University of Alberta

Solubility of Sulphur Dioxide in Mixed Polyethylene Glycol Dimethyl Ethers

by

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To Andy, Carol and Holly

Abstract

Selexol, a mixture of polyethylene glycol dimethyl ethers, was found to be an excellent solvent for removing sulphur dioxide emissions. The solubility measurements of sulphur dioxide in tetraethylene glycol dimethyl ether at 40°C were shown to be consistent with the results from previous literature investigations. The solubility of sulphur dioxide was experimentally determined in Selexol at 25, 40, 70 and 100°C.

Activity coefficients of sulphur dioxide were determined from the solubility data. The NRTL equation correlated the data well with an average error of approximately 10% and was used to calculate the excess Gibbs energy, entropy and enthalpy of the liquid mixture over the full range of composition. Heats of mixing and solution at infinite dilution were also determined for the (sulphur dioxide-Selexol) system. The effect of water on the solubility of sulphur dioxide was investigated with a 6.04 wt% water solution. As expected the solubility decreased with an increased presence of water.

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Nomenclature

A_{ij}	Margules and van Laar parameters
f_i	fugacity of component i
f_i°	reference fugacity of component i
G	Gibbs energy
G^E	excess molar Gibbs energy
G_{ij}	NRTL equation parameter
g_{ij}	intermolecular interaction parameter
H^E	excess molar enthalpy
H^{MX}	enthalpy of mixing
H^{SOLN}	enthalpy of solution
$H_{1,2}$	Henry's constant of solute in solvent
k_{12}	binary interaction parameter
L	liquid phase
n_i	mole number of component i
P	total pressure
P_c	critical pressure
P_i^{SAT}	saturation pressure of i
P_i	fitted parameter of vapour-liquid equilibrium equations
p_i	partial pressure of i
q_i	molecular geometric area parameter of pure component i
q_i'	modified molecular geometric area parameter of pure component i
R	gas constant (8.314 J/mol K)
r_i	molecular volume parameter of pure component i
S^E	excess molar entropy
T	temperature
T_c	critical temperature
T_r	reduced temperature
u_{ij}	UNIQUAC energy parameter

V	vapour phase
V	total volume in Equation (12.11)
v_i	molar volume of component i
x_i	mole fraction of component i in liquid
y_i	mole fraction of component i in vapour
w_i	mass fraction of component i in liquid
Z_m	compressibility factor
z	lattice coordinate number; here = 10

Greek Symbols

α	NRTL non-randomness parameter
α	vapour or liquid phase in Equation (12.2)
γ_i	activity coefficient of component i
θ_i	average segment fraction of component i (UNIQUAC)
Λ_{ij}	Wilson and T-K Wilson parameter
λ_{ij}	Wilson and T-K Wilson energy parameter
τ_{ij}	NRTL and UNIQUAC parameter
ϕ_i	fugacity coefficient of component i
ϕ_i^{SAT}	saturation fugacity coefficient of component i
ω	acentric factor

1. Introduction

SO₂ emissions have long been a source of concern since the burning of coal became a prominent energy source. According to Wilson (1976), King Edward I of England banned the burning of coal in his kingdom because of the noxious fumes it produced. It was not until the 1920's that sulphur dioxide limits were imposed on SO₂ emitting facilities. In 1920, smelters in the Salt Lake district of Utah were limited to emissions of 1 ppm on an hourly average at vegetation levels during the growing season (Kohl and Riesenfeld, 1985). One of the first legal requirements for controlled sulphur dioxide emissions was at the Battersea station of the London Power Company which was constructed in 1929. The statutory consent granted in 1927 to the erection of the power station was subject to:

“The company shall in the construction and use of the said generating station take the best known precautions for the due consumption of smoke and for the preventing as far as reasonably practicable the evolution of sulphur oxides”
(Hewson et al., 1933).

Over the years, the conditions of operating a facility which emits SO₂ have become increasingly more stringent. For example, the province of Alberta has adopted the most stringent of Environment Canada's objectives for SO₂ (MacDonald and Bietz, 1996). Presented in Table 1.1 are Alberta's ambient guidelines for sulphur dioxide which, as can be seen, are much lower than those originally set forward in the 1920s.

Table 1.1 Alberta's 1996 Ambient Air Quality Guidelines for SO₂
(MacDonald and Bietz, 1996)

Averaging Time	Guideline Level
Annual	0.01 ppm (30µg/m ³)
24 hour	0.06 ppm (150µg/m ³)
1 hour	0.17 ppm (450µg/m ³)

Alberta also has very stringent sulphur dioxide source emission standards which affect sour gas plants, petroleum refineries, and the oil sands industry. For new plants, which have 2,000 tonnes per day of sulphur (inlet) or larger, the requirement is that 99.8% of the sulphur is to be recovered. Smaller plants (between 1 and 10 tonnes per day) are required to remove 70% to 90% of the sulphur. These regulations have been set up to protect the health of humans and the environment from deterioration due to increasing energy and chemical processing demands.

As regulations are becoming more strict and the penalty for violation increases, new and economical ways of sulphur dioxide removal are becoming increasingly important to everyday operations. Many different techniques have been proposed for scrubbing of sulphur dioxide from tail gas streams. The most common type is the non-regenerable processes. The use of regenerable and recyclable organic solvents has been a popular technique in many other acid gas (H_2S and CO_2) treating facilities. Regenerable solvents can be used to help to reduce the environmental impact of removing SO_2 and achieving the regulations mentioned above. For these processes, knowledge of the solubility of SO_2 in the solvent is of paramount importance for the design of practical gas removal systems.

The purpose of this study is to investigate the harmful effects of increased sulphur dioxide in the atmosphere and to select an appropriate solvent for the regenerable removal of SO_2 from tail gas streams. The solubility of SO_2 will be measured in the selected solvent at a variety of temperatures and pressures. Heats of mixing and absorption will be calculated and discussed in the context of solubility enhancement and solvent-solute interactions.

