressure, however, can be quite difficult. Cook (Clever and Battino, 1975) found that temperature control to within ±0.1 °C was quite adequate for most measurements and that usually the temperature could be controlled fairly easily at this level of precision.

The influence of temperature on gas solubility measurements requires consideration of the following coefficients (Clever and Battino, 1975): the temperature coefficient of the solvent vapor pressure and the temperature coefficient of solubility. The temperature coefficient of solvent vapor pressure was not a major concern in the present work since the vapor pressures of all the aqueous solutions were experimentally determined, at the temperature of the solubility measurement. On the other hand, for oxygen solubilities in the hydrocarbons, vapor pressures were available in the literature. For regular solutions, as defined by Hildebrand and Scott (1964) the temperature coefficient of solubility can be determined as the slope of the logarithm mole fraction solubility versus logarithm of the absolute temperature plot.

Most of the errors in solubility measurements are due to the last four factors in the list shown above. Errors associated with the determination of the true volume of gas dissolved and control of contamination during any transferring procedure can be minimized through proper design of the equilibrium apparatus and calibration of the gas burettes (Battino and Clever, 1966).

Complete saturation of solvent with gas is crucial in order to obtain reliable solubility measurements. Complete saturation or equilibrium can be attained in flow systems through control of the solvent infusion rate. Complete saturation can be verified by repetition of solubility measurements using a range of solvent flow rates. For example, if the solubility determined at a solvent rate of 1.0 ml/minute and at a solvent rate of 0.5 ml/minute was the same within experimental error, then equilibrium has been attained in both experiments (Battino and Clever, 1966). However, if the measured gas solubility at the two solvent infusion rates was not the same then the solvent was not completely saturated. In this case, the solvent infusion rate was lowered and the solubility of the gas was determined again.

The final major factor affecting the accuracy of solubility measurements was the adequacy of the deaeration of the solvent. It is often considered that deaeration of the solvent was perhaps the most important source of error in solubility determinations. In general, a solvent was considered degassed when the residual gas pressure is approximately 100 microns. One of the main difficulties with deaeration was the inability to actually measure the degree of deaeration. It was difficult to ascribe a numerical value to indicate completeness of degassing. Therefore, the reproducibility of the solubility results with different times of deareation served as a means of verifying adequate deareation.

1.3 VAPOR PRESSURE OF THE AQUEOUS SOLUTIONS

The vapor pressure of a liquid is function of temperature and increases rapidly with temperature. The presence of nonvolatile components in the liquid, results in a reduction of the vapor pressure of the solvent. Reliable values of solution vapor pressures are required to calculate gas solubilities. Typically, these vapor pressures are calculated by means of Raoult's law. Raoult's law, however, is an ideal relationship, applicable to dilute and ideal solutions only. Therefore, to increase the precision of the solubility measurement, the vapor pressures of the aqueous sulphuric acid and copper salt solutions were experimentally determined. The vapor pressure of the aqueous solutions was measured using the apparatus of Gibbs and Van Ness (1972). The aqueous solutions under consideration included water, 75 and 150 g/L sulphuric acid, 30 and 60 g/L hydrated cupric sulphate salt, as well as binary mixtures of 30 g/L cupric sulphate salt with 150 g/L sulphuric acid and 60 g/L cupric sulphate salt with 150 g/L sulphuric acid. The vapor pressures were determined at a temperature of 333.15 K. These vapor pressure data were then used to verify the extent to which Raoult's law could be applied.

1.4 DENSITIES OF AQUEOUS SOLUTIONS

A knowledge of solution densities was necessary to calculate gas solubilities. Solution densities allow one to convert a volumetric flow rate to a mass flow rate or vice versa. Furthermore, tabulated densities are generally limited to binary mixtures for a specific temperature range. Tabulated densities of sulphuric acid (Sohnel et al., 1985, Perry et al., 1984) and cupric sulphate (Sohnel et al., 1985) are available up to a maximum temperature of 373.15 K and any extrapolations beyond this range are extremely questionable. Correlations for such mixtures tend to have a rather narrow range of applicability and some are quite difficult to apply. Furthermore, the densities of three component mixtures such as water, acid and salt are virtually non-existent. Hence, experimental determinations of the densities for the aqueous solutions were undertaken.

A series of dilatometer tubes were employed to determine the densities of the aqueous solutions (Kimweri, 1990). Essentially, the dilatometer tubes allow for the accurate determination of the change in volume of the aqueous solutions resulting from an increase in the temperature. Furthermore, since the dilatometer tubes are sealed, the mass of the aqueous solutions remains constant. Hence densities can be calculated from the amount of expansion of the solutions.

1.5 SCOPE OF THE RESEARCH

The objective of the present work was to measure the equilibrium solubilities of oxygen in several aqueous solutions as well as in selected normal alkanes. To improve the reliability and accuracy of the solubility measurement for the aqueous system, the corresponding vapor pressures, at the temperature of the solubility measurement, were also determined. The aqueous system consisted of the following solutions:

- Water at 298, 333 and 353 K at atmospheric pressure.
- 75 g/L H_2SO_4
- 150 g/L H_2SO_4
- 30 g/L Cu^{2+}
- 60 g/L Cu^{2+}
- 30 g/L Cu^{2+} and 150 g/L H_2SO_4
- 60 g/L Cu^{2+} and 150 g/L H_2SO_4

Solubility measurements for all of the above sulphuric acid and cupric sulphate salt solutions were carried out at 333.15 K and at atmospheric pressure. In addition, the densities of all of the aqueous solutions were also measured for a range of temperatures between 313.15 K and 413.15 K, at 20 degree temperature intervals. Due to the corrosive nature of the aqueous solutions, the electronic digital densimeter could not be used without damaging the densimeter. The concentrations of copper salt and sulphuric acid were chosen so as to simulate typical electrolytic solutions found in electrorefining operations for copper to obtain ultra pure copper metal.

The second phase of this research project dealt with the determination of oxygen solubilities in selected alkanes. The alkanes studied included the normal alkanes: hexane, octane, decane, dodecane and hexadecane. The solubilities of oxygen were determined at 273.15 K, 298.15 K and 323.15 K at atmospheric pressure. Because of its relatively high vapor pressure, the maximum temperature for the solubility determination in hexane was reduced to 313.15 K from 323.15 K used for the other solvents. Also because the approximate freezing point of hexadecane is 291.15 K, oxygen solubilities in hexadecane were only determined at 298.15 K and 323.15 K.

2. THEORY

Solubility data have been measured and expressed in numerous ways. However, in order for meaningful comparisons to be made, some standard unit must be adopted. An examination of the methods of expressing gas solubility is warranted. In addition, the nature of the temperature effect on the solubilities of oxygen in the n-alkanes is presented. Also considered are the methods of expressing the interaction between the electrolytes in solution and the dissolving gas. Finally, the vapor pressure of the electrolytic solutions, at the temperature of the solubility measurement, must be determined to accurately express the solubility of oxygen in the aqueous solutions. Hence, methods of expressing the vapor pressures for real, non ideal solutions are also presented.

2.1 METHODS OF EXPRESSING GAS SOLUBILITY

The solubilities of gases in liquids can be expressed in a variety of ways. Some of the more common methods include the Ostwald coefficient, the Bunsen coefficient, the mole fraction solubility, and the Henry's law constant (Clever and Battino, 1975).

The Ostwald coefficient, usually denoted as L, has been defined in many different ways. Ostwald defined L as the ratio, at equilibrium, of the volume of gas absorbed by a unit volume of pure solvent at a specified temperature and total pressure (Battino, 1984). Quite often, however, the determination of the pure solvent volume is difficult, leading to a second definition of the Ostwald coefficient; in this case, the Ostwald coefficient is defined as the volume of gas (V_g) absorbed by a volume of saturated solution (V_L), at the specified temperature and total pressure (Battino, 1984):

$$L_v = \left(\frac{V_g}{V_L}\right)_{equilibrium.} \qquad [E-1]$$

For dilute solutions, however, these two definitions give essentially the same result. The Ostwald coefficient calculated in this work employed equation [E-1].

The second method for expressing gas solubility is the Bunsen coefficient, usually denoted by α. The Bunsen coefficient is defined as the volume of gas, reduced to STP, (273.15 K and 101.325 kPa) absorbed by a volume of solvent at the temperature of measurement at a partial pressure of 101.325 kPa. Assuming ideal gas behavior, the Bunsen coefficient may be expressed by:

$$\alpha = \frac{V_g}{V_L}\frac{273.15}{T}. \qquad [E\text{-}2]$$

If the partial pressure of the gas is not 101.325 kPa, it may be corrected to this pressure by Henry's law (Clever and Battino, 1975).

The extent of ideality of the gas can be determined by inspection of the correction factors that result when utilizing the second viral coefficient of the gas. A correction factor based on the compressibility factor for oxygen at 200 K was found to be 0.27% and at 300 K the correction factor decreased further to 0.063% (Battino et al., 1983). A correction for the nonideality of oxygen or the use of the second viral coefficient is thus only warranted in solubility determinations of extreme precision.

Solubilities are also expressed in terms of the mole fraction of gas absorbed by the solvent:

$$x_g = \frac{n_g}{n_g + n_s}. \qquad [E\text{-}3]$$

To avoid ambiguity in any of the results, the partial pressure of the gas and the temperature of measurement must also be specified.

Another useful method of expressing gas solubility is the Henry's law constant, K_H. Henry's law is a limiting law and is strictly applicable only in the extrapolation to infinite dilution or to very low partial pressures:

$$\lim_{x \to 0} \frac{P_g}{x_L} \approx \lim_{x \to 0} \frac{f_g}{x_L} = K_H . \qquad \text{[E-4]}$$

In many practical situations, particularly for gases of low solubility, a negligible error in gas solubility is observed in equating f_g with P_g. Thus in dilute solutions, Henry's law becomes (Clever and Battino, 1975):

$$K_H = \frac{P_g}{x_L} = \frac{P_g}{x_g} = \frac{1\,(P_g = 1)}{x_g}. \qquad \text{[E-5]}$$

The relations for converting from one set of units to another are given below (Clever and Battino, 1975):

$$L = \frac{\alpha T}{273.15}, \qquad \text{[E-6]}$$

$$K_H = \frac{17.033 \times 10^6 \rho_s}{\alpha M_s}, \qquad \text{[E-7]}$$

$$x_g = \left[\frac{RT}{LPgV_1^\circ} + 1 \right]^{-1}. \qquad \text{[E-8]}$$

2.2 SALT EFFECTS

The behavior of real solutions of interest to chemical engineers cannot always be adequately represented by the ideal solution models. The introduction of the activity coefficient allows for a more general treatment of real solutions (Smith and Van Ness, 1987).

The influence of salts on the activity coefficient of a non-electrolyte (dissolved gas) in the aqueous solution can be represented by a power series in the electrolyte concentration, C_S and the non-electrolyte solute gas concentration, C_i (Long and McDevit, 1952):

$$\log \gamma_i = \sum_{m,n=0}^{\infty} K_{mn} C_s^m C_i^n . \qquad [E\text{-}9]$$

Expanding the above power series to show the first few terms yields the following:

$$\begin{aligned} \log \gamma_i = {} & K_{10} C_s + K_{20} C_s^2 + K_{30} C_s^3 + \dots \\ & + K_{01} C_i + K_{02} C_i^2 + K_{03} C_i^3 + \dots \\ & + K_{11} C_s C_i + K_{12} C_s C_i^2 + K_{13} C_s C_i^3 + \dots \\ & + K_{21} C_s^2 C_i + K_{22} C_s^2 C_i^2 + K_{23} C_s^2 C_i^3 + \dots \end{aligned} \qquad [E\text{-}10]$$

In dilute solutions for low C_S and C_i values, only the linear terms are important. Thus in dilute solutions and assuming no chemical interaction between solute species, equation [E-10] reduces to:

$$\log \gamma_i = K_s C_s + K_i C_i . \qquad [E\text{-}11]$$

Generally, salt effect studies are concerned with the calculation of K_S, the ion-non-electrolyte interaction parameter or the salting out parameter and not with K_i, which represents the interaction of the non-electrolyte with itself.

Solubility measurements allow a direct calculation of gas activity coefficients. At a given temperature and pressure, the non-electrolyte solute activity is the same in both pure solvent and salt solution, that is:

$$\gamma_i S_i = \overset{\circ}{\gamma}_i \overset{\circ}{S}_i. \qquad \text{[E-12]}$$

It follows that:

$$\log \gamma_i = \log \overset{\circ}{\gamma}_i + \log \frac{\overset{\circ}{S}_i}{S_i} = K_s C_s + K_i C_i. \qquad \text{[E-13]}$$

Furthermore, the following relationship can be used to simplify equation [E-13]:

$$\log \overset{\circ}{\gamma}_i = \overset{\circ}{K}_i \overset{\circ}{S}_i. \qquad \text{[E-14]}$$

Combining equations [E-13] and [E-14] gives:

$$\log \frac{\gamma_i}{\overset{\circ}{\gamma}_i} = \log \frac{\overset{\circ}{S}_i}{S_i} = K_s C_s + K_i \left(S_i - \overset{\circ}{S}_i\right). \qquad \text{[E-15]}$$

The values of S_i and $\overset{\circ}{S}_i$ are generally low, even if K_i and K_S are of similar magnitude. In situations where the non-electrolyte solute is a gas, the second term in equation [E-15] is normally omitted with negligible error. The assumption of low non-electrolyte concentration reduces the above equation to the well known Setschenow equation, shown below:

$$\log \frac{\gamma_1}{\gamma_1^\circ} = \log \frac{S_1^\circ}{S_1} = K_s C_s. \qquad \text{[E-16]}$$

Salts which increase the activity coefficient of the dissolved gas are said to "salt-out" the gas; that is, addition of these salts to the solvent decreases the solubility of the gas in the salt solution as compared to the pure solvent. Salts resulting in decreased activity coefficients of the dissolved gas are said to "salt-in" the gas (Long and McDevit, 1952).

The salt effect parameter can be rewritten in any one of several forms. For example, the salt effect parameter in terms of the Bunsen coefficient is (Battino et al., 1982):

$$K_{sc\alpha} = \frac{1}{C_2} \log \frac{\alpha_1^\circ}{\alpha_1}, \qquad \text{[E-17]}$$

or in terms of the Ostwald coefficient,

$$K_{scL} = \frac{1}{C_2} \log \frac{L_1^\circ}{L_1}. \qquad \text{[E-18]}$$

2.3 IDEAL AND NON-IDEAL SOLUTIONS

As mentioned in section 1.3, the vapor pressure of a mixed solvent solution influences the solubility of gases in the liquid solution. For ideal gases and liquids, the vapor pressure is typically calculated by means of Raoult's law. Introduction of a nonvolatile component in the solvent, such as an acid or a salt, decreases the vapor pressure of the solution when compared with the vapor pressure of the pure solvent. The decrease in vapor pressure is proportional to the mole fraction of nonvolatile solute added. In terms of the mole fraction of solvent, Raoult's law is expressed as:

$$P = x_a P^{o}. \qquad \text{[E-19]}$$

For real or non ideal solutions, however, one cannot use Raoult's law as stated above. In real solutions, there is a complex interaction (such as, solute-solute or solute-solvent interactions) between charged particles which may cause the solute concentration in solution to vary. Thus one needs to obtain the effective active mass in the solution (Moore, 1981). This effective active mass is represented by the activity. For an ideal solution the activity of each component in solution is equal to the mole fraction. In non-ideal solutions, one needs to define the activity coefficient of a component in solution (Smith and Van Ness, 1987):

$$\gamma_i \equiv \frac{\hat{f}_i}{x_i f_i} = \frac{a_i}{x_i}. \qquad \text{[E-20]}$$

The activity may be expressed as:

$$a_i = \frac{\hat{f}_i}{f_i}. \qquad \text{[E-21]}$$

The activity of a component is the ratio of its fugacity in a particular solution to its fugacity in some standard state. The choice of the standard state is arbitrary and is invariably represented by the pure liquid at a specified temperature and pressure (Shinoda, 1978).