2. Sulphur Dioxide Emissions into the Atmosphere

Before discussing the effects of SO_2 emissions, it is important to know where these emissions arise from. Sulphur oxides are naturally emitted into the atmosphere by volcanoes and biogenic behaviour. Oxidation of hydrogen and diethyl sulphides from decaying vegetation is considered to be the principal natural sources of sulphur oxides (National Academy of Sciences, 1975). Oceans also contribute significant amounts of sulphates from sea spray which are converted in the atmosphere to form SO_2 (National Academy of Sciences, 1975). On a global scale, the amount of sulphur emitted from natural sources is about equal to that of man made emissions, excluding sea spray (Harter, 1985). Harter (1985) also suggests that natural inland sulphur emissions amount to only $\frac{1}{4}$ of global emissions. Figure 2.1 illustrates the world's sulphur cycle in more detail.

Sulphur emissions from human activities over land are about 4 times as great as natural emissions. The majority, 85%, of these man made emissions are from the combustion of fossil fuels (coal and oil) used for power generation (Harter, 1985). Other emitters of SO_2 include (in order of importance): non ferrous metal ore smelting (such as copper, zinc, and lead), petroleum refining and production, sulphuric acid plants, and pulp and paper mills. Over ninety percent of the man made sulphur emissions is SO_2 with the remainder being neutralized sulphates, SO_3 and sulphates (Harter, 1985). This SO_3 quickly becomes oxidised with water vapour to form H_2SO_4 . Naturally, most of these man made sources of SO_2 are located near large population densities. The increased amount of man made SO_2 in the atmosphere has been shown to have serious detrimental effects to wildlife, humans and to the environment.

Figure 2.1 Sulphur Cycle (Seinfeld, 1975)

3. Health Effects of SO₂ Emissions

Sulphur dioxide is widely known to the public as a harmful substance to both humans and animals. This concern has been reflected in the scientific community by vast amounts of literature on the subject. Many good reviews have been written about the toxicity of sulphur oxides: Greenhill (1978), Moss (1996), Lippman (1979), National Academy of Sciences (1975), and Harter (1985). The results from experimental studies are often confusing and contradictory. This section summarises some of the agreed upon health effects of these compounds.

Sulphur dioxide is a highly soluble gas in aqueous systems and is, therefore, irritating to the eyes, throat, and respiratory tract. The irritant effects of SO₂ are caused by its reaction with water to produce HSO₃⁻ (Greenhill, 1978). It is accepted that the major physiological consequence of SO₂ inhalation is bronchoconstriction. Increased airway resistance occurs at about 1 ppm of SO₂. At higher concentrations, as illustrated in Figure 3.1, irritation of the throat and eyes, and constriction of the chest occur which can lead to death. Because SO₂ constricts the bronchi and increases air flow resistance, asthmatics, the elderly, and people with damaged lungs are particularly at risk. Prolonged exposure to SO₂ has been shown to have permanent detrimental effects on the respiratory tract. Workers exposed daily to SO₂ have had high frequencies of cough, shortness of breath and dryness of the eyes and throat (Greenhill, 1978).

Other serious effects of SO₂ exposure include mutagenicity, carcinogenicity, low birth weight and a higher risk of infection. Tests by Schneider (1970) show that when SO₂ (5.7 ppm in air) is bubbled through cultures of lymphocytes (cells which play a

Figure 3.1 Health Effects Due to Various Exposures to SO_2 (Seinfeld, 1975)

role in disease resistance) fewer of the cells synthesized DNA, divided or grew. The cells grown in pure air were larger than those in a SO₂ environment. Further, 20% of these cells have altered chromosome structures. Ukai (1977) has shown that mice have increased viral infections when exposed to SO₂ at low concentrations (0.03-0.1 ppm) over several days.

Gaseous SO₂ produces lung tumours in mice exposed to massive doses, usually much higher concentrations than are generally found in the atmosphere (Harter, 1985). Sulphur dioxide acts as a co-factor in benzo(a)pyrene (BaP) and cigarette smoke carcinogenicity (Harter, 1985). This is suggested to occur because SO₂ is a bronchoconstrictor which would reduce the cross section for air flow within the larger bronchial airways, greatly increasing the surface density of the carcinogenic aerosol deposition on the bronchial bifurcations (Lippmann, 1979). This interference by SO₂ (of insoluble particles removal from the bronchial bifurcations), along with the decreased clearance from the lung, has implications to the pathogenesis of emphysema (Lippmann, 1979).

Sulphur dioxide and suspended sulphates in the atmosphere block out UV sunlight which is used in formation of Vitamin D in the skin. SO₂ absorbs and sulphates reflect UV rays in the range of (290-310 nm) which is the most active ingredient in Vitamin D production in the skin (Moss, 1996). This is suggested to lead to Vitamin D deficiencies when high sulphur oxide concentrations are found in the acid haze associated with air pollution. Vitamin D, based on laboratory evidence, plays an important role in reducing the risk of colon and breast cancer (Moss, 1996). These two forms are the second and third leading causes of cancer death in North

America (Moss, 1996). This has been shown in independent studies (Gorham et al., 1989), where significant positive associations were found for colon cancer in women and men, and also breast cancer in women. This association may explain the differences between urban and rural risk of colon and breast cancer, although an indirect association with industrialised urban lifestyle may also explain these findings (Gorham et al., 1989).

High SO_2 levels are often associated with high particulate concentrations (Seinfeld, 1975). Submicron particles in the atmosphere have been shown to potentiate the irritant effects of SO_2 . The fact that a three to four fold increase in the irritant response to SO_2 is observed in the presence of particulate matter is attributed to the ability of aerosol particles to transport SO_2 deep into the lung (Seinfeld, 1975). Experimental data also indicate that atmospheric oxidation of small amounts of SO_2 will result in particulate aerosols more toxic than the pure SO_2 acting alone. Aerosols of H_2SO_4 have been shown to be ten times more potent than SO_2 alone in constricting bronchial tubes, this response is also more rapid and prolonged (National Academy of Sciences, 1975). Table 3.1 illustrates the relative potency of sulphates to cause irritant effects on guinea pigs.