Introduction of the activity coefficient into Raoult's law, yields the modified Raoult's law (Smith and Van Ness, 1987):

$$P = x_a\gamma_a P^\circ. \qquad \text{[E-22]}$$

In terms of the solute:

$$P = (1 - x_b\gamma_b)\, P^\circ. \qquad \text{[E-23]}$$

The activity coefficient is a measure of the deviation from ideality. Thus γ_i is essentially a correction for non-ideality. Note that γ_i is defined such that, as $x_{solvent} \rightarrow 1$, $\gamma_{solvent} \rightarrow 1$, and the modified Raoult's law becomes identical to equation [E-19] (Carroll, 1991).

Similar to Raoult's law, Henry's law expresses the variation of the partial pressure of a gas with the mole fraction of gas in the liquid. Henry's law is a limiting law and applicable in the limit of infinite dilution. Henry's law constant for oxygen in aqueous solution can be written as,

$$K_H = \frac{P_g}{\gamma_2 x_2}. \qquad \text{[E-24]}$$

By convention, as the mole fraction of the solute, x_2, tends towards zero, the activity coefficient, γ_i, tends towards unity (Wilhelm et al., 1977). For systems where the gas solubility is low, as in the present work, the activity coefficient is assumed to be unity. Then Henry's law constant is simply the ratio of the partial pressure of the gas to the mole fraction of the gas in the liquid solution.

3. EXPERIMENTAL EQUIPMENT AND PROCEDURE

A detailed description of the experimental equipment and procedures will now be presented. The gas solubility experiments were separated into two sections, the deaeration section and the absorption section. For the deaeration section, two types of apparatus were used. Similarly for the second stage, two types of apparatus for measuring the solubilities of oxygen were employed. Finally, the apparatus for measuring the vapor pressures of water and the aqueous solutions as well as the apparatus for determining solution densities will be discussed..

3.1 SOLUBILITY APPARATUS

The essential design features of the solubility apparatus for both the aqueous solvent solutions and the hydrocarbon solvents are similar. However, since the solubility of oxygen in the aqueous solvent solutions is significantly lower than the solubility of oxygen in the normal alkanes, a separate solubility apparatus was required for each solvent system. The solubility apparatus for the aqueous solutions had to accommodate larger solvent volumes since the solubility of oxygen in the aqueous solvent solutions is lower. Hence, the solubility apparatus for the aqueous solutions and the normal alkane solvents varies in the volumes and sizes of the components of the equipment involved. Nevertheless, the solubility measurement process for both the aqueous solutions and the hydrocarbon solvents was similar. The apparatus utilized for the gas solubility measurements can be divided into two sections. In section one the solvent is deaerated and subsequently stored for the second stage. The second section, meanwhile, allowed for intimate contact between the deaerated solvent and dry oxygen in order to fully saturate the solvent.

3.1.1 DEAERATION APPARATUS

A schematic representation of the deaeration apparatus is shown in Figure 1. Equipment specifications for the deaeration apparatus for both the aqueous solvent solutions and the n-alkane solvents are shown in Table 1. The design objectives of the deaeration apparatus was to ensure adequate deaeration of the solvent as well as to minimize the amount of solvent lost during degassing. The deaeration apparatus consisted of a glass bottle wrapped with electric tape for heating purposes. Initial solvent deaeration was carried out in the glass bottle, and was referred to as stage one. The glass bottle was connected to the top of a packed column, which forms the second stage of deaeration.

The deaeration procedure for the aqueous solvent solutions and the n-alkane solvents was similar, with one notable difference which was observed during the first stage of deaeration. This difference in the deaeration procedure is described below. In stage one of the deaeration procedure, the solvent in the glass bottle was degassed with the aid of a vacuum pump. The vacuum pump removes the bulk of the dissolved contaminant gases in the solvent. Upon subjecting the solvent to vacuum, the solvent begins to boil violently. The method of boiling the solvent under vacuum was an effective way to ensure adequacy of deaeration, but was wasteful of solvent. For pure solvents, such as the hydrocarbon solvents, this method of boiling the solvent proved satisfactory. However, the aqueous solvent solutions which contained components assumed to be nonvolatile, such as sulphuric acid and cupric sulphate salts, boiling was considered to be equivalent to removing just the water from the solutions. Hence, boiling the aqueous solutions can significantly alter the initial concentration of the sulphuric acid and cupric sulphate salt in the aqueous solvents; that is, the concentration of the acid and the salt in the deaerated solvent solutions would become unknown. Therefore, to minimize aqueous solvent losses, the deaeration apparatus was modified to allow for purging of the aqueous solvents prior to degassing with the vacuum pump during stage one. The aqueous solvents were purged with helium. The solubility of helium in water at 298.15 K was approximately 200% lower than the solubility of oxygen in water, at the same temperature (Wilhelm, et al., 1977). Hence, to achieve adequate deaeration, the amount of time required to boil the aqueous solvent solutions under vacuum was reduced. The main difference in the deaeration procedure between the n-alkane solvents and the aqueous solvent solutions was that the aqueous solvents were purged with helium. The combination of purging the solvent with helium followed by degassing with the vacuum pump resulted in solvent losses of less than two percent.

Table 1. Specifications of equipment for the deaeration and the absorption apparatus.

	Hydrocarbon system	Aqueous system
Deaeration apparatus:		
Length of packed column	0.61 m (61 cm)	1.18 m (118 cm)
Diameter of packed column	0.025 m (2.5 cm)	0.065 m (6.5 cm)
Column packing	0.003 m glass beads	0.003 m glass beads
Vol. of vessel for stage 1	2.50×10^{-4} m^3 (250 ml)	1.00×10^{-3} m^3 (1000 ml)
Absorption apparatus:		
Length of column	0.78 m (78 cm)	1.14 m (114 cm)
Vol. of burette for dry O_2	0.5000 m (50.00 cm)	0.1000 m (10.00 cm)
Vol. of burette for liquid solution	0.1000 m (10.00 cm)	0.1000 m (10.00 cm)
Solvent infusion rate	1.2×10^{-6} m^3/minute (1.2 cm^3/minute)	2.1×10^{-6} m^3/minute (2.1 cm^3/minute)

The glass bottle is connected to the top of the packed column which forms the second stage of the deaeration apparatus. The solvent from stage one was allowed to flow, under vacuum, into the packed column. The column packing consisted of Pyrex glass spheres with a diameter of 0.003 m. The solvent formed a thin film as it flowed through the packed column, resulting in rapid and thorough degassing of the solvent.

The packed column also served as a reservoir for the deaerated solvent until it was needed in the absorption apparatus. To pump the deaerated solvent from the packed column to the top of the absorption apparatus, the vacuum pump had to be shut off and the contents of the packed column exposed to atmospheric pressure. Exposure of the deaerated solvent to the atmosphere, results in contamination of the solvent with air. However, only the top one-third portion of the packed column was assumed contaminated, leaving the bottom portion adequately degassed for the solubility determination.

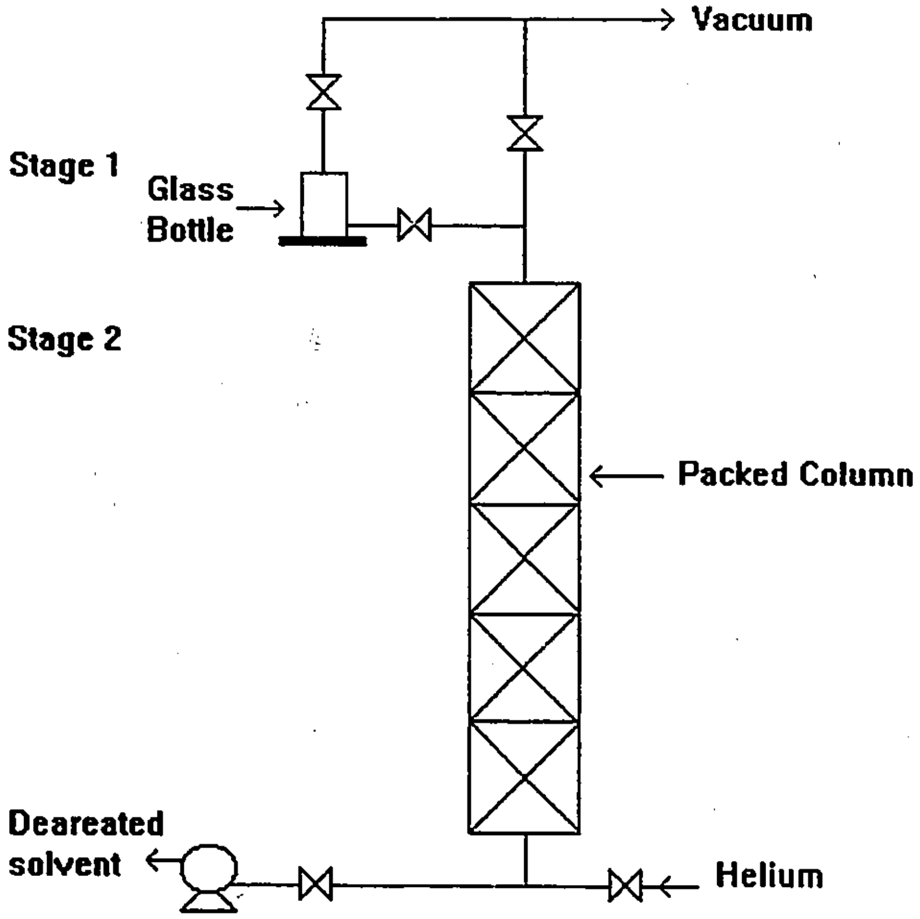

Figure 1. Deaeration apparatus representing the first stage of the solubility apparatus.

3.1.2 GAS ABSORPTION APPARATUS

The solubility apparatus was divided into two sections: the deaeration section and the gas absorption section. A schematic representation of the absorption apparatus is shown in Figure 2. Specifications for the components of the absorption apparatus are given in Table 1. The essential components of the absorption apparatus are the gas burettes, the spiral absorption tube, the U-tube to control pressure in the spiral tube and the mercury leveling bottle. As illustrated in Table 1, the absorption apparatus for the aqueous solvent solutions and the hydrocarbon solvents were not of the same size. The difference in the size and volume of the components of the absorption apparatus was necessary because the solubility of oxygen in the aqueous solvents is lower than the solubility of oxygen in the n-alkane solvents. Hence, the aqueous absorption apparatus had to accommodate smaller gas volumes.

The procedure for measuring the solubility of either the normal alkane solvents or the aqueous solvent solutions was identical. The absorption column was maintained at a constant temperature by circulating constant temperature water through the water jacket. During the latter stages of the deaeration procedure, the absorption column was purged with the test gas, namely dry oxygen. Thus deaeration of the solvents in the packed column and purging of the absorption apparatus with dry oxygen occurred simultaneously. During the purging procedure, the level of mercury was maintained below the gas inlet tee. The absorption apparatus was purged for approximately 15 minutes.

After the initial purging period, the degassed solvent was pumped into the top of the absorption apparatus. The solvent infusion rates for both the aqueous solvent solutions and the n-alkane solvents are indicated in Table 1. The dry gas and the degassed solvent flowed co-currently down the spiral absorption tube. The solvent was completely saturated with the dry oxygen prior to reaching the U-tube. Methods for ensuring

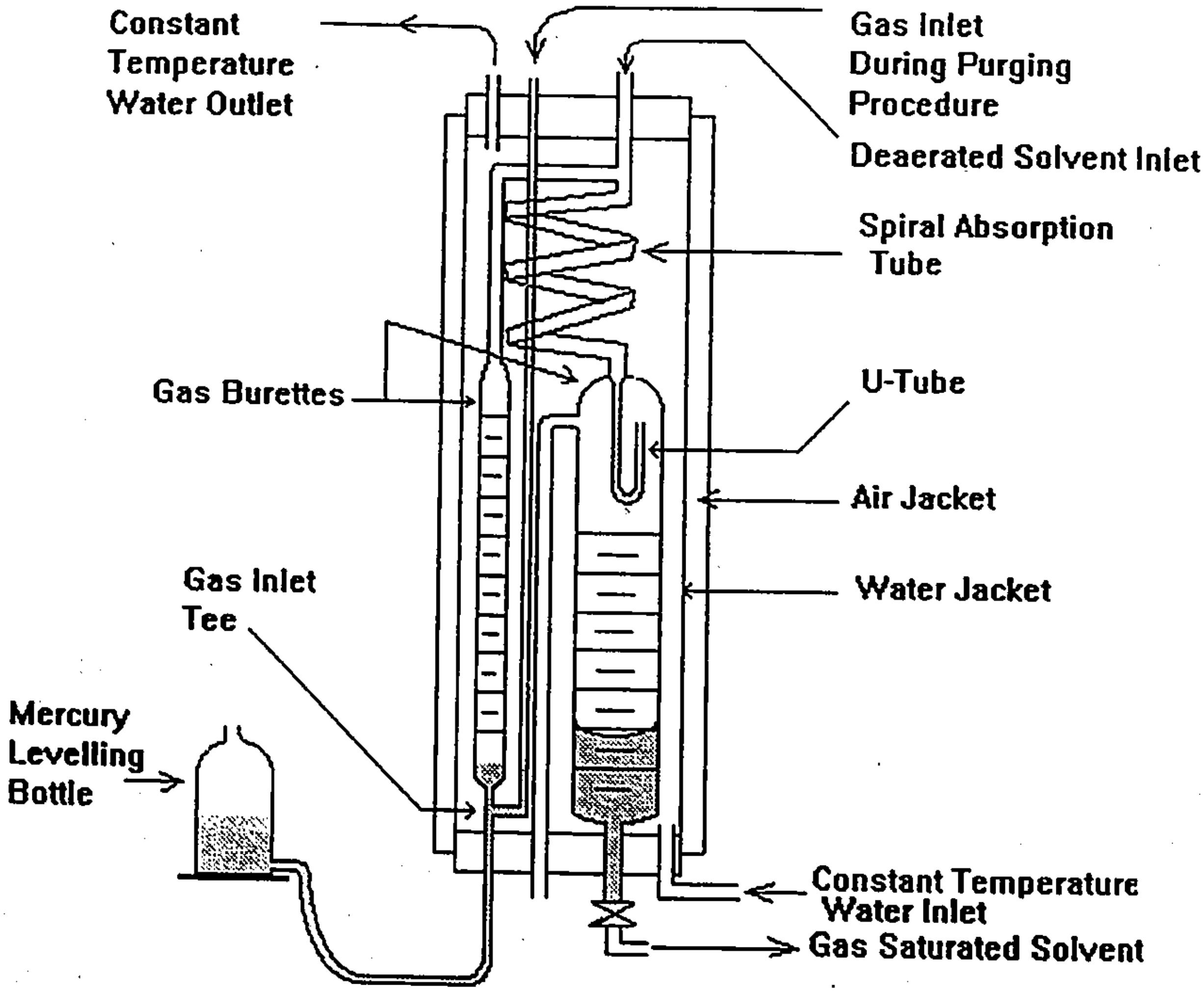

Figure 2. Gas absorption apparatus representing the second stage of the solubility apparatus.

complete saturation of the solvent were discussed in Section 1.2. The initial 15 to 20 cm^3 of solvent was discarded. Rejection of this initial volume of solvent served to remove any contaminant air that may have been in the tubing connecting the deaeration apparatus to the absorption apparatus, as well as to allow for additional purging to occur.

The next step in the determination of gas solubilities was to confine the oxygen in the absorption apparatus. This was accomplished by raising the level of mercury in the gas burette to a level above the gas inlet tee. The oxygen then was trapped between mercury at one end, and saturated solvent in the U-tube at the outlet of the absorption spiral. The supply of oxygen gas was cut off and the gas inlet tube opened to the atmosphere. The inlet tube effectively became one arm of a manometer. The pressure in the absorption spiral was controlled by raising the mercury level in the gas burette. Pressure deviations from atmospheric are indicated, in the absorption column, as differences in the levels of saturated solvent in the U-tube. The mercury was raised at a rate proportional to the rate of oxygen absorption, as dictated by the level of saturated solvent in the U-tube.

The mercury level had to be adjusted frequently throughout the course of the solubility measurement. The mercury level was raised by placing the bottle on a platform attached with a spring loaded half nut to a rotating, threaded shaft. The threaded shaft was rotated by a variable speed motor whose speed (0-400 rpm) was manually adjusted. In this manner, the gas volume could be accurately controlled, resulting in accurate measurement of gas volume by means of the gas burette.

At least 15 pairs of readings of dry gas volume and saturated solution volume were recorded, at suitable time intervals, for each solubility measurement. After the experiment was completed, a linear plot of volume of gas absorbed versus volume of solution collected, was constructed. The slope of the line on such a plot yielded the Ostwald coefficient. The solubility data for the n-alkane solvents and the aqueous solvent solutions were collected for a period of time between 60 to 90 minutes, ensuring that a steady-state absorption rate had been measured.

3.2 VAPOR PRESSURE APPARATUS

A schematic diagram of the experimental apparatus is shown in Figure 3. The diagram represents a simplified version of the vapor pressure apparatus described by Gibbs and Van Ness (1972). The vapor pressure of the aqueous solvent solutions was measured at a temperature of 333.15 K (60 °C). The vapor pressure apparatus consisted of a 100 cm^3 glass bottle fitted with a rubber stopper and attached to the pressure transducer with (1/8-inch) tubing. The glass bottle was used as a degassing chamber as well as a storage vessel for the aqueous solvent solutions while the vapor pressure was being measured.

Water has been extensively studied; hence its vapor pressure was used to calibrate the pressure transducer. The absolute pressure transducer, supplied by MKS, was subjected to vacuum for approximately four hours and then zeroed. To calibrate the transducer, the glass bottle was filled with approximately 50 cm^3 of distilled water and submerged in the water bath. The distilled water was thoroughly degassed by means of a vacuum pump. Then with the aid of the zero control, the digital readout connected to the pressure transducer was set to the literature value of the vapor pressure of water at 333.15 K (60 °C); that is, the transducer was set to 2.90 psi (19.995 kPa). To check the reproducibility and drift with time of the pressure transducer, the vapor pressure of water at 333.15 K was measured over a period of one week. The results were found to be reproducible, indicating that the vapor pressures measured by the transducer during the course of the week were reliable.

To perform a vapor pressure measurement, approximately 50 cm^3 of the aqueous solvent solution was placed in the glass bottle. The aqueous solution and the entire length of line connecting the glass bottle to the pressure transducer was submerged in the water bath to maintain a constant temperature of 333.15 K. The solution in the glass bottle was deaerated and the vapor pressure measured by reading the digital readout connected to the pressure transducer.

Prior to deaerating the aqueous solvents, the stainless steel tubing connecting the glass bottle to the vacuum pump was evacuated. Deaeration of the aqueous solvents was performed in a batchwise fashion; that is, the solvents were intermittently subjected to the vacuum pump by means of a valve which was opened and then closed repeatedly for about 20 minutes. The valve was closed when the aqueous solvent in the glass bottle began to boil violently. The valve was opened again when the aqueous solution stopped boiling. The purpose for deaerating the aqueous solvent in a batchwise fashion was to minimize water loss. Excessive water loss would significantly alter the composition of the aqueous solvent solution, producing a more concentrated solution. The solvent vapor was condensed in a vacuum condensate trap and the water losses due to deaeration were consistently less than 1% of the total volume of solution.

The connecting lines were evacuated for a minimum of 10 hours and the residual vapor pressure in the connecting lines was recorded. The residual pressure in the connecting lines was approximately 1.4 kPa (10 mmHg), and was ascribed to be the vapor pressure of the vacuum oil. The residual pressure in the connecting lines gradually increased with time, indicating an increased water content in the oil. Hence, to obtain vapor pressures, reproducible to within 1%, the vacuum oil required changing every week.

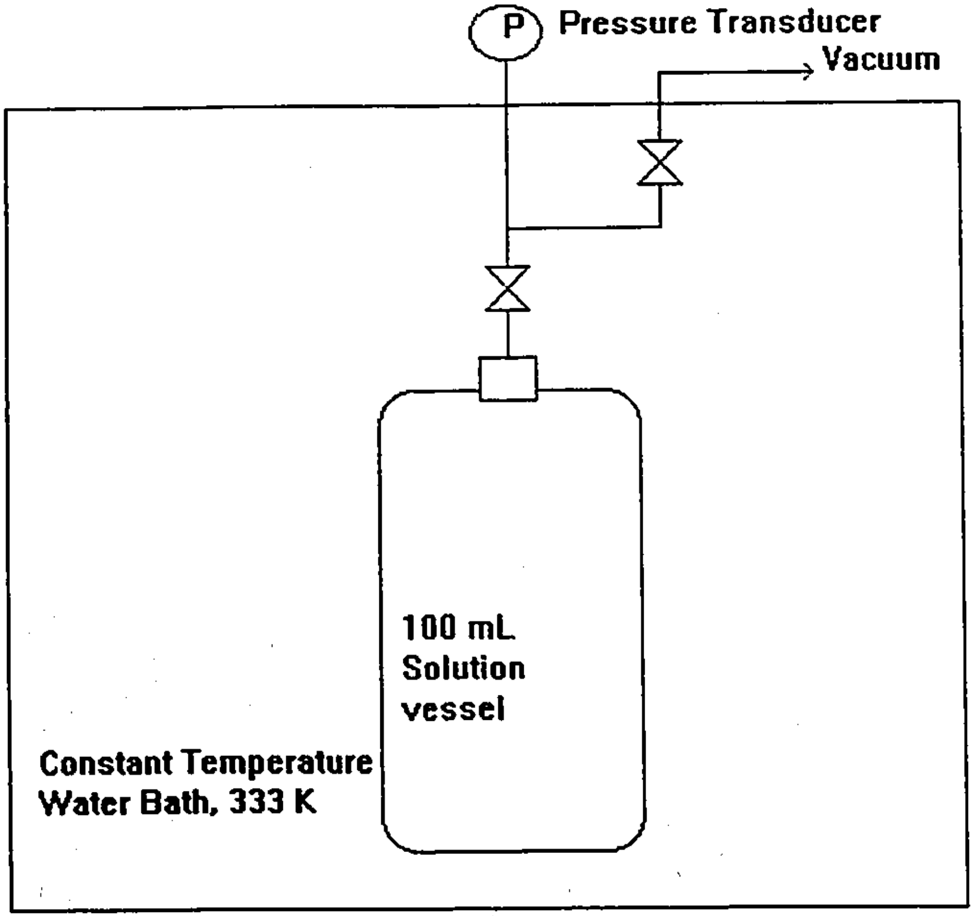

Figure 3. Schematic representation of the vapor pressure apparatus.

3.3 PROCEDURE AND DESCRIPTION OF THE APPARATUS FOR THE DETERMINATION OF SOLUTION DENSITIES

The densities of the aqueous solutions were measured for a range of temperatures between 313.15 K (40 °C) to 413.15 K (140 °C), at 20 degree temperature intervals. The electronic densimeter, available in the department, could not be employed to determine solution densities because of the corrosive nature of the salt and the acid aqueous solutions. Instead, a series of dilation tubes were used. A schematic representation of a typical capillary dilation tube (dilatometer) is shown in Figure 4. The capillary tubes (I.D. of approximately 0.001 m) were made of Pyrex glass with a uniform internal cross sectional area. One end of the capillary tube was permanently sealed, while the other end was slightly tapered by the application of heat and attached to a stainless steel reducing union to allow the capillary tube to be pressurized. The tubes were approximately 50 cm long. This length was desirable to allow an accurate measurement of liquid dilation. However, due to the limited depth of the oil bath, the tubes were bent at a 90° angle to allow them to be completely submerged in the constant temperature bath. Three dilation tubes were available, allowing simultaneous density determinations of three different aqueous solutions. The amount of solution dilation, as temperature was increased, was measured by means of a cathetometer. The cathetometer was capable of measuring increases in lengths of liquid to within 0.01 mm.

Density determinations utilizing dilatometer tubes are based essentially on the law of mass conservation. The tubes are made of capillary Pyrex glass tubing. The tubes must first be calibrated with a liquid of known density to account for any thermal expansion. Pure water was used to calibrate the tubes. From the measurements with water, a correction factor, r, was calculated for each tube at every temperature:

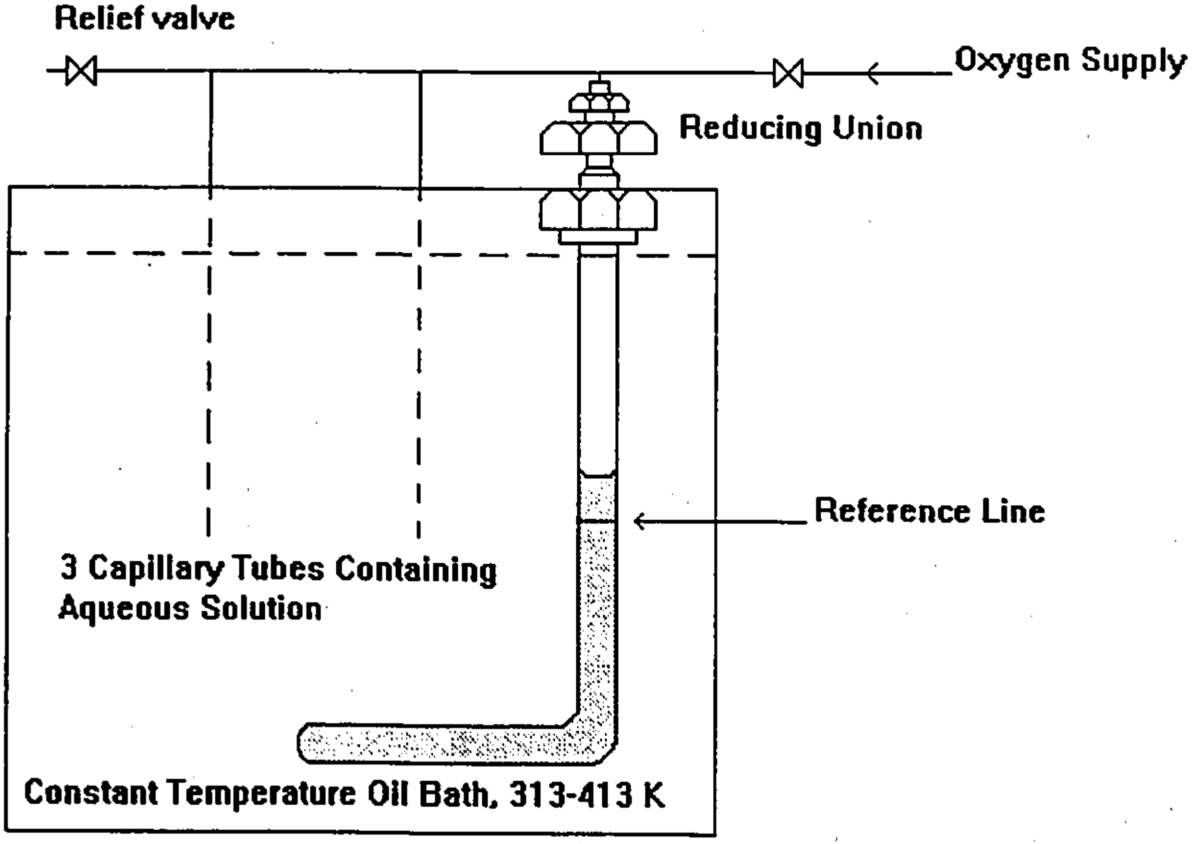

Figure 4. Density apparatus, schematic representation of the dilatometer tubes.

$$r = \frac{\rho_{actual}}{\rho_{measured}} = \frac{L_{measured}}{L_{actual}}. \qquad [E\text{-}25]$$

From a material balance on the sealed dilatometer tubes, the mass of the aqueous solution at two different temperatures must be the same. Expressing mass in terms of densities the following relation was obtained:

$$\rho_1 V_1 = \rho_2 V_2 . \qquad [E\text{-}26]$$

The subscripts 1 and 2, denote mass of solution at temperatures T_1 and T_2, respectively. Assuming a smooth tube with uniform internal cross sectional area, the density of solution the can be rewritten in terms of length of solution in the tube:

$$\rho_1 L_1 = \rho_2 L_2 \qquad [E\text{-}27]$$

$$\rho_2 = \frac{\rho_1 L_1}{L_2}. \qquad [E\text{-}28]$$

It is apparent from the above relation that a solution density at an initial temperature must be known. The initial solution density at room temperature was measured by determining the weight of 5.00 cm^3 of solution with an analytical balance.

The solution was injected into the capillary dilatometer tubes with a 10 cm^3 plastic syringe. The syringe was attached to a thin, flexible Teflon tube which could deliver the aqueous solution into the capillary tube without introducing any air bubbles. A reference line was marked on each capillary tube with a permanent marker. The tubes were then placed in the oil bath at room temperature and pressurized to approximately 5 atmospheres. Pressurizing the tubes to a pressure above the vapor pressure of the solution, reduced the possibility of the evaporation of the solution. Evaporation of the solution would decrease the volume of liquid solution from its initial value, resulting in an erroneous density measurement. The initial height of solution was measured from the reference line. The temperature of the oil bath was increased to 313.15 K (40 °C) and the change in height of the liquid solution from the reference line was recorded. The temperature was again increased by 20 °C and the change in height determined. The procedure was repeated until the maximum temperature of 413.15 K (140 °C) was reached. The reference line served to standardize all measurements to the initial height of liquid. Thus any movement of the capillary tubes as the result of convection currents generated during mixing, would not interfere with the determination of actual heights of the liquid in the capillary tubes.