Japanese studies have found a significant direct dependence of chronic bronchitis with SO_2 pollution. Results were more significant for smokers (Wilson, 1976). Increased deaths and respiratory injuries have been strongly linked to periods of high sulphur dioxide pollution. Increased deaths in London are commonly associated with periods of high pollution lasting only one or two days (Harter, 1985). Respiratory diseases in Yokkaichi, Japan have been associated with emissions of large

Table 3.1 Ranking of Sulphates for Irritant Potency for a Constant Size Particle of $0.3\mu\text{m}$ (Wilson, 1976)

Compound	% Increase Resistance $/(\mu\text{g SO}_4\cdot\text{m}^{-3})$
H_2SO_4	0.410
$\text{Zn}(\text{NH}_4)_2(\text{SO}_4)_2$	0.135
$\text{Fe}_2(\text{SO}_4)_3$	0.106
ZnSO_4	0.079
$(\text{NH}_4)_2\text{SO}_4$	0.038
NH_4HSO_4	0.013
CuSO_4	0.009
FeSO_4	0.003
MnSO_4	-0.004

quantities of highly concentrated sulphuric acid in residential areas (Harter, 1985). Similar studies in the United States during the 1960's have linked air pollution with increased morbidity and mortality. It was estimated that a reduction in SO_x and particulate matter by 88% and 58%, respectively, would result in a 7% decrease in mortality (Harter, 1985).

4. Acid Precipitation

Another consequence of man made sulphur dioxide emissions is acid precipitation and deposition. The widespread occurrence of acid precipitation and dry deposition results, in large part, from man made emissions of sulphur and nitrogen oxides (Cowling, 1982). The detrimental effects associated with "acid rain" were not fully realised until the 1970's. Since the 1980's acid rain has become a major environmental concern among private businesses, scientists, engineers and the general public.

The term "acid rain" generally classifies precipitation which has a pH less than the normal pH of precipitation ($\text{pH} \approx 5.6$). Pure rain is slightly acidic due to atmospheric carbon dioxide. "Acid rain" is caused by atmospheric conversion, in the presence of water, of emitted sulphur oxides and nitrogen oxides to sulphuric and nitric acid. The chemistry of these transformations is complex and is reviewed elsewhere (Harter, 1985). Dry deposition of sulphates occurs when no moisture in the air is available for the sulphur oxides to react with. Approximately 65-70% of the acidity of acid rain in the eastern United States is from sulphuric acid (EPA, 1980).

Aquatic ecosystems have shown the most susceptibility to acid precipitation. Many lakes in eastern Canada and the United States are now fishless because of acid precipitation. These effects were first noticed in the vicinity of Sudbury's (Ontario, Canada) notorious metal smelters where it is estimated that 200-400 lakes within a 50 mile radius are without fish (EPA, 1980). Some reasons for the declining or elimination of fish populations due to acidification of lakes and streams are: failure of the reproductive cycle (EPA, 1980), abnormal rates of growth (Harvey, 1996), high mortality in adult fish (Harvey, 1996), impairment of body organs (Mayer and Schreiber, 1984), and death from accumulations of heavy metals such as mercury and aluminium (Ibid., and EPA, 1980). Reproduction of salamanders and frogs has also been affected by atmosphere acidification of surface waters (Cowling, 1982).

Harmful effects to other forms of wildlife have been indirectly linked to acid rain. Soil acidification breaks the bonds of metals (aluminium, magnesium, lead and zinc) to soils, allowing these metals to be rapidly leached into ground water and aquatic ecosystems where they are ingested by animals, especially birds (St. Louis and Barlow, 1996), which feed in that environment.

Vegetation is harmed, both directly and indirectly by acid precipitation. Acidification of the soil leaches important nutrients such as calcium and magnesium. Phosphorous availability is also reduced (Cowling, 1982) while toxic metal (aluminium and cadmium) solubility is increased, leading to increased up take by plants. Nitrogen fixation and breakdown of organic matter is also decreased in soils which have been acidified (Cowling, 1982).

Direct acidification to plants has reduced yields and caused deformations in the plant structure. Some plants exposed to acid have exhibited a reduction in carbohydrate production which is used by plants for food (EPA, 1980). Decrease in the yield of root crops (such as radish, carrot, beet), the marketability of leaf crops (such as spinach and lettuce) by severe foliar injury, and visible injury to tomatoes are all detrimental results of simulated acid rain within ambient concentrations (Lee, 1982). Similarly, western pine and yellow birch trees have shown damaging effects from simulated acid rain (EPA, 1980). Forest dieback is also a concern from acid rain where oak, beech, and maple have also been affected (Mayer and Schreiber, 1984). These trees are important habitat for nesting, cover and food for wildlife. Because aluminium becomes more soluble in soils due to acidic deposition, widespread decline in spruce, fir and beech forests have been noticed in Germany due to build up of aluminium in the roots (Cowling, 1982). Similarly, lichen, mosses, and mushrooms have accumulated toxic, heavy metals from acid deposition which may be transferred to creatures eating them (Cowling, 1982).

Experiments with synthetic rain (similar in chemical composition and rate of deposition to normal rain) have been performed. The biological effects on crops were: morphological changes in foliage, loss of nutrients in foliar organs due to leaching, accelerated erosion of wax on leaf surfaces, decreased nitrogen fixation by symbiotic bacteria, reduced rates of decomposition of leaf litter leading to decreased mineralisation of chemically bound nutrients, increased mortality of pine seedlings (inhibited formation of terminal buds) and interference with normal reproductive processes.