3.4 INNOVATIONS TO THE EXPERIMENTAL PROCEDURE NECESSARY FOR OBTAINING RELIABLE RESULTS

Some of the experimental innovations found useful in measuring gas solubilities will now be discussed. These innovations are not obvious at first, but are nevertheless important in assuring reliable results as well as extending the life of the experimental equipment. The first factor pertains to the maintenance of the constant temperature water bath. Initially, the water bath was filled with tap water. At elevated temperatures of 333.15 K (60 °C) and above, a fine precipitate or growth appeared in the water bath; the tap water became cloudy and turbid within three days at the elevated temperature. The growth was problematic since in the solubility measurements a clear view of the U-tube and the spiral absorption tube was required. To inhibit growth in the water bath, commercial bleach was employed. The concentration of the bleach was initially maintained at approximately 5% by volume of the total bath volume. The growth in the water bath was not observed for about two weeks; however, although the bleach alleviated the problem of fungal growth, it introduced another difficulty. After approximately four days of continuous operation, a reddish, rust colored precipitate was deposited in the absorption column. This new deposition was also undesirable because it obscured the view of the gas absorption spiral, thus preventing visual confirmation of film flow through the spiral tube. The precipitate was believed to be the result of oxidation and precipitation of dissolved ions in the tap water. Therefore, the next step was to use distilled water in the constant temperature bath. Distilled water proved to be quite satisfactory in terms of inhibiting fungal growth as well as reducing the formation of the reddish precipitate. The water bath, filled with distilled water, was usable for approximately three weeks before the appearance of any noticeable growth or precipitate. The use of distilled water in the constant temperature bath was considered to be a useful innovation for a satisfactory experimental procedure.

Another innovation that was developed concerns the ice trap for the deaeration apparatus. Upon applying vacuum to the solvent under study, a definite quantity of solvent necessarily evaporated. The solvent vapor had to be condensed before it reached the vacuum pump. The first design of the ice trap consisted of an Erlenmeyer flask submerged in ice, through which the vacuum line passed prior to reaching the vacuum pump. The temperature in the ice trap reached a minimum of about 277 K. It was found with this arrangement that the vacuum oil required changing every week. The oil change was necessary because some solvent vapor escaped through the ice trap and condensed in the vacuum pump. When water was deaerated, the above design of trap served fairly well. However, with the aqueous copper salt and sulphuric acid solutions, it was necessary to be concerned about corrosion of the pump. It was not recommended to leave salt and acid solutions in the vacuum pump for long periods of time because of their corrosive nature. Furthermore, changing the vacuum oil at a frequency of more than once a week was time consuming as well as wasteful of vacuum pump oil. It appeared necessary to decrease the temperature of the vacuum condensate trap. Ethylene glycol was used for this purpose.

Ethylene glycol was cooled to approximately 268 K with the aid of an auxiliary refrigeration coil. Aqueous and organic solvent losses were found to be greatly reduced to the extent of being negligible.

A third innovation dealt with attaining the lower temperature of 273.15 K in the absorption apparatus for the determination of oxygen solubility in the n-alkane solvents. The lowest temperature attainable with the available refrigeration coil was about 268 K. Therefore, to obtain a temperature of 273 K for the solubility determinations, antifreeze was pumped through the jacket of the absorption apparatus. Furthermore, commercial antifreeze, ethylene glycol, which is a rich green color, tended to obscure the view of the U-tube and the spiral absorption tube. Therefore, diethylene glycol, which is colorless, was employed to obtain the lower temperature of 273.15 K for the low temperature solubility determinations.

Installation of an air jacket to minimize the temperature drop across the length of the absorption apparatus was another important innovation. The initial design of the absorption apparatus lead to a temperature drop across the length of the absorption apparatus. The temperature drop observed in the absorption apparatus was dependent upon the temperature of the solubility measurement. For example, the solubility measurement at a temperature of 333.15 K (60 °C) produced a temperature drop along the length of the absorption apparatus of about 1 °C. Thus, to compensate for the 1 °C temperature drop, the inlet temperature was raised by 0.5 °C yielding an outlet temperature which was 0.5 °C lower than the set point. The average temperature in the column then was at the set point. Furthermore, as the temperature of the solubility measurement was raised, the temperature drop along the length of absorption apparatus became larger. To better control the temperature of the absorption apparatus it was fitted with an air jacket. The air jacket reduced the temperature drop in the absorption apparatus to negligible levels for solubility measurements up to 333.15 K (60 °C). At a temperature of 353.15 K (80 °C), the temperature drop across the column was observed to be less than 0.2 °C. Hence, a significant improvement in temperature control was obtained by installing the air jacket.

4. PROPERTIES OF MATERIALS

The solubilities of oxygen were determined for the hydrocarbon solvents and the aqueous solvent solutions using ultra pure carrier grade oxygen, with a specified purity of 99.994%, obtained from Air Products Canada Limited. At atmospheric pressure and in the range of temperatures used in this research project, oxygen was assumed to be an ideal gas, as discussed in Section 2.1. Furthermore, use of the ideal gas law, at low and moderate pressure, was recommended by Battino et al. (1981).

The principle supplier of the paraffinic hydrocarbons was Aldrich. However, n-hexane obtained from BDH, was available in the department and was also used. All of the hydrocarbon solvents were of analytical grade and had a specified purity of 99+%. The n-alkanes were colorless liquids at normal temperatures. Useful physical properties of the hydrocarbon solvents are given in Table 2. The boiling point and freezing point temperatures for the organic solvents were obtained from the Material Safety Data Sheets supplied by the manufacturer. The densities of the pure n-alkane solvents were obtained from Rossini et al. (1953). The uncertainty in the densities of the alkane solvents was reported to be less than 0.2%. The vapor pressures of the n-alkane solvents were obtained from Zwolinski and Wilhoit (1971). The Antoine constants reported by Zwolinski and Wilhoit were valid down to a minimum vapor pressure of 1.4 kPa (10 mmHg). Since the vapor pressures for some of the n-alkane solvents were less than 1.4 kPa (10 mmHg), the Antoine constants could not be employed. To overcome this limitation in the reported Antoine constants, a graph of the logarithm of the solvent vapor pressure versus the reciprocal of the temperature was constructed and is included in Appendix A. The dependence of the vapor pressure on temperature was assumed linear over a small temperature range, thus allowing extrapolation of the required vapor pressures from the graph in Appendix A.

The two components which composed the aqueous solvent solutions included: 99.5% pentahydrate cupric sulphate salt ($CuSO_4 \cdot 5H_2O$) and 96% concentrated sulphuric acid (H_2SO_4). The inorganic copper sulphate salt and the sulphuric acid were purchased from BDH. The vapor pressures and the densities of the aqueous solvent solutions were measured in the current work and are presented in the Results and Discussion section. All of these chemicals were of analytical grade.

The method of preparing the aqueous solutions will be now outlined. The required amount of copper sulphate salt was weighed by means of a Mettler analytical balance. The weight could be accurately determined with the analytical balance to 1×10^{-8} kg (0.01 mg). Appropriate amounts of the copper sulphate salt were added to a volumetric flask which was approximately half filled with distilled water. Complete dissolution of the copper sulphate salt in the distilled water was facilitated by the application of heat. The concentrated sulphuric acid was then accurately titrated into the copper sulphate solution. The sulphuric acid was titrated into the volumetric flask by means of a burette readable to within 0.05 cm^3. Finally, additional distilled water was added to the volumetric flask producing an electrolytic solution with the required concentrations of copper sulphate salt and sulphuric acid. Sample calculations for determining the required amounts of copper sulphate salt and sulphuric acid are given in Appendix B.

Helium gas was another important material used in this work. Helium was used to remove dissolved air from the aqueous solvent solutions during the first stage of deaeration. Ultra pure carrier grade helium which had a specified purity of 99.999% was obtained from Air Products Canada Ltd. The solubility of helium in water at 298.15 K and at a gas partial pressure of 101.325 kPa, expressed in terms of the Ostwald coefficient is very low, at 0.009540. Furthermore, the Ostwald coefficient for oxygen at the same temperature and pressure is 0.03098 (Wilhelm, 1977). The solubility of helium in water is approximately 3.25 times lower than the solubility of oxygen in water.

Table 2. Physical properties of the normal hydrocarbon solvents.

	n-hexane	n-octane	n-decane	n-dodecane	n-hexadecane
MW	86.18	114.23	142.29	170.34	226.45
b.p. (K)	342 (69 °C)	399 (126 °C)	447 (174 °C)	489 (216 °C)	560 (287 °C)
f.p. (K)	178 (-95 °C)	216 (-57 °C)	243 (-30 °C)	261 (-12 °C)	291 (18 °C)
ρ (kg/m^3):					
T = 273.15 K	676.9	718.9	745.4	763.7	-
T = 298.15 K	654.8	698.5	726.3	745.1	770.0
T = 313.15 K	641.1	-	-	-	-
T = 323.15 K	-	678.4	707.3	727.1	752.8
P_{vap}(kPa):					
T = 273.15 K	6.06	0.58	0	0	-
T = 298.15 K	20.20	2.14	0.24	0	0
T = 313.15 K	37.30	-	-	-	-
T = 323.15 K	-	6.41	0.75	0	0

5. RESULTS AND DISCUSSION

The objective of this work was to determine the equilibrium solubilities of oxygen in selected normal alkane solvents as well as in several aqueous solvent solutions. The aqueous solvent solutions were made to simulate solutions typically found in the electrorefining of copper. Furthermore, to increase the accuracy and reliability of the solubility measurements, the vapor pressures and the densities of the aqueous solutions were also measured.

5.1 SOLUBILITY OF OXYGEN IN THE NORMAL ALKANES

The solubility of oxygen in the n-alkanes has been studied by numerous researchers with surprisingly poor agreement. In fact, oxygen solubilities reported by Makranczy et al. (Battino et al., 1981) decreased as the linear length of the hydrocarbon was increased. Meanwhile, the data of Blanc and Batiste (Battino et al., 1981) showed the opposite trend; that is, their data predicted an increase in the solubility of oxygen as the carbon number was increased. The present work therefore, was an effort to resolve the discrepancy found in the literature. The equilibrium solubilities of oxygen in the following alkanes were measured: hexane, octane, decane, dodecane and hexadecane. The solubility measurements were performed at temperatures of 273.15 K, 298.15 K and 323.15 K and at atmospheric pressure. The solubility of oxygen in the n-alkanes were measured at least twice. At least fifteen pairs of readings of the volume of oxygen absorbed and the volume of liquid solution collected were fitted by a least squares relation to yield the oxygen solubility. The least squares relation was used to calculate the Bunsen coefficient as well as other common methods of expressing gas solubilities. The least-squares FORTRAN program to calculate the solubility of oxygen can be found in Appendix B. The average results for the solubility of oxygen in the n-alkanes are presented in Table 3.

Table 3. Solubilities of oxygen in normal alkanes at a gas partial pressure of 101.325 kPa.

	Temperature, K		
Solvent	273.15	298.15	313.15
n-hexane:			
α	0.427	0.370	0.315
$K_H\ (10^{-5})$	3.179	3.378	3.470
$x\ (10^3)$	$2.391\ (\pm 0.73\times10^{-5})$	$2.250\ (\pm0.37\times10^{-5})$	$2.191\ (\pm1.64\times10^{-5})$
	Temperature, K		
	273.15	298.15	323.15
n-octane:			
α	0.313	0.292	0.276
$K_H\ (10^{-5})$	3.449	3.632	3.662
$x\ (10^3)$	$2.204\ (\pm2.57\times10^{-5})$	$2.122\ (\pm1.90\times10^{-5})$	$2.076\ (\pm1.77\times10^{-5})$
n-decane:			
α	0.262	0.250	0.235
$K_H\ (10^{-5})$	3.399	3.475	3.596
$x\ (10^3)$	$2.236\ (\pm3.08\times10^{-5})$	$2.187\ (\pm0.0)$	$2.113\ (\pm0.0)$
n-dodecane:			
α	0.227	0.213	0.206
$K_H\ (10^{-5})$	3.379	3.517	3.548
$x\ (10^3)$	$2.250\ (\pm0.17\times10^{-5})$	$2.161\ (\pm0.22\times10^{-5})$	$2.142\ (\pm1.01\times10^{-5})$
n-hexadecane:			
α	-	0.183	0.179
$K_H\ (10^{-5})$	-	3.177	3.172
$x\ (10^3)$	-	$2.392\ (\pm0.0)$	$2.396\ (\pm0.65\times10^{-5})$

To test the solubility apparatus, the solubility of oxygen in decane at 298.15 K and a gas partial pressure of 101.325 kPa was compared with the value reported by Battino et al. (1981). The measured mole fraction solubility of oxygen in decane was 2.187×10^{-3} and the value reported in the literature was 2.200×10^{-3}, corresponding to a relative error of about 0.6%. Comparison of the measured mole fraction solubility of oxygen in hexane with the solubility reported by Naumenko (Battino et al., 1981) yielded a relative error of about 0.4%. Finally, the largest relative error between measured and literature values for the solubility of oxygen was about 2%, observed for octane at 298.15 K (Battino et al., 1981). Solubility data from the literature served as a reference to confirm the accuracy of the solubility apparatus and method. The maximum standard deviation between replicates was $\pm 3.08 \times 10^{-5}$, observed for decane at 273.15 K. The standard deviations between replicates, for the n-alkane solvents are shown in parentheses in Table 3.

As mentioned previously, the lack of agreement amongst researchers concerning the solubility of oxygen in the n-alkanes, provided the motivation for measuring additional solubility data. Figure 5 illustrates this discrepancy as well as the solubility measurements determined in this work. It should be noted that most errors in solubility measurements tend to lower the solubility of a gas in the solvent. In general, the measured solubilities were found to be greater than the corresponding literature solubility values, indicating that the measured solubilities of oxygen in the n-alkanes were probably more accurate and reliable. Furthermore, the results indicate that the solubility of oxygen in the n-alkane solvents increased as the carbon number of the hydrocarbon was increased, in accordance with the findings of Blanc and Batiste as shown by curve 2 in Figure 5. The solubility data of Makranczy et al. (Battino et al., 1981), curve 1 in Figure 5, were lower than the solubility data determined in this work. Some possible explanations for the lower solubility data of Makranczy et al. (Battino et al., 1981) could be incomplete saturation of the solvent with the gas or insufficient deaeration of the solvents.

Figure 5 illustrates a decrease in the mole fraction solubility of oxygen for the hydrocarbon solvents with a carbon number lower than eight. This observation is supported by other researchers, as shown in Figure 5. However, the relationship between gas solubility and solvent carbon number cannot be easily generalized. There is a consistent increase in the solubility of some other gases in the normal alkane and alkanol solvents with increasing carbon number. For example, the solubility of ethane in the normal alkane solvents, with a carbon number greater than five, was shown to increase by Hayduk and Cheng (1970). Also, the solubility of oxygen in some alkanol solvents increases for a carbon number greater than two (Battino et al., 1983).

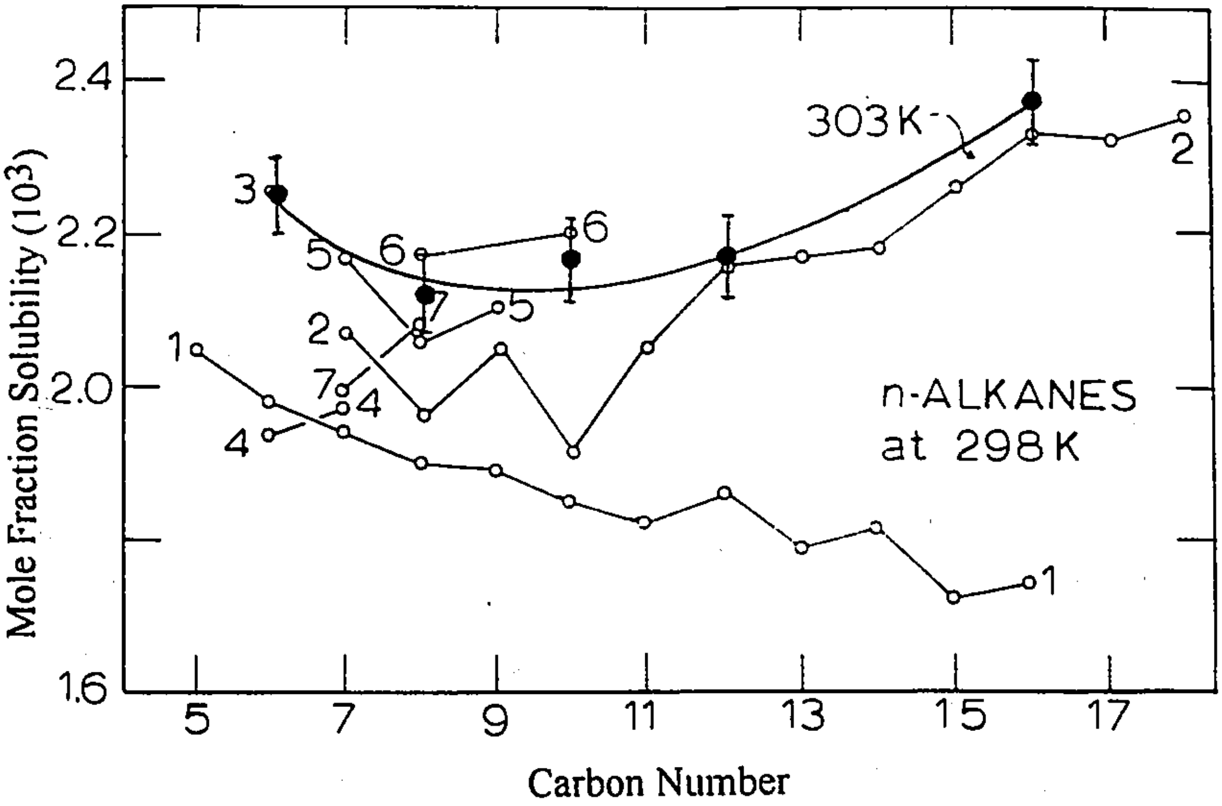

Figure 5. Mole fraction solubility of oxygen in the normal alkanes at a gas partial pressure of 101.325 kPa. (Reproduced from Battino et al. (1981). Curves 1 through 7 represent the results of several different researchers whose experimental data was compiled by Battino et al. (1981). • This work, with ± 2% error bars).

The solubilities of oxygen were determined at three different temperatures, allowing for the evaluation of the temperature coefficient of solubility. The effect of temperature on solubility can be directly related to the entropy of solution. The entropy of solution, also referred to as the Hildebrand entropy, can be determined as the slope of the logarithm mole fraction versus logarithm of the absolute temperature plot (Hayduk and Buckley, 1971). Hildebrand and Scott (1962) have shown that the entropy of solution could be related to the solubility of the gas in the solvent. A positive temperature coefficient would indicate that oxygen gas was only sparingly soluble in the n-alkane solvents. On the other hand, a negative temperature coefficient would indicate that oxygen was moderately soluble in the n-alkane solvents. In fact, comparison of the solubilities of oxygen in the n-alkanes with the solubility of oxygen in water showed that the solubilities of oxygen in the n-alkanes were approximately ten times greater than the solubilities of oxygen in water. The entropies of solution or the temperature coefficients of solubility were calculated from Figure 6 and are summarized in Table 4. The magnitude of the temperature coefficients for the n-alkane solvents were found to be small; that is, the effect of temperature on gas solubility was minor. For example, the solubility of oxygen in n-hexane decreased by approximately 9% when the temperature was increased from 273.15 K to 323.15 K. Furthermore, the solubility of oxygen in n-dodecane decreased by approximately 5% for the same temperature range. To illustrate the magnitude of the effect of temperature on the solubility of oxygen in the n-alkanes, consider the effect of temperature on the solubility of oxygen in water. The data of Benson et al. (1979) showed that the solubility of oxygen in water decreased by about 134% as the temperature was raised from 273 K to 323 K. Therefore, the effect of temperature on the solubility of oxygen in the n-alkanes was indeed small. Furthermore, the effect of temperature on gas solubility in several normal alkanes was also studied by Hayduk and Buckley (1971). Their findings were consistent with the findings of this work, namely the temperature coefficients for solvents with a carbon number between 6 and 16 were small.

The correlation coefficient, r, reported in Table 4 illustrates the strong linear relation between solubility and temperature. Therefore, estimation of the temperature coefficient of solubility from a plot of the logarithm of the mole fraction solubility versus the logarithm of the absolute temperature could be considered satisfactory.

Table 4. Summary of the temperature coefficients of solubility, as calculated from Figure 6.

Solvent	Temperature Coefficient	Correlation Coefficient, r
Hexane	-0.6467	0.9981
Octane	-0.3581	0.9919
Decane	-0.3353	0.9895
Dodecane	-0.2930	0.9451
Hexadecane	-0.0229	1.0000

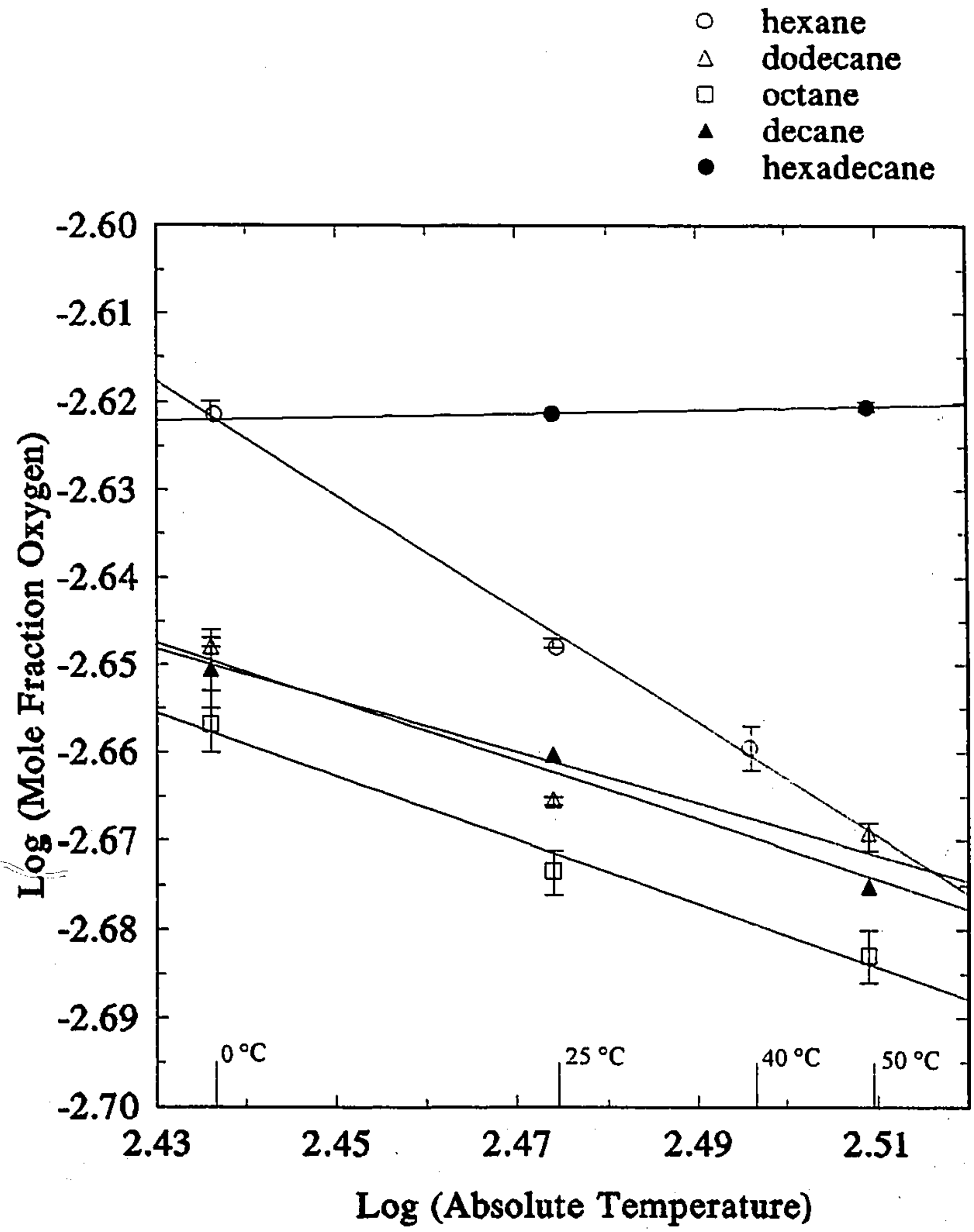

Figure 6. Solubility of oxygen versus temperature for the hydrocarbon solvents.

5.2 SOLUBILITY OF OXYGEN IN THE AQUEOUS SOLVENT SOLUTIONS

The experimental solubility data obtained were evaluated to determine the effect of electrolytes on the solubility of oxygen in the electrorefining solutions. The equilibrium solubilities were calculated by the least-squares FORTRAN program included in Appendix B. Solubility of oxygen in water was determined at temperatures of 298.15 K, 333.15 K and 353.15 K, at atmospheric pressure. The solubilities of oxygen in the aqueous solvent solutions were determined at a temperature of 333.15 K and at atmospheric pressure. Oxygen solubilities in water and in the aqueous solvent solutions were measured at least twice.

The results of oxygen solubility in water were consistently within 2% of the solubility values reported in the literature. The mole fraction solubility of oxygen in water at a temperature of 298.15 K is 2.288×10^{-5} (Wilhelm et al., 1977) whereas the solubility measured in the present work at the same temperature was 2.283×10^{-5} ($\pm1.00\times10^{-7}$), corresponding to a relative error of about 0.2%. The standard deviation between replicates is indicated in parenthesis. The value of the solubility of oxygen at 298.15 K also served to confirm that the solubility apparatus and procedures were satisfactory.

The mole fraction solubilities of oxygen in water at temperatures of 333.15 K and 353.15 K were reported by Wilhelm et al. (1977) to be 1.5753×10^{-5} and 1.4403×10^{-5}, respectively. The measured mole fraction solubility of oxygen in water at a temperature of 333.15 K was 1.596×10^{-5} ($\pm1.00\times10^{-7}$), which represented a relative error between the measured solubility and the solubility reported in the literature of about 1.3%. At a temperature of 353.15 K the mole fraction solubility of oxygen gas was measured to be 1.455×10^{-5} ($\pm7.85\times10^{-8}$), corresponding to a relative error of approximately 1%. The effect of temperature on the solubility of oxygen in water is complex. The solubility of oxygen in water was measured at three temperature levels and in general the solubility of oxygen in water decreased as the temperature was raised.

An analysis of the effect of temperature on gas solubility in water was reported by Hayduk and Laudie (1973). The work of Hayduk and Laudie showed that the solubilities of a number of sparingly soluble gases in water exhibit a minima. Furthermore, it was shown that the solubility of oxygen in water tends to a minimum at a temperature of about 373 K. The solubility of oxygen in water increased at higher and lower temperatures. The reduction in solubility was attributed to hydrogen bonding in the solvent. The H-bonds were believed to exclude solute molecules. Experimental data for a number of gases in associating solvents have shown that the gas solubilities passed through a minimum and then increased as the temperature was raised (Hayduk and Laudie, 1973).

The solubility of oxygen in the aqueous solvent solutions was similar to that of oxygen in water. The average solubility results for the aqueous solvent solutions are shown in Table 5 below. Limited solubility data available in the literature does not permit a comparison of the measured solubility with literature values. As mentioned previously, known solubilities of oxygen in water served to verify the accuracy of the solubility apparatus, therefore reproducibility between experiments served as an indication of the accuracy and reliability of the measured solubility. The maximum standard deviation in the measured solubility of oxygen in the aqueous solvent solutions was 1.68×10^{-7}. Furthermore, the densities and vapor pressures of the aqueous solvent solutions were experimentally determined, hence the measured solubilities of oxygen were considered more accurate than those appearing in the literature.

The solubility of oxygen in pure water represented the maximum equilibrium solubility for the aqueous solvents. The electrolytes, cupric sulphate salt and sulphuric acid, reduced the solubility of oxygen in the aqueous solvent solutions as compared to the maximum solubilities in water. Electrolytes which cause a reduction in oxygen solubility are said to "salt out" the oxygen. The salting out of oxygen by the addition of the salt and the acid is illustrated in Figure 7.

Table 5. Summary of the results for the solubility of oxygen in the aqueous solvent solutions, at a temperature of 333.15 K and at a gas partial pressure of 101.325 kPa.