The terrestrial and aquatic ecosystems are together ultimately bound. Since the effects of acidic precipitation in aquatic ecosystems affect the terrestrial ecosystem and vice versa, it is difficult to consider the effects independently. Examples are vegetation loss, soil leaching and animal feeding. Acid rain and deposition is not a local issue alone, the creation of tall stacks has alleviated some of the problems near industrial plants, but the sulphates travel for miles staying aloft from the stack before they are deposited to the earth. Tall stacks generally indirectly oxidise most of the SO_2 to SO_3 , which is converted to sulphates. Figure 4.1 indicates that acid rain is predominantly found in more industrialised areas. In 1980, the most rapid increases of acid precipitation were found in the southeast U.S.A., paralleling the expansion of south-eastern urban and industrial activities (EPA, 1980).

It can be shown that there is a real need for sulphur dioxide removal. Detrimental effects to the environment and the health of humans and wildlife can be reduced if man made emissions of SO_2 are reduced.

5. Sulphur Dioxide Removal

As described earlier, SO_2 is detrimental to the health and well being of humans, wildlife and the environments they live in. This threat to the environment has been realised by legislators, politicians, scientists, and engineers. Legislators have responded by imposing and enforcing laws on sulphur dioxide emissions. These laws have limited the amount of SO_2 released into the environment. Nations have come together to limit world wide emissions, noticing that it is not merely a local problem. For example, about thirty nations signed an agreement under the United Nations

Figure 4.1 Acidic Precipitation and Geographical Association in the United States (EPA, 1980)

Economic Commission for Europe. The terms require these nations to reduce their 1980 levels of SO_2 emissions by 60-80% by 2010 (Kwong and Meissner, 1995).

Scientists and engineers are studying sulphur dioxide absorbents and designing new and economical facilities.

Sulphur dioxide is typically released in tail gas streams from power plants (flue gases) and smelters. Other emitters are catalytic cracking regenerators, sulphuric acid plants, and Claus recovery plants (Astarita et al., 1983). Flue gases usually have low amounts of SO_2 associated with high volumetric flow rates. Smelters, on the other hand, have high relative concentrations of SO_2 at low flow rates. Typical concentrations are shown in Table 5.1. The most popular form of flue gas de-sulphurisation is non regenerable (throwaway) scrubbing using a calcium-based alkali salt as a sorbent (Soud, 1994). Kohl and Riesenfeld (1985) discuss the different removal processes in detail and is recommended to the reader. Presented in Figure 5.1 is a general chart on the different processes available. The economically feasible choices for SO_2 removal by scrubbing have usually been between lime/limestone slurries or regenerable processes.

In the lime/limestone processes and other non-regenerable processes, SO_2 is permanently bound to the sorbent and must be disposed of. This waste from the older lime processes consisted of calcium sulphate/sulphite and fly ash had to be entirely disposed of in a land fill. New modifications in the 1970's have resulted in a low value saleable by-product, gypsum. These permanent processes are becoming less feasible because of low value byproducts and shrinking landfills and increased environmental regulations regarding them. Therefore, regenerable processes which

Table 5.1 Representative Influent Flue Gas for Desulphurisation
(Astarita et al., 1983)

Fuel	SO ₂ in flue gas (%)
Coal 4% sulphur	0.35
Fuel oil 2% sulphur	0.12
Fuel oil 5% sulphur	0.31
Refinery acid sludge 40% sulphur	2.0
Smelters handling sulphide ores	8.0
<i>Representative flue gas composition</i>	
Component	Mole %
CO ₂	12.60
SO ₂	0.22
SO ₃	0.001
NO	0.045
NO ₂	0.005
O ₂	1.78
N ₂	73.44
H ₂ O	11.90

Figure 5.1 Categorization of Sulphur Dioxide Removal Processes
(Kohl and Riesenfeld, 1985)

lessen the environmental impact of conventional throw away processes are of interest.

Regenerable processes are characterised by chemically or physically bonding the solute to the solvent which is regenerated by either chemical or thermal means. The SO_2 is removed from the sorbent and the regenerated sorbent is used again to absorb more SO_2 . The recovered SO_2 is then processed and sold or reused to recover some of the operation costs. These higher value by-products are elemental sulphur, liquid SO_2 , or sulphuric acid. The Wellman-Lord process is the most widely used regenerable process for gas desulphurisation. It is based on absorption of the SO_2 in a sodium sulphite solution. Other recyclable processes based on aqueous electrolyte systems are also available (Kwong and Meissner, 1995). Regenerable processes such as the sodium sulphite and MgO processes have found limited success because of high associated costs (Barnett and Sarlis, 1992).

Other acid gases (H_2S and CO_2) have been successfully removed from gas streams with a regenerable organic solvent. Operation of these plants has been done with relative ease and have become the most widely used form of acid gas removal. Many reviews and texts have been written on this subject. Kohl and Riesenfeld (1985), and Astarita et al. (1983) are very complete and suggested to the reader. These reviews recommend regenerable organic solvents for bulk and selective removal of the acid gases mentioned before. Sulphur dioxide, a Lewis acid, is expected to behave in a similar manner with organic solvents.

Organic solvents have found limited success in the removal of SO_2 from smelter gas streams. Aromatic amines (xylidine and dimethylaniline) have been commercially used for many years now. The American Smelting and Refining

Company (ASARCO) has been using dimethylaniline-water mixtures since 1947 (Kohl and Riesenfeld, 1985). Three units were running in the United States and Norway. Recently, Union Carbide developed an aqueous amine based regenerative gas desulphurisation process called CANSOLV. This system was tested at the Suncor facility in Fort McMurray (Alberta, Canada) and proved to be very successful at removing low ppm SO_2 from high flue gas velocities (removal efficiency of 99%) (Barnett and Sarlis, 1992). As of 1994, there were no planned or operating commercial applications on coal fired plants (Soud and Takeshita, 1994). These aromatic amines (chemical absorbents) are good for sulphur dioxide removal but regeneration costs are high. Therefore a physical solvent for SO_2 is of interest for lower operational costs.