Solvent	Solubility
75 g/L H_2SO_4	
α	0.0169
K_H (10^{-7})	4.169
x (10^5)	1.178 (±0.0)
$k_{sc\alpha}$ $(dm^{-3}/mole)$	0.0995
150 g/L H_2SO_4	
α	0.0152
K_H (10^{-7})	3.938
x (10^5)	1.091 $(\pm 6.00\times10^{-9})$
$k_{sc\alpha}$ $(dm^{-3}/mole)$	0.0802
30 g/L Cu^{2+}	
α	0.0144
K_H (10^{-7})	2.740
x (10^5)	1.018 $(\pm 5.29\times10^{-7})$
$k_{sc\alpha}$ $(dm^{-3}/mole)$	0.308
60 g/L Cu^{2+}	
α	0.0110
K_H (10^{-7})	2.534
x (10^6)	8.112 (±0.0)
$k_{sc\alpha}$ $(dm^{-3}/mole)$	0.277
30 g/L Cu^{2+}/150 g/L H_2SO_4	
α	0.0124
K_H (10^{-7})	2.876
x (10^6)	9.321 $(\pm 1.68\times10^{-7})$
$k_{sc\alpha}$ $(dm^{-3}/mole)$	0.105
60 g/L Cu^{2+}/150 g/L H_2SO_4	
α	0.00955
K_H (10^{-7})	2.827
x (10^6)	7.550 $(\pm 3.15\times10^{-7})$
$k_{sc\alpha}$ $(dm^{-3}/mole)$	0.131

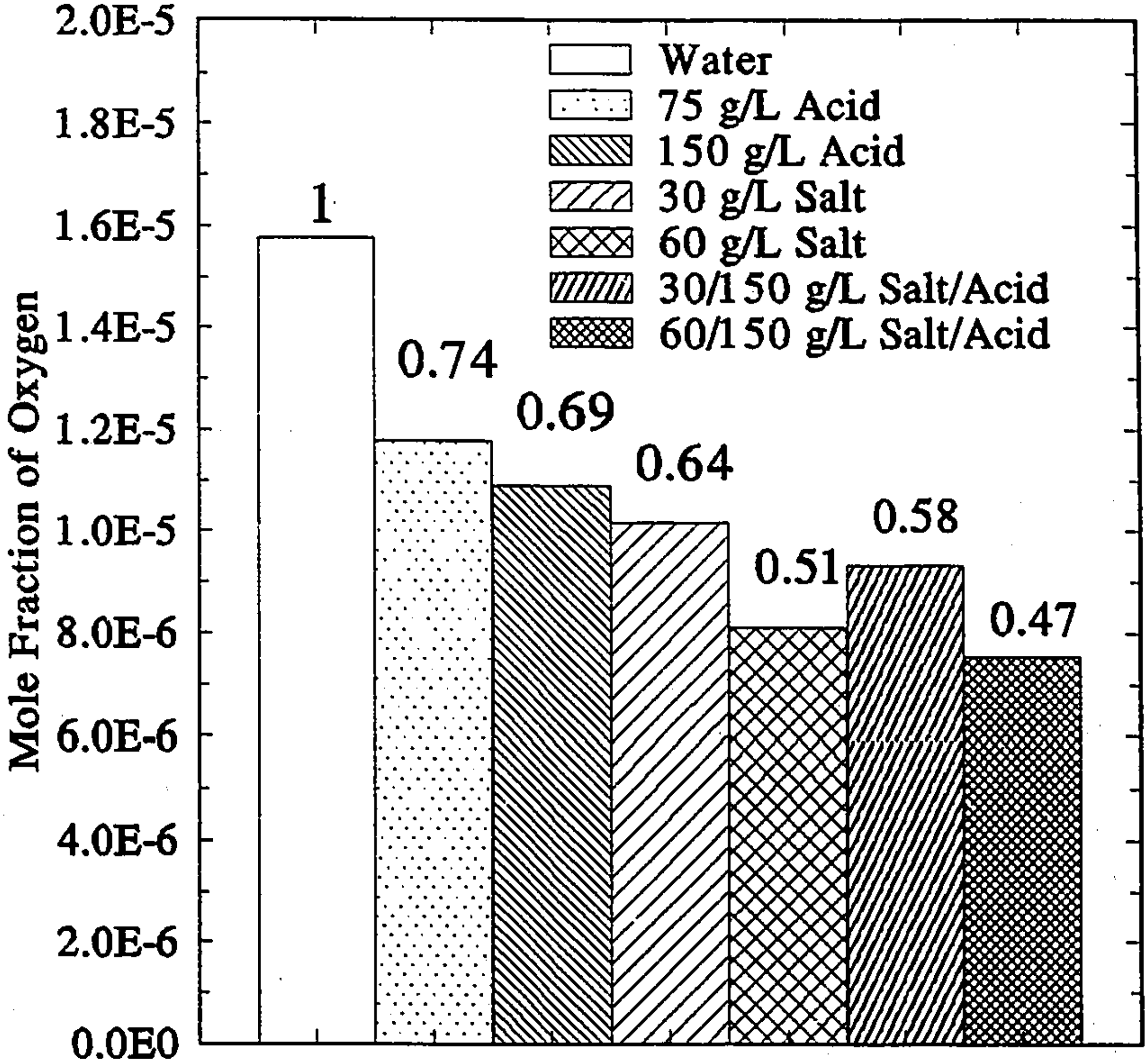

Figure 7. Plot of the mole fraction solubility of oxygen in water and the aqueous solvent solutions at a temperature of 333.15 K for a gas partial pressure of 101.325 kPa. An illustration of the salting out effect of the electrolytes.

The reduction in oxygen solubility upon addition of 75 g/L (0.778 mole/L) sulphuric acid was approximately 26% of the maximum solubility value for oxygen in pure water. Increasing the concentration of the acid to 150 g/L (1.540 mole/L), reduced the solubility of oxygen by an additional 5%, producing a net salting out effect of about 31%. Similarly, addition of 30 g/L (0.0472 mole/L) and 60 g/L (0.0944 mole/L) Cu^{2+} reduced the solubility of oxygen by 36% and 49%, respectively. The salting out effect for the electrolytic solvent solutions containing both the salt and the acid was not linearly additive. The solubility of oxygen in the electrolytic solution containing 30 g/l Cu^{2+} and 150 g/L sulphuric acid was reduced by about 42%. Finally, a decrement in oxygen solubility of 53% was observed for the electrolytic solution containing 60 g/l Cu^{2+} and 150 g/L sulphuric acid.

It should be noted from the above table that a doubling of the electrolyte concentration does not double the salting out effect. Rather, doubling the salt or acid concentration resulted in a reduction of oxygen solubility of a few percent. The decrement in oxygen solubility, as a result of the addition of the salt or the acid, can be represented by the Setschenow salt effect parameter, shown in Table 5 as $k_{sc\alpha}$. A positive Setschenow would indicate salting out of the gas. The Setschenow salt effect parameter has been used to convert the solubility data to a common basis, allowing for the comparison of data from various sources. The Setschenow constants, based on the Bunsen coefficients, were calculated using the total electrolyte concentrations in each solvent solution.

For moderate concentrations of the electrolyte, the Setschenow constant was shown to exhibit a linear dependence on electrolyte concentration. In fact, Bruhn et al. (Battino et al., 1981) have indicated that $k_{sc\alpha}$ tended to decrease slightly as the concentration of the electrolyte was increased. The dependence of the Setschenow constant on electrolyte concentration could be evaluated from a plot of $k_{sc\alpha}$ versus electrolyte concentration. If the resulting slope on such a plot was zero, then the

Setschenow salt effect parameter was considered independent of electrolyte concentration. The slopes for the sulphuric acid solutions, the cupric sulphate solutions, and the electrolytic solutions containing both the acid and the salt were determined to be 0.025, 0.066 and 0.055, respectively. The dependence of the Setschenow constants on electrolyte concentrations appears to be small. In fact, for the concentration range and the temperature at which the solubilities of oxygen were determined, the Setschenow constant could be considered independent of electrolyte concentration. The calculated Setschenow constants served to illustrate the salting out of oxygen gas as the electrolyte concentration was increased. The salting out effect was also illustrated in Figure 7.

The precision of the solubility results was estimated. Solubility measurements obtained by volumetric means typically contain errors of up to 2%. In fact, determination of known solubilities of oxygen in water indicated that the solubility measurements were accurate to within 1.3%.

5.3 VAPOR PRESSURES OF THE AQUEOUS SOLVENT SOLUTIONS

The vapor pressure of ideal solutions could be evaluated by means of Raoult's law. However, Raoult's law is an ideal relation and cannot be applied to real solutions which contain nonvolatile solutes, such as the sulphuric acid and copper sulphate salt. Therefore, to correctly express the solubility measurements, the vapor pressures of the aqueous solvent solutions were measured at a temperature of 333.15 K. The measured vapor pressures allowed for the evaluation of the activity coefficients for the aqueous solutions. Reproducibility of the vapor pressure measurements was approximately 1%. The vapor pressure results and the calculated activity coefficients are shown in Table 6.

Table 6. Summary of the experimental results for the vapor pressure of the aqueous solutions at 333.15 K.

Solution	Vapor Pressure, kPa (psi)	Activity Coefficient
75 g/L H_2SO_4	19.443 (2.82)	1.9131
150 g/L H_2SO_4	18.547 (2.69)	2.1582
30 g/L Cu^{2+}	19.926 (2.89)	0.3988
60 g/L Cu^{2+}	19.719 (2.86)	1.0033
30 g/L Cu^{2+}/150 g/L H_2SO_4	18.478 (2.68)	-
60 g/L Cu^{2+}/150 g/L H_2SO_4	18.409 (2.67)	-

The activity coefficients for the salt and the acid solutions were calculated by means of equation [E-23]. The activity coefficient accounted for nonideality of the aqueous solution due to the presence of the copper salt and the sulphuric acid. Furthermore, the effect of each of the nonvolatile components was assumed additive; that is, the reduction in the vapor pressure of the two component aqueous solutions could be calculated from the knowledge of the activity coefficients of the individual salt and acid solutions. In this manner, the estimated vapor pressures of the solutions containing 30 g/L Cu^{2+}/150 g/L H_2SO_4 and 60 g/L Cu^{2+}/150 g/L H_2SO_4 were calculated to be 18.685 kPa (2.71 psi) and 18.409 kPa (2.67 psi), respectively. The estimated vapor pressures using the modified Raoult's law are considered to be accurate to within 1%.

5.4 DENSITIES OF THE AQUEOUS SOLUTIONS

The densities of the aqueous solvent solutions were measured for six temperatures in the range between 313.15 K and 413.15 K. Due to the corrosive nature of the aqueous solutions, the densities were measured in dilatometer tubes. Dilation of the solutions inside the dilatometer tubes were measured with moderate accuracy, by means of a cathetometer, as the temperature was increased. Prior to the determination of the unknown densities of the aqueous solutions, the dilatometer tubes needed to be calibrated.

Thus water was used to calibrate the tubes, since the densities of water are known precisely. The measured water densities allowed for the calculation of a correction factor for each of the three dilatometer tubes. The densities of the aqueous solutions were measured at least twice. The experimental results of water densities and the calculated correction factors are tabulated in Appendix A. The density results for the aqueous solvent solutions are shown in Table 7. Table 7 shows the measured densities of the aqueous solutions; the correction factor, r; the densities of the aqueous solution as reported in the literature (Sohnel et al., 1985); and the relative errors between the measured densities and the densities found in the literature.

As discussed previously in Section 3.3, the correction factor, r, accounted for thermal expansions of the capillary tubes as the temperature was raised. For the aqueous solutions containing both the sulphuric acid and copper sulphate salt, densities were not available in the literature. Furthermore, the densities found in the literature were reported to a maximum temperature of 373.15 K. Hence comparison of experimental densities with literature densities at temperatures above 373.15 K was not possible.

A graphical representation of the density results was found useful in order to illustrate the effect of the acid and the salt on the density of pure water. The effects of temperature and electrolyte concentration on the densities of the aqueous solvent solutions is illustrated in Figure 8. It can be observed from Figure 8 that the densities of water and the aqueous solutions decreased as the temperature was increased, as expected. The decrease in the densities was initially small for the lower temperatures but became significantly larger at the higher temperatures. Furthermore, the aqueous solution densities were larger than the densities of pure water. Hence, the densities of the aqueous solutions increased with the addition of the salt and the acid. Furthermore, the effects of the copper sulphate salt and the sulphuric acid appeared to be additive. The additive effect of the salt and the acid on solution densities could most easily be illustrated by means of an

Table 7. Average density (kg/m^3) results for the aqueous solvent solutions.
Solvent concentrations are expressed as g/L Cu^{2+} / g/L H_2SO_4
r denotes the correction factor for each dilation tube
R.E. (%) denotes percent relative error.

Solvent	Temperature, K						
	296.15	313.15	333.15	353.15	373.15	393.15	413.15
0/75							
Measured	1044.5	1041.5	1031.5	1016.6	1007.7	989.7	976.4
r	-	1.001	1.000	0.996	0.999	0.991	0.988
Literature	1046.8	1039.4	1029.4	1017.5	1003.9	-	-
R.E. (%)	0.22	0.20	0.20	0.09	0.38	-	-
0/150							
Measured	1089.0	1085.4	1073.8	1060.3	1041.8	1029.5	1009.3
r	-	1.004	1.004	1.002	0.997	0.999	0.995
Literature	1092.6	1084.5	1072.9	1060.7	1047.7	-	-
R.E. (%)	0.33	0.08	0.08	0.04	0.56	-	-
30/0							
Measured	1075.0	1069.9	1060.1	1046.0	1036.8	1014.2	1000.5
r	-	1.001	1.000	0.996	0.999	0.991	0.988
Literature	1074.2	1067.4	1056.4	1044.4	1030.9	-	-
R.E. (%)	0.07	0.23	0.35	0.15	0.57	-	-
60/0							
Measured	1143.0	1138.5	1128.4	1113.9	1099.9	1084.2	1060.8
r	-	1.002	1.003	1.002	1.004	1.007	1.005
Literature	1144.7	1138.0	1127.0	1115.0	1100.3	-	-
R.E. (%)	0.15	0.04	0.12	0.10	0.04	-	-
30/150							
Measured	1157.0	1151.7	1138.5	1125.6	1113.5	1093.9	1073.6
r	-	1.004	1.004	1.002	0.997	0.999	0.995
Literature	-	-	-	-	-	-	-
R.E. (%)	-	-	-	-	-	-	-
60/150							
Measured	1223.0	1211.9	1200.8	1185.6	1170.8	1157.4	1139.3
r	-	1.002	1.003	1.002	1.004	1.007	1.005
Literature	-	-	-	-	-	-	-
R.E. (%)	-	-	-	-	-	-	-

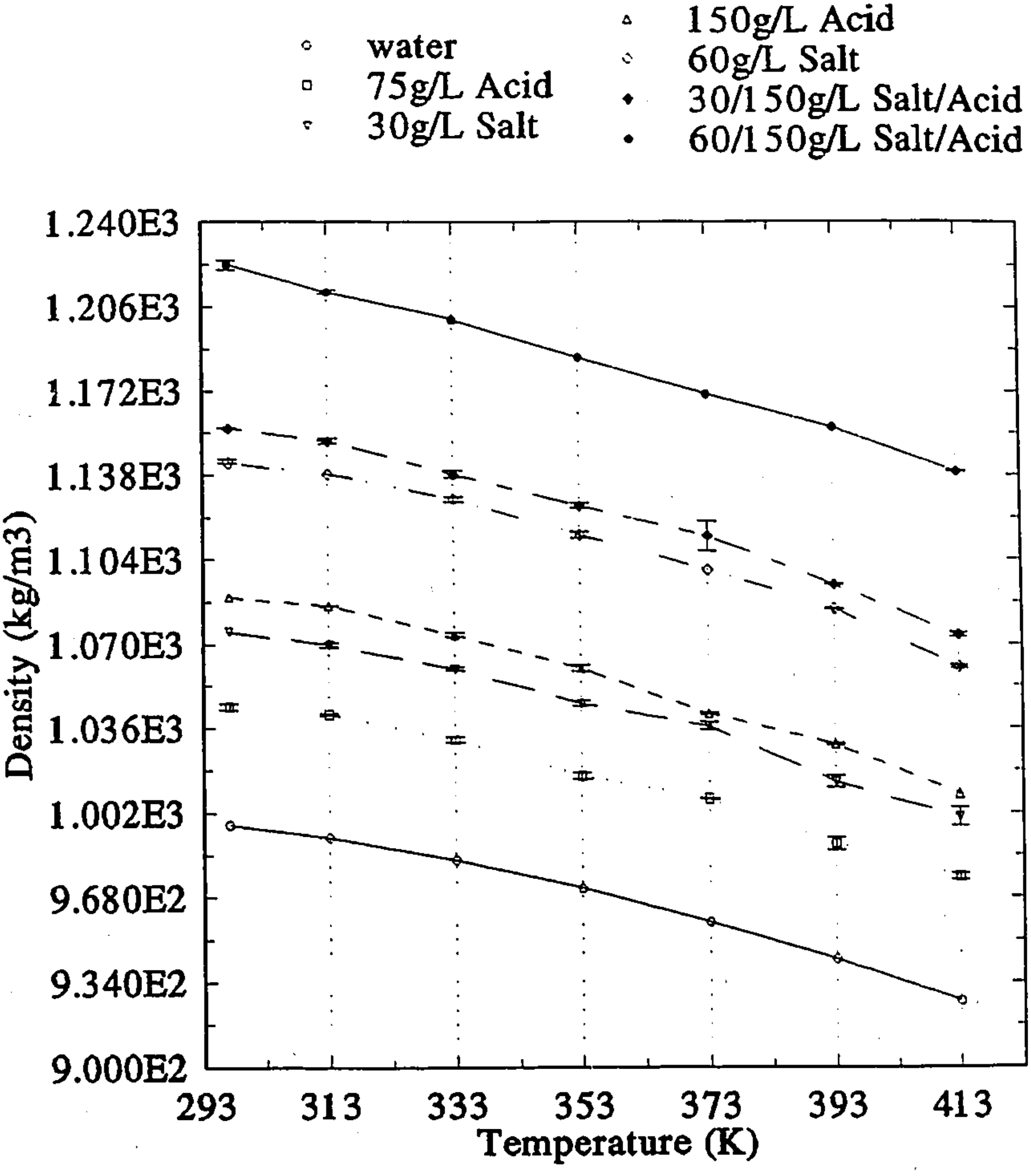

Figure 8. Densities of water and the aqueous solvent solutions determined by means of dilatometer tubes.

example. Consider, for example, the effect of the salt and the acid on the density of water at a temperature of 333.15 K. The density of water was found to have increased by 76.86 kg/m^3 upon addition of 30 g/L Cu^{2+}. Furthermore, addition of 150 g/L H_2SO_4 increased the density of water by 90.56 kg/m^3. If the effects of the salt and the acid were additive, then a two component solution composed of both the salt and the acid of the same concentrations as above, would have produced an increase in density of 167.42 kg/m^3. In fact, for the aqueous solution containing both the 30 g/L Cu^{2+} and the 150 g/L H_2SO_4, the increase in the density was determined to be 155.26 kg/m^3. Therefore, the density determined by assuming the effects of the salt and the acid to be additive was found to be within 7% of the experimental density for the two component aqueous solution. In fact, 7% was the largest error between the experimentally determined density and the density found by summing the effects of the individual salt and acid solutions.

6. CONCLUSIONS AND RECOMMENDATIONS

6.1 CONCLUSIONS

1. The solubility apparatus proved to be a reliable and accurate instrument with which to determine solubilities of gases in liquids.

2. The solubility of oxygen in the alkane solvents with a carbon number greater than six was found to increase, in accordance with the findings of Blanc and Batiste (Battino et al., 1981).

3. The temperature coefficient of solubility was small; that is, the solubility of oxygen showed little dependence on temperature between the temperature range of 273.15 K to 323.15 K.

4. The solubility of oxygen in water approaches a minimum at about 373.15 K.

5. Addition of the copper sulphate salt and the sulphuric acid reduced the solubility of oxygen in the aqueous solution; that is, the oxygen was salted out.

6. The salting out of oxygen from the aqueous solutions was found to be function of the type of electrolyte added. However, the Setschenow salt effect parameter, for a given electrolyte, was found to decrease slightly as the concentration of the electrolyte was increased.

7. The aqueous solutions did not closely obey Raoult's law, hence the activity coefficients for the electrolytes were calculated from the vapor pressure data.

8. The dilatometer tubes provided density measurements of moderate accuracy for corrosive solutions at elevated temperatures.

9. The densities of the aqueous solutions increased as the concentration of electrolyte was increased. The effect of the salt and the acid on solution density was additive, allowing approximation of the density of three component (salt/acid/water) mixture. Furthermore, for the temperature range investigated, the densities decreased as the temperature was increased as expected.

6.2 RECOMMENDATIONS

1. In this work, the mercury lift was adjusted manually to compensate for pressure changes in the absorption tube during solubility measurements. The use of a pressure transducer and a control device for the mercury lift would perhaps increase the accuracy of the solubility results.

2. Straight dilatometer tubes for the density determinations may be used if an oil bath with greater depth was available.

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APPENDICES

APPENDIX A: EXPERIMENTAL DATA FOR THE DETERMINATION OF THE DENSITIES OF THE AQUEOUS SOLVENT SOLUTIONS

Additional experimental density data is presented in this Appendix. Table A.1 summarizes the corrected experimental measurements recorded in the determination of the densities of the aqueous solutions. The correction factor used to calculate the lengths in Table A.1 was presented in Table 7, in the Results and Discussion section. Table A.2 shows additional data which describes the composition of the aqueous solutions.

Table A.1. Corrected lengths of the aqueous solvent solutions in the dilatometer tubes (m). Solvent concentrations are expressed as g/L Cu^{2+} / g/L H_2SO_4.

Solvent	Temperature, K						
	296.16	313.15	333.15	353.15	373.15	393.15	413.15
Water							
Tube 1	-	0.33808	0.33803	0.33945	0.34421	0.34793	0.35400
Tube 2	-	0.33170	0.33212	0.33493	0.33880	0.34475	0.35019
Tube 3	-	0.35507	0.35673	0.36509	0.37071	0.37664	0.38328
0/75	0.31966	0.32044	0.32336	0.32804	0.33126	0.33649	0.34152
	0.31656	0.31762	0.32088	0.32564	0.32817	0.33493	0.33909
0/150	0.34936	0.35056	0.35401	0.35843	0.36500	0.36942	0.37473
	0.34844	0.34955	0.35364	0.35828	0.36440	0.36831	0.37361
30/0	0.36608	0.36752	0.37105	0.37581	0.37903	0.38704	0.39197
	0.36116	0.36316	0.36640	0.37158	0.37496	0.38378	0.38944
60/0	0.38550	0.38702	0.39009	0.39513	0.40016	0.40933	0.41564
	0.38550	0.38703	0.39086	0.39604	0.40104	0.40646	0.41520
30/150	0.32979	0.33162	0.33561	0.33930	0.34085	0.34886	0.35569
	0.32853	0.32974	0.33341	0.33466	0.34321	0.34741	0.35380
60/150	0.33768	0.34103	0.34441	0.34877	0.35317	0.35924	0.36296
	0.33575	0.33858	0.34197	0.34635	0.35072	0.35683	0.36051

Table A.2. Summary of the total number of moles in the aqueous solution and the mole concentration of the electrolyte in solution. Solvent concentration is expressed as g/L Cu^{2+} / g/L H_2SO_4.

Solution	Total solution (mole/L)	Electrolyte only (mole/L)
0/75	53.9684	0.7784
0/150	52.9577	1.5398
30/0	55.2239	0.4759
60/0	55.5686	0.9517
30/150	53.1906	2.0148
60/150	52.9256	2.4906

APPENDIX B: EXTRAPOLATION OF THE VAPOR PRESSURES FOR THE HYDROCARBON SOLVENTS

Figure B.1 was constructed to allow extrapolation of the vapor pressures of the hydrocarbon solvents to a region where the Antoine equation was not applicable. Vapor pressure values above 1.4 kPa (10 mmHg) were obtained from Zwolinski and Wilhoit (1971). Vapor pressure values lower than 1.4 kPa (10 mmHg) were assumed linear in the pressure range between 0 to 1.4 kPa and hence were linearly extrapolated from Figure B.1.

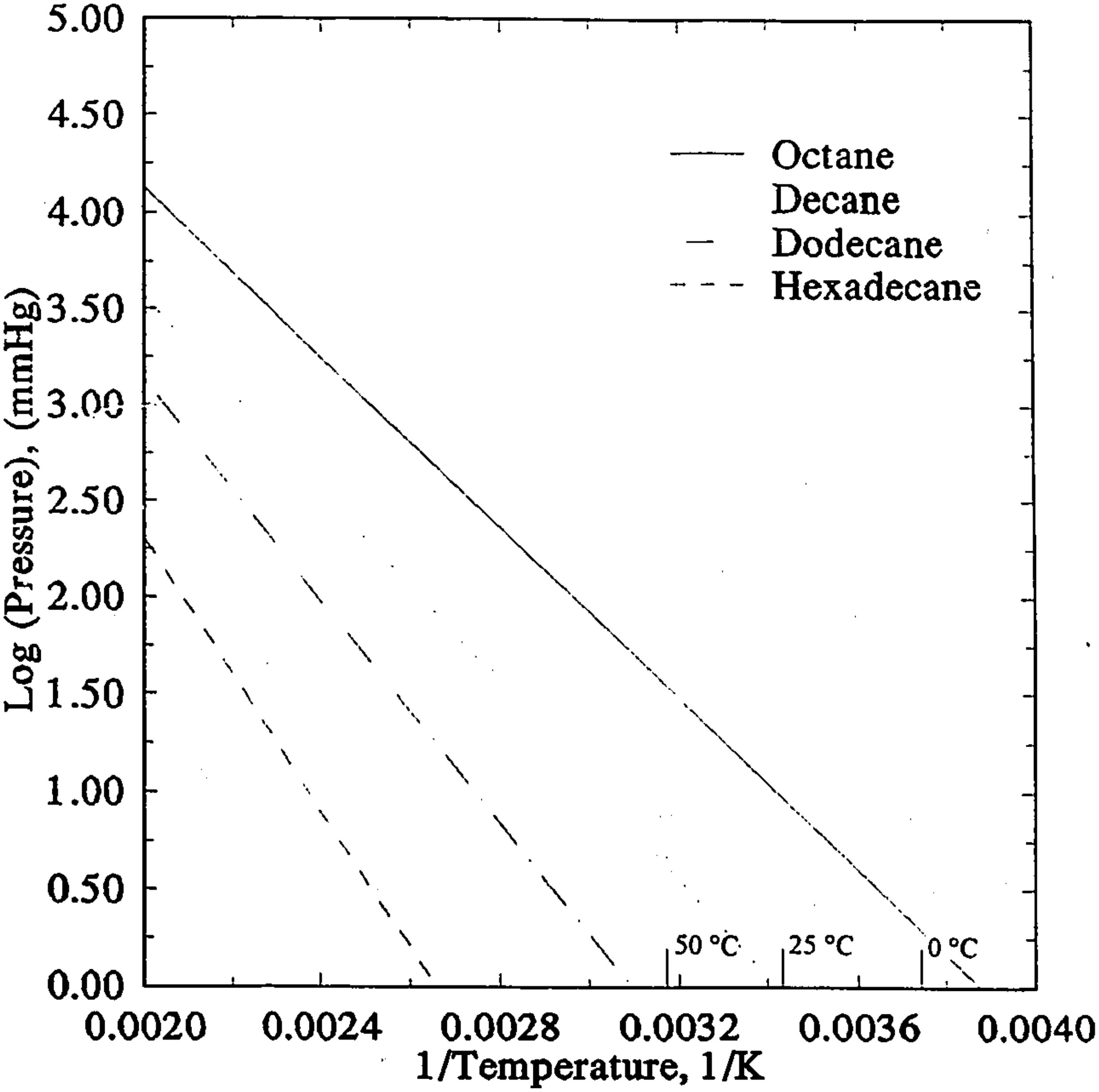

Figure B.1. Plot of the vapor pressures of the hydrocarbon solvents for low pressures.

APPENDIX C: SAMPLE CALCULATIONS FOR SOLUTION PREPARATION

Sample calculations for the amount of chemicals used in the preparation of the aqueous solvent solutions will now be shown. The 30 g/L Cu^{2+} with the 150 g/L sulphuric acid will be taken as the basis for the calculations shown. Moreover, the sample calculations are shown for a total solution volume of 1000 cm^3.

C1.1 AMOUNT OF SULPHURIC ACID

To evaluate the amount of sulphuric acid required, the density and purity of the acid was needed. The sulphuric acid was specified to be 96 % pure. Furthermore, the density of the sulphuric acid was determined by accurately weighing a known volume of acid in a Mettler balance. The density of the acid was determined to be 1828.0 kg/m^3 (1.828 g/cm^3). Therefore, to produce a solution with a 150 g/L of pure sulphuric acid, as specified for the solution above, the required volume of acid can be found by:

$$1\ m^3 \times \frac{96}{100} \times 1828\ kg/m^3 = 1754.88\ g \text{ of pure sulphuric acid,}$$

then 0.150 kg of pure acid can be obtained from:

$$\frac{1\ m^3}{1754.88\ kg} \times 0.150 = 8.5475 \times 10^{-5}\ m^3 = 85.48\ ml \text{ of sulphuric acid.}$$

Therefore, to make a solution of 150 g/L sulphuric acid, 85.48 ml of the 96 % pure sulphuric acid would be diluted to a volume of 1000 cm^3.

C1.2 AMOUNT OF CUPRIC SULPHATE

To determine the amount of hydrated cupric sulphate crystals required to produce a solution containing 30 g/L of Cu^{2+}, the molecular weight of the anhydrous salt and the purity of the hydrated salt were required. Also, the atomic weight of copper was needed for the calculation.

The molecular weight of the hydrated cupric sulphate salt is 249.68 kg/kmole, and the percentage purity of the salt was specified at 99.5 %. Hence the corrected molecular weight of the hydrated copper salt was 249.68/0.995 = 250.935 kg/kmole. Each molecule of cupric sulphate contains a single copper atom and the atomic weight of copper is 63.54 kg/kmole. Therefore, 250.935 kg of the copper salt crystals contain 63.54 kg of pure copper metal. Then,

$$\frac{250.935}{63.54} \times 0.03 \text{ kg} = 0.1184771 \text{ kg} = 118.477 \text{ g of hydrated copper sulphate salt.}$$

Thus, a 30 g/L Cu^{2+} solution was made by dissolving 118.477 g of the hydrated crystals in 1000 cm^3 of water.