6. Sulphur Dioxide Solubility Literature Survey

The solubility of SO_2 in organic solvents has been extensively studied by numerous investigators with good reviews and data evaluations available: (Young, 1984), (Gerrard, 1972), (Gerrard, 1976), Gerrard (1980), and (Fogg and Gerrard, 1991). Amines and sulphur dioxide have been studied since the late 19th century (Schiff, 1866) with the early interest being solid (adduct) formation. Foote and Fleisher (1934) found that solids were formed with SO_2 and amines. Solids were found with methyl, ethyl and dimethyl aniline, but not with diethylaniline. Hill and Fitzgerald (1935) measured the vapour pressures over 15 amines and found solids formed in most of them at room temperature. Amines are, however, excellent sulphur dioxide absorbers because of their Lewis base properties.

One of the largest studies of SO_2 was performed by Sano (1968) and Sano and Nakamoto (1968). Bunsen absorption coefficients were determined for over 100 solvents through static and dynamic absorption techniques. The results for the top ten compounds are presented in Table 6.1. The absorption capacity of these solvents was determined at 30°C . Lenoir et al. (1971) determined the Henry's constants of 12 gases in 19 solvents using gas chromatography. Results from this study based on Henry's constants are presented in Table 6.2. Gerrard (1972) measured the solubility of SO_2 in 26 compounds at 1 atm at 0, 10, 20, and 25°C using a bubbler tube described in the original work. Included in his study were five older investigations used for comparison. Table 6.3 lists the ten best solvents for SO_2 absorption based on moles of SO_2 in solution. Bogeatzes and Tassios (1973) measured the infinite dilution activity coefficients of SO_2 in nine organic solvents at temperatures around 40°C using gas chromatography. The results from this study are presented in Table 6.4. Henry's constant was also determined for 17 aprotic solvents at 25°C by Benoit and Milanova (1978). The ten best solvents are listed for comparison in Table 6.5. The solubility of 15 gases including SO_2 was determined in normal alkanes from n-pentane to n-hexadecane by Makranczy et al. (1976). They determined that there is an inverse relationship between the solubility of a gas (expressed either as an Ostwald or a Bunsen coefficient) and increasing carbon number.

An interesting study of SO_2 solubility was performed by Gel'perin et al. (1958). This study was concerned with the absorption of SO_2 in ditolylmethane, dicumylmethane, and diisopropylbenzene. Experimental solubility, densities and heat capacities, amongst others were determined. Included in this study was a detailed

Table 6.1 **SO₂ Absorption Capacities of Polar Organic Solvents at 30°C**
(Sano and Nakamoto, 1968)

Rank	Solvent	Absorption Coefficient (mL SO₂/mL solvent)
1	Dimethylsulphoxide	447.0 b
2	Pyridine	424.0 b
3	Monoethanolamine	380.0 c
4	n-Butylamine	350.0 c
5	d-Picoline	335.5 b
6	Methyl formate	331.0 a
7	N-methylpyrrolidone	309.6
8	Methylal	304.0 a
9	N, N-Dimethylformamide	303.0 b
10	Benzylamine	288.0 d

a) extrapolated from low temperature

b) extrapolated from high temperature

c) resinous precipitate

d) extrapolated from high temperature, solidified at 30°C

Table 6.2 Henry's Constants in atm (Lenoir et al., 1971)

Solvents	T(°C)	Henry's Constant (atm)
Dimethylsulphoxide	25	0.117
Tripropyl phosphate	50	0.621
Tripropyl phosphate	70	1.45
Trisobutyl phosphate	52	0.695
Propylene carbonate	25	1.20
Triethyl phosphate	52	1.41
Nitrobenzene	25	1.64
Benzyl alcohol	25	2.08
Propylene carbonate	25	3.17
Ethylene glycol	25	3.41
Phenol	50	7.07
Hexadecane	25	12.9
Heptadecane	50	16.4
Decahydronaphthalene	25	18.8
Decahydronaphthalene	50	25.6

Table 6.3 Mole Ratio (Moles SO₂ /Mole Solvent) at 25°C (Gerrard, 1972)

Solvent	Pressure (mmHg)	Mole Ratio
C ₅ H ₅ N Pyridine	757	1.56
HCON(CH ₃) ₂ N,N dimethyl formamide	767	1.50
(CH ₃ CO) ₂ O Ethylene glycol	747	0.76
C ₆ H ₅ CN Benzonitrile	754	0.50
C ₁₅ H ₁₆ Ditolylmethane (4°C)	760	0.46
C ₆ H ₅ NO ₂ Nitrobenzene	772	0.45
C ₁₉ H ₂₄ Dicumylmethane	760	0.43
<i>m</i> -C ₆ H ₄ (CH ₃) ₂ <i>m</i> -xylene	765	0.40
Raoult's law (ideal)	760	0.34
C ₆ H ₆ Benzene	760	0.278

Table 6.4. Infinite Dilution Activity Coefficients, γ^∞ , for SO₂
(Bogatzes and Tassios, 1973)

Solvent	T (°C)	(γ^∞)
Xylidine-Dimethyl-aniline (1:1)	40	0.040
Dimethylformamide	40	0.081
N,N-Dimethylacetamide	41.5	0.036
" "	66	0.070
" "	93	0.077
N,N-Dimethylaniline	41	0.027
Trimethylpyridine	39	0.123
Xylidine	40	0.140
Benzonitrile	39	0.532
3-Methylsulfolane	40	0.609
3-Methoxysulfolane	39	1.090
Triethylenetetramine	41	1.580
N, N-Bismethylamine	42	1.590
Nitrobenzene	25.5	0.910

Table 6.5 Henry's Law Constants for SO₂ in Polar and Non-Polar Aprotic Solvents at 25°C (Benoit and Milanova, 1979)

Solvent	H (atm)
Pyridine	0.088
Dimethylsulfoxide	0.109
Dimethylformamide	0.172
Tetrahydrofuran	0.392
Sulfolane (30°C)	1.01
Ethyl acetate	1.09
Propylene carbonate	1.51
Acetonitrile	1.91
Nitromethane	2.33
Nitrobenzene	3.18
1,2-Dichloroethane	4.23

corrosion analysis. This paper is very complete and can be used for the complete design of sulphur dioxide removal facilities.