APPENDIX D: SAMPLE CALCULATION FOR GAS SOLUBILITY

D1.0 BUNSEN COEFFICIENT

The Bunsen coefficient was evaluated by means of the least squares FORTRAN program, which solved equation [E-2]. The volume of oxygen absorbed and the volume of absorbing solvent was determined from the experimental solubility data. The gas volume was reduced to 101.325 kPa by means of Henry's law. For example, the solution containing 30 g/L Cu^{2+} and 150 g/L H_2SO_4 absorbed 1.98×10^{-6} m^3 (1.98 cm^3) of oxygen per 1.56×10^{-4} m^3 (156.6 cm^3) of solvent. The experiment was performed at an atmospheric pressure of 100.286 kPa (752.0 mmHg), the total saturated oxygen pressure was 118.776 kPa (890.652 mmHg). Therefore, applying Henry's law yields:

Equivalent volume of O_2 absorbed $= (1.98 \times 10^{-6}) \dfrac{118.776}{100.286} = 2.35\times10^{-6}\ m^3 = 2.35$ cm^3.

$$\therefore \text{ the Bunsen coefficient, } \alpha = \frac{(2.35 \times 10^{-6})\,273.15}{(1.56 \times 10^{-4})\,333.15} = 0.01235.$$

The above calculation was repeated for the second solubility measurement. The value of the Bunsen coefficient reported in Table 5, was an average of the two experimental solubility values.

D2.0 SETSCHENOW SALT EFFECT PARAMETER

The Setschenow salt effect parameter was calculated based on the Bunsen coefficients of pure water and the aqueous solvent solutions. The Setschenow salt effect parameter was calculated by means of equation [E-17]. For the solution containing 30 g/L cupric metal ions and 150 g/L sulphuric acid, the average Bunsen coefficient at 333.15 K and at atmospheric pressure was reported to be 0.01244. Similarly, the Bunsen coefficient for pure water was 0.02024. The total number of moles of electrolyte in this solution was 2.0148, as shown in Table 8. Equation [E-17] then yields:

$$k_{sc\alpha} = \frac{1}{2.0148} \log\left(\frac{0.02024}{0.01244}\right) = 0.1046.$$

APPENDIX E: SAMPLE CALCULATION FOR THE DETERMINATION OF THE DENSITIES OF THE AQUEOUS SOLVENT SOLUTIONS

The densities of the aqueous solutions were determined by means of the dilatometer tubes. The length of solution dilation in the tube, as the temperature was increased, was measured with a cathetometer. The density of the solution at each temperature was evaluated with equation [E-28]. For the aqueous solution consisting of 30 g/L cupric metal ions and 150 g/L sulphuric acid, at a temperature of 333.15 K, the length of solution, from Table A.1, was 0.33341 m. The average length of the same solution at 296.15 K was 0.32853. The density of the solution at 296.15 (23 °C) was determined volumetrically by accurately weighing a known volume of solution in a Mettler balance, and was found to be 1157.0 kg/m^3 (1.1570 g/cm^3). Therefore, the density of the two component solution at 333.15 K, as calculated by means of equation [E28] was:

$$\rho = \frac{0.32853}{0.33341} \times 1157.0 \text{ kg/m}^3 = 1140.07 \text{ kg/m}^3.$$

Similar calculations with the second set of experimental data would yield the average solution density value shown in Table 7.

APPENDIX F: SAMPLE CALCULATION FOR THE DETERMINATION OF THE ACTIVITY COEFFICIENT FROM VAPOR PRESSURE DATA

The vapor pressures of the aqueous solvent solutions were determined at the temperature of the solubility measurement (333.15 K), allowing for the evaluation of the activity coefficient for all the aqueous solutions. The modified Raoult's law, equation [E-23], was utilized to determine the activity coefficients. The number of moles of water in a 100 cm^3 of 150 g/L sulphuric acid solution = 5.1418. The number of moles of sulphuric acid added was = 0.15389;

$$\therefore \text{ the mole fraction of } H_2SO_4 = \frac{0.15389}{0.15389 + 5.1418} = 0.02906.$$

Rearranging equation [E-23] to solve for the activity coefficient yields:

$$\gamma_{H_2SO_4} = \frac{1 - \frac{P}{P^\circ}}{x_{H_2SO_4}} = \frac{1 - \frac{2.69}{2.87}}{0.02906} = 2.1582.$$

Similarly for 30 g/L Cu^{2+}: $\gamma_{CuSO_4} = 0.3988$.

The above activity coefficients are used to calculate the vapor pressure of the aqueous solution containing both the acid and the salt. For example, in a solution containing 30 g/L Cu^{2+} and 150 g/L H_2SO_4, the mole fractions of the copper salt, and the sulphuric acid were 0.008945, and 0.02893, respectively. Thus the calculated vapor pressure of the two component aqueous solution was:

$$P = \{1 - [(0.3988)(0.008945) + (2.1582)((0.02893)]\}2.90 = 2.71 \text{ psi.}$$

The measured vapor pressure for the same solution was 2.68 psi, corresponding to a relative error between the measured and calculated vapor pressures of approximately 1.1%.

APPENDIX G: LEAST-SQUARES FORTRAN PROGRAM

The least-squares FORTRAN program used to calculate the solubilities in terms of the Ostwald coefficient, the Bunsen coefficient, Henry's law constant and the mole fraction of oxygen is included herein. The program also evaluates the correlation coefficient between the volume of oxygen absorbed and the volume of absorbing solvent.

```
      PROGRAM SLBLTY
*
*
*A       SLOPE OF CURVE CORRESPONDING TO THE OSTWALD COEFFICIENT
*ALPHA   BUNSEN COEFFICIENT
*BETA0   INTERCEPT FROM LINEAR REGRESSION PERFORMED ON THE EXPERIMENTAL
*        DATA
*BETA1   SLOPE FROM LINEAR REGRESSION PERFORMED ON THE EXPERMINETAL DATA
*EQVLO2  EQUIVALENT VOLUME OF OXYGEN CORRECTED TO P BY HENRY'S LAW, ML
*HATM    HENRY'S LAW CONSTANT AT ATMOSPHERIC PRESSURE
*HPP     HENRY'S LAW CONSTANT AT O2PP
*N       NUMBER OF SOLUBILITY DATA PAIRS COLLECTED
*O2ML    VOLUME OF OXYGEN ABSORBED, ML
*O2MOL   MOLES OF OXYGEN ABSORBED
*O2PP    PARTIAL PRESSURE OF OXYGEN AT THE TEMPERATURE OF THE SOLUBILITY
*        MEASUREMENT
*OSTWLD  OSTWALD COEFFICIENT
*P       TOTAL PRESSURE, MMHG
*PATM    ATMOSPHERIC PRESSURE, MMHG
*R       CORRELATION COEFFICIENT
*RESDUL  RESIDUAL, DIFFERENCE IN VOLUME OF GAS BETWEEN FITTED EQUATION
*        AND EXPERIMENTAL DATA COLLECTED
*RHOT2   DENSITY OF SOLVENT AT TAVE, G/ML
*SOLML   VOLUME OF SOLVENT, ML
*SOLMOL  MOLES OF SOLVENT
*SOLVMW  MOLECULAR WEIGHT OF THE SOLVENT
*SSR     SUM OF THE SQUARED RESIDUALS
*SUMX    TOTAL VOLUME OF ABSORBING SOLVENT, ML
*SUMXY   SUM OF THE PRODUCT OF VOLUME OF LIQUID AND GAS
*SUMY    TOTAL VOLUME OF ABSORBED GAS, ML
*TAVE    AVERAGE TEMPERATURE OF SOLUBILITY MEASUREMENT, CELCIUS
*TERCEPT Y-INTERCEPT, SAME AS BETA0
*VOLME   MOLAR VOLUME OF OXYGEN AT THE TEMPERATURE OF THE SOLUBILITY
*        MEASUREMENT
*VPSOLV  VAPOR PRESSURE OF THE SOLVENT AT TAVE
*XATM    MOLE FRACTION OF GAS AT ATMOSPHERIC PRESSURE
*XBAR    AVERAGE VOLUME OF ABSORBING GAS
*XPP     MOLE FRACTION OF GAS O2PP
*YBAR    AVERAGE VOLUME OF GAS ABSORBED
*
*
*
*

      IMPLICIT DOUBLE PRECISION (A-H, O-Z)
      DIMENSION X(50), Y(50), RESDUL(50)
*
*

      DATA N, TAVE, PATM/16, 60.0, 752.0/
      DATA SOLVMW, VPSOLV, RHOT2/25.191, 138.135, 1.2008/
*
      WRITE (9,*) 'RUN 1,TEMP = 60.0 C, 60 G/L SALT/150 G/L ACID'
*
      READ (8,*) (X(I), I = 1, N)
      READ (8,*) (Y(I), I = 1, N)
*
```

```
      O2ML = Y(N) - Y(1)
      SOLML = X(N) - X(1)
      O2PP = PATM - VPSOLV
      P = PATM + VPSOLV
      CALL SLOPE (A, TERCPT, X, Y, R, SSR, RESDUL, N)
      VOLME = VOLUME (TAVE, O2PP)
      O2MOL = O2ML/VOLME
      SOLMOL = (SOLML*RHOT2)/SOLVMW
      CALL SOLUB (O2MOL, SOLMOL, O2PP, PATM, P, TAVE, A, O2ML,
     C           XPP, XATM, HPP, HATM, EQVLO2, SOLML, ALPHA, OSTWLD,
      CALL DAT (O2ML, SOLML, O2PP, XATM, HPP, HATM, P,
     C   EQVLO2, A, TERCPT, R, SSR, X, Y, RESDUL, N,
     C   O2MOL, SOLMOL, XPP, ALPHA, OSTWLD, PATM)
      END
*
*
*
* SUBROUTINE CALCULATES THE MOLE FRACTION SOLUBILITY AND HENRY'S LAW
* CONSTANTS AT THE EXPERIMENTAL PRESSURE AND AT 760.0 MMHG.
*
*
      SUBROUTINE SOLUB (O2MOL, SOLMOL, O2PP, PATM, P, TAVE, A, O2ML,
     C           XPP, XATM, HPP, HATM, EQVLO2, SOLML, ALPHA,OSTWLD)
*
      IMPLICIT DOUBLE PRECISION (A-H, O-Z)
*
*
      XPP = O2MOL/(SOLMOL + O2MOL)
      XATM = XPP*760.0/O2PP
      HPP = O2PP/XPP
      HATM = 760.0/XATM
      EQVLO2 = O2ML*P/PATM
      OSTWLD = A*P/PATM
*
* CALCULATE THE BUNSEN COEFFICIENT
*
      ALPHA = (EQVLO2*273.15)/(SOLML*(TAVE + 273.15))
      RETURN
      END
*
*
*
* FUNCTION CALCULATES THE VOLUME OF GAS, USING IDEAL GAS LAW
*
*
      FUNCTION VOLUME (TAVE, O2PP)
*
      IMPLICIT DOUBLE PRECISION (A-H, O-Z)
*
*
      R = 82.06
      T = TAVE + 273.15
      P = O2PP/760.0
      VOLUME = R*T/P
      RETURN
      END
```

```
*
*
* SUBROUTINE CALCULATES REGRESSION VALUES FOR THE EXPERIMENTAL DATA
*
*
      SUBROUTINE SLOPE (A, TERCPT, X, Y, R, SSR, RESDUL, N)
*
      IMPLICIT DOUBLE PRECISION (A-H, O-Z)
      DIMENSION X(50), Y(50), RESDUL(50)
*
      SUMX = 0.0
      SUMY = 0.0
      SUMXY = 0.0
      SUMX2 = 0.0
      DO 10 I = 1, N
         SUMX = SUMX + X(I)
         SUMY = SUMY + Y(I)
         SUMXY = SUMXY + X(I)*Y(I)
         SUMX2 = SUMX2 + X(I)**2
   10 CONTINUE
*
      YBAR = SUMY/N
      XBAR = SUMX/N
      BETA1 = (SUMXY - N*XBAR*YBAR)/(SUMX2 - N*XBAR**2)
      BETA0 = YBAR - BETA1*XBAR
      A = BETA1
      TERCPT = BETA0
*
      SSR = 0.0
      XDIFF2 = 0.0
      YDIFF2 = 0.0
      XYDIFF = 0.0
      DO 20 J = 1, N
         RESDUL(J) = Y(J) - (BETA0 + BETA1*X(J))
         SSR = RESDUL(J)**2 + SSR
         YDIFF2 = YDIFF2 + (Y(J) - YBAR)**2
         XDIFF2 = XDIFF2 + (X(J) - XBAR)**2
         XYDIFF = XYDIFF + (X(J) - XBAR)*(Y(J) - YBAR)
   20 CONTINUE
*
      R = XYDIFF/(XDIFF2*YDIFF2)**0.5
      RETURN
      END
*
*
*
* SUBROUTINE PRINTS ALL DATA TO AN OUTPUT FILE.
*
*
      SUBROUTINE DAT (O2ML, SOLML, O2PP, XATM, HPP, HATM, P,
    C   EQVLO2, A, TERCPT, R, SSR, X, Y, RESDUL, N,
    C   O2MOL, SOLMOL, XPP, ALPHA, OSTWLD, PATM)
*
*
      IMPLICIT DOUBLE PRECISION (A-H, O-Z)
      DIMENSION X(50), Y(50), RESDUL(50)
```

```
*
*
      WRITE (9,90) PATM
      WRITE (9,100) O2ML, O2MOL
      WRITE (9,110) SOLML, SOLMOL
      WRITE (9,120) O2PP, XPP, HPP, XATM, HATM
      WRITE (9,130) P, EQVLO2, OSTWLD
      WRITE (9,135) ALPHA
      WRITE (9,140) N, A, TERCPT, SSR, R
      WRITE (9,150)
      DO 10 I = 1, N
         WRITE (9,160) X(I), Y(I), RESDUL(I)
 10   CONTINUE
 90   FORMAT (//'ATMOSPHERIC PRESSURE (MMHG) = ', F9.3)
100   FORMAT (//, 'MOLES OF OXYGEN IN ', F5.2, ' ML OF GAS = ',
    C        D12.7,/)
110   FORMAT ('MOLES OF SOLVENT IN ', F9.2, ' ML OF SOLVENT = ',
    C        D12.7,/)
120   FORMAT ('AT OXYGEN PARTIAL PRESSURE OF ', F9.3,/'THE MOLE',
    C        ' FRACTION OF OXYGEN IS = ',D12.7,/, 'HENRYS CONSTANT',
    C        ' AT THIS PARTIAL PRESSURE IS = ', D12.7,//'AT 760 MMHG',
    C        ' MOLE FRACTION OXYGEN = ', D12.7,/, 'AND HENRYS',
    C        ' CONSTANT = ', D12.7/)
130   FORMAT ('TOTAL SATURATED OXYGEN PRESSURE = ', F9.3,/,
    C        'CORRESPONDING TO AN EQUIVALENT VOLUME = ', F9.2,/,
    C        'OSTWALD COEFFICIENT = ', D12.7,/)
135   FORMAT ('BUNSEN COEFFICIENT = ', D12.7, ///)
140   FORMAT ('REGRESSION ANALYSIS YIELDS: ', ///, 'NUMBER OF ',
    C        'OBSERVATIONS = ', I2,/, 'SLOPE = ', D15.7,/,
    C        'INTERCEPT = ',D15.7,/, 'SUM OF THE SQUARE RESIDUALS = ',
    C        D15.7,/, 'CORRELATION = ',D15.7)
150   FORMAT ('VOLUME OF SOLVENT (ML)', 5X, 'VOLUME OF OXYGEN (ML)',
    C       10X, 'RESIDUAL', //)
160   FORMAT (D12.7,20X, D12.7, 12X, D14.7)
      RETURN
      END
```