The solubility of seventy mono-functional organic compounds containing oxygen, nitrogen, sulphur, and phosphorous were studied by Kurochkin et al. (1984). The temperatures ranged from -10°C to 120°C at a pressure of 100 kPa. Experimental techniques/apparatus were not discussed. The ten best solvents from this study are listed in Table 6.6. It was shown that the structure of the hydrocarbon skeleton had a negligible effect of the solvent power. Table 6.7 illustrates this for the dimethyl sulphoxide family. However, the presence of a double bond or an aromatic nucleus in the α position with respect to the electron donor group of the solvent molecule is more substantial because of the resulting decrease in basicity. The solvent power of the heteroatomic compounds for absorbing SO_2 increases with the electron-donor properties (Kurochkin et al., 1984).

The Kuenen coefficients and the solubility coefficient of SO_2 in eleven organic solvents were measured in 1983 (Gestrich and Reinke, 1983). The solubility was measured at 20°C , 50°C , and 120°C . The results are shown in Table 6.8. Correlations are also presented in this paper for the solubility of SO_2 in polyethylene glycol. A complete review of sulphur dioxide solubility in organic solvents is given in a PhD thesis produced in 1984 (Demyanovich, 1984) and subsequent papers (Demyanovich and Lynn, 1987 and 1991). These works are also very complete for determining the best solvents for SO_2 absorption. Solubilities were determined and correlated in 1984 and 1991 for eight solvents: dimethylaniline, quinoline, diglyme, triglyme, tetraglyme, tributyl phosphate, sulpholane, and three mixtures. Experiments

Table 6.6 Solubility of Sulphur Dioxide in Mono-functional Heteroatomic Organic Compounds at 50°C. (Kurochkin et al., 1984)

Solvent	S (mole SO ₂ /mole of solvent)
N-Butylpiperidine	1.70
Hexamethylphosphorotriamide	1.29
N,N-Dimethyl-aniline	1.12
4-Benzyl-pyridine	0.98
Dipentyl-sulphoxide	0.93
Tributyl-phosphate	0.85
N,N-Dimethylformamide	0.69
<i>m</i> -Ethylaniline	0.63
Sulpholane	0.387
Dipentyl ketone	0.264

Table 6.7 Solubility of SO₂ in the Sulphoxide Family (Kurochkin et al., 1984)

Skeleton	Mole Fraction
dimethyl-	0.626
diethyl-	0.636
dipropyl-	0.647
dibutyl-	0.640
dipentyl-	0.637
dihexyl-	0.631
dicyclohexyl-	0.634
diisopentyl-	0.637
methylnonyl-	0.637
n-propylheptyl-	0.632
isopropyl heptyl-	0.637

Table 6.8 Solubility of Sulphur Dioxide in Several Low Vapour Pressure Solvents
(Gestrich and Reinke, 1983)

Solvent	Temperature (°C)	Solubility (mg gas/g solvent*bar)
PEG P200	20	510
PEG P200	50	196
Sulfolane	120	23.9
Polyethyleneglycolmonomethylether	120	21.2
Polyethyleneglycol P200	120	21.5
Tetraethyleneglycol	120	20.8
Triethyleneglycol	120	20.0
1,10-Dicyanodecane	120	16.5
Tricresylphosphate	120	11.0
Dibenzylether	120	11.0
1,4-Bishydroxymethylcyclohexane	120	7.8

were performed in a recirculating still with constant SO₂ liquid mole fractions with a temperature range of 30-95°C. The activity coefficients at 50°C are shown in Figure 6.1. The decreasing order of solvent capacity is.

In the 1991 paper and the 1984 thesis, predictions of the infinite dilution activity coefficient were made based on the Gutmann donor number and Arnett heat of hydrogen bonding. Results were obtained for over 80 organic solvents. Table 6.9 shows the twenty two best solvents for sulphur dioxide based on the infinite dilution activity coefficient. The accuracy of these predictions are $\pm 20\text{-}25\%$. The solubility results obtained by Demyanovich in 1984 were later correlated by Sciamanna in 1988 (Sciamanna and Lynn, 1988).

Another recent study of the solubility of sulphur dioxide in multiple organic solvents was performed in 1987 (Hayduk and Pahlevanzadeh, 1987). The solubility was measured in a constant solvent flow apparatus. The results at 298.15 K are presented in Table 6.10. In an older work the solubility of SO₂ was studied in the pure solvents: Tetraethylene glycol dimethyl ether, N,N-dimethylformamide, N,N-dimethyl acetamide, 2-octanone, ethyl laurate, nitrobenzene, and n-heptyl alcohol by Albright et al. (1963). Activity coefficients were calculated from the experimental results and presented in Figure 6.2 for a temperature of 65.6°C.

A critical review of the experimental solubility results for SO₂ in non-aqueous organic solvents was performed by Fogg and Gerrard (1991). The results for non-aromatic hydrocarbons, aromatic hydrocarbons, compounds containing halogens and compounds containing sulphur were compared with the reference line.

Figure 6.1 Experimental Activity Coefficients for SO_2 vs. SO_2 Mole Fraction in Organic Solvents at 50°C (Demyanovich, 1984)

Table 6.9 Predictions of Infinite Dilution Activity Coefficients of Sulphur Dioxide
Using the Gutmann Donor Number at 25°C (Demyanovich, 1984)

Rank	Solvent	Predicted Activity Coefficient
1	Ammonia	3 e-4
2	tert-Butylamine	4 e-4
3	Ethylamine	.001
4	Ethylenediamine	.001
5	Piperidine	.001
6	Hydrazine	.003
7	Hexamethylphosphoric triamide	.007
8	Pyridine	.018
9	N,N-Dimethylacetamide	.021
10	Triethylamine	.022
11	N,N-Diethylformamide	.028
12	Dimethyl sulfoxide	.030
13	1,1,3,3,-Tetramethylurea	.031
14	N,N-Dimethylacetamide	.042
15	Methyl-2-pyrrolidone	.045
16	N,N-Dimethylformamide	.050
17	Pentaethylene glycol dimethyl ether	.070
18	Formamide	.076
19	Tetraethylene glycol dimethyl ether	.080
20	Ethylene glycol dimethyl ether	.080
21	Tributyl phosphate	.080
22	Triethylene glycol dimethyl ether	.084

Table 6.10 Solubilities of SO₂ Expressed as Ostwald Coefficients at a Gas Partial Pressure of 101.35 kPa, 298.15 K (Hayduk and Pahlevanzadeh, 1987)

Solvent	Ostwald Coefficient
N,N-Dimethyl-formamide	452
N,N-Dimethyl-acetamide	384
Acetone	377
Acetonitrile	275.1
Methanol	215.5
Ethyl acetate	202.4
Ethylene glycol	99.1
Chlorobenzene	53.9

Figure 6.2 Activity Coefficients of Sulphur Dioxide in Solution With Various Solvents (Albright et al., 1963)

The reference is defined by Raoult's law and is given by:

$$x_i = \frac{P_i}{P_i^{SAT}} \quad (6.1)$$

It is useful for a base reference line when comparing solubilities. Being below the reference line indicates lower solubility while being above indicates higher solubilities. All the following evaluations were made at 1.013 bar and varying temperature by Fogg and Gerrard (1991).

Hydrocarbons

The solubility of SO₂ in non-aromatic hydrocarbons falls well below the reference line; however, the presence of a double bond increases the solubility. The liquid mole fraction of SO₂ in aromatic hydrocarbons is higher than those in alkanes. As with all groups the behaviour of SO₂ in substituted molecules is similar to the non-substituted molecules.

Compounds Containing Oxygen

The presence of oxygen in a molecule increases the solubility because the dissolution of SO₂ is favoured due to the fact that oxygen atoms tend to be electron donors in organic solvents. However, if the oxygen atom takes part in hydrogen bonding between the solvent molecules, the solubility will be reduced. The alkanols have a higher capacity for SO₂ compared to the alkanes which they are derived from, but, again the solubility is lower than the reference line. The straight chained alkanols

capacity (on a mole fraction basis) decreases with increasing chain length. Secondary alkanols show similar trends as the straight chained alkanols. The mole fraction of sulphur dioxide in aromatic alcohols is greater than in aliphatic alcohols.

The presence of an ether linkage significantly increases the solubility. The presence of a second ether linkage (1,4 dioxane) significantly increases the solubility again. This trend is also noticed in aromatic ethers. Monoethers typically lie above or close to the reference line. Ketones have been shown to be good solvents for SO_2 with the solubility lying above the reference line. Monocarboxylic acids lie below the reference line indicating lower solubility. The mole fraction of SO_2 in these compounds decreases with increasing chain length. Hydrogen bonding between the solvent inhibits SO_2 from entering between the solvents thus lowering the solubility. The esters of monocarboxylic acids are higher (the solubility of tributyl phosphate is very high, $x = 0.567$) than the reference line and have a wide range of solubility above this line.

Compounds Containing Nitrogen

Mole fractions at a partial pressure of 101.3 kPa lie above the reference line for compounds containing nitrogen as presented in Figure 6.3. and in some cases very high as these compounds act as electron donor solvents. Pyridine exhibits solid structure formation with SO_2 . As expected, substituted compounds are similar to non-substituted compounds at the same temperature. Aromatic amines have an excellent ability to absorb SO_2 as illustrated in Figure 6.3.

Figure 6.3 General Pattern of Solubilities of SO_2 in Aromatic Amines
(Fogg and Gerrard, 1991)

Compounds Containing Halogens

The solubility of SO_2 in alkanes which contain halogens is higher than those alkanes which contain no halogens. In general, a higher dipole moment in aliphatic chlorocompounds increases the mole fraction of sulphur dioxide in the solvent at 1.013 bar. In benzene, the substitution of chlorine lowers the solubility. The mole fraction is higher, however, than benzene substituted with iodine. A second substituted halogen group lowers the solubility further.

Tables which summarise the literature solubility data have been prepared by Fogg and Gerrard (1991). The top ten solvents based on mole fraction and weight fraction at 1.013 bar and 298 K obtained from this summary are presented in Tables 6.11 and 6.12. As shown from these tables, the best compounds for SO_2 absorption are nitrogen, oxygen, phosphorous, and sulphur-based compounds. The absorption capacity ranking made by Demyanovich is reasonable. Based on Fogg and Gerrard (1991) at 101.3 kPa and 298 K, the solubility fractions decrease, with respect to groups, in the following order:

mole fractions	glycol ether > amine > sulphoxide > phosphate
weight of SO_2	amine > sulphoxide > carbonyl > dioxane > glycol ether

Table 6.11 Mole Fraction Solubilities of SO₂ in Various Solvents for a Partial Pressure of Sulphur Dioxide at 1.013 bar and 298.15 K
(Fogg and Gerrard, 1991)

Rank	Solvent	Mole Fraction
1	Tetraethylene glycol dimethyl ether	0.700
2	N,N-Dibutylbutanamine	0.669
3	Pyridine	0.621
4	N,N-Dimethylacetamide	0.616
5	1-Butanamine	0.615
6	N,N-Dimethylaniline	0.610
7	Dimethylsulfoxide	0.607
8	N,N-Dimethylformamide	0.568
9	Tributyl phosphate	0.567
10	Methylaniline	0.561
11	Ethylaniline	0.560
12	Aniline	0.534
13	1,4-Dioxane	0.532
14	Diethylaniline	0.531
15	2-Aminoethanol	0.520

Table 6.12 Weight Ratio Solubilities of SO₂ in Various Solvents for a Partial Pressure of Sulfur Dioxide at 1.013 bar and 298.15 K
(Fogg and Gerrard, 1991)

Rank	Solvent	Weight of SO ₂ in 100g solvent
1	1-Butanamine	139.91
2	Pyridine	132.96
3	Dimethylsulfoxide	126.58
4	N,N-Dimethylacetamide	118.16
5	N,N-Dimethylformamide	115.03
6	2-Aminoethanol	113.62
7	Acetone	100.70
8	1,4-Dioxane	82.58
9	N,N-Dimethylaniline	82.14
10	Aniline	78.82
11	Methylaniline	76.40
12	N,N-Dibutylbutanamine	69.85
13	Ethylaniline	67.28
14	Tetraethylene glycol dimethyl ether	67.15
15	Methyl acetate	66.80

7. Organic Solvent Selected for this Study

For practical industrial recyclable removal of SO₂ from tail gas streams, the solvent should have the following characteristics:

- chemically and thermally stable
- low vapour pressure
- high absorptive capacity for SO₂
- non-toxic and non-carcinogenic
- widely available at a reasonable cost
- no solid adducts
- easily regenerable

The solvent which meets all the above requirements is tetraethylene glycol dimethyl ether (tetraglyme). As shown in the previous section, tetraglyme has a high absorption capacity for SO₂. Tetraglyme is also non-toxic (Becker and Linde, 1985) and has a low vapour pressure. The other top solvents listed in Tables 6.11 and 6.12 have characteristics which make them undesirable for selection.

In the study by Sano and Nakamoto (1968), most of the top ten solvents have a vapour pressure too low for practical uses as an absorbing solvent (2, 4, 5, 6, 7, 8) (Demyanovich, 1984). Solvents ranked (3, 4, 10) form solid adducts with SO₂ which is undesirable for a plant operation. The best solvent in Table 6.1 is dimethyl sulphoxide but according to Smedslund (1950) this compound is a poor choice for industrial applications because it dissociates in the presence of acids. Similarly, most of the compounds listed in Table 6.11 are either toxic (2, 3, 4, 6, 10, 11), carcinogenic (5, 7, 8, 12), have too high a vapour pressure (2, 3, 5, 6, 8, 13), have a high melting point (7, 13), or form solids with SO₂ (6, 10, 11, 12).

By using similar criteria as those above, Linde in 1985 (Becker and Linde, 1985) used tetraethylene glycol dimethyl ether in a pilot plant for SO₂ removal from flue gases. The reason for the selection of tetraglyme was because the solvent met the following requirements:

- solubility must be highly temperature dependent
- scrubbing agent must be highly selective
- thermally and chemically stable
- unaffected by trace impurities in flue gases
- low vapour pressure
- non-polluting and non-toxic for flora and fauna
- available in sufficient quantities at an acceptable price

The pilot plant was run with low concentrations of SO₂ (up to 2 mole %) in the flue gas stream and proved to be very successful. The valuable by-products from this type of absorption are elemental sulphur, sulphuric acid, or concentrated sulphur dioxide. The pilot plant tests must have been very successful because in Legnica, Poland, a Solinox plant is being used in two locations.

In 1993, a 36 MWe coal fired plant was fitted with a Linde Solinox unit with tetraglyme as the recycled absorbing agent (Soud and Takeshita, 1994). The state owned copper works Huta Miedzi Legnica has also employed this gas de-sulphurisation unit with Genosorb 1900 (a mixture of glymes) to remove 99% of the SO₂ from 250, 000 cubic metres of flue gas per hour (Vennan, 1995). The attached sulphuric acid plant produces 45 metric tons of sulphuric acid per hour which is then used on the same site for further refining of copper.

The solubility of sulphur dioxide in tetraglyme has been extensively studied: Albright et al. (1963), Härtel (1985) and Demyanovich and Lynn (1987) and, therefore, not of interest to be further studied. Because of the success of tetraglyme and Genosorb 100, a mixture of polyethylene glycol dimethyl ether (Selexol) was selected for this investigation. Selexol was chosen without sacrificing any of the above criteria and, in addition, Selexol has the following advantageous properties:

- non-corrosive and non-fouling
- high selectivity of SO₂ over N₂, O₂ and CO₂
- biodegradable
- some lubricity (Woelfer, 1977)
- is used as received, without any further mixing or addition of any additives
- water miscibility

Selexol also has broad applicability and is a physical solvent with sulphur dioxide and, therefore solvent regeneration is easily done. The solvent is fully regenerable and recirculated in a closed loop therefore, minimising losses to the environment. The operation is solids-free which results in little maintenance because there is no plugging of the lines. Because it is a physical solvent, the operation of the plant is essentially the same with varying SO₂ inlet concentrations which adds to the ease of the operation and lowers the cost. Some other advantages of physical scrubbers can be found in Heisel and Belloni (1991).

As shown in Table 7.1, Selexol is much more selective to sulphur dioxide than nitrogen and carbon dioxide, the major constituents of flue gas streams. Some physical properties of Selexol are given in Table 7.2. Another advantage of Selexol is

Table 7.1 Relative Solubility of Gases in Selexol Solvent (Shah, 1988)

Compound	Solubility Ratio
H ₂ (least soluble)	1.0
N ₂	1.5
CO	2.2
CH ₄	5
CO ₂	76
COS	175
H ₂ S	670
SO ₂	7,000
H ₂ O (most)	55,000

Table 7.2 Physical Properties of Selexol

Structure:	$\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{-CH}_3$ $n=2,3,4,\dots,11$
Molecular Weight:	≈ 280
Density at 25°C	1031 kg/m ³
Specific Heat at 5°C	2.05 kJ/kg°C
Specific Heat at 100°C	2.14 kJ/kg°C
Freezing Point	-22°C to -29°C
Flash Point	151°C
Viscosity at 20°C	8.93 mPa·s
Viscosity at 70°C	1.25 mPa·s
Vapour Pressure at 25°C	1.1×10^{-4} kPa
Vapour Pressure at 100°C	0.13 kPa
Odour	very mild
Toxicity	none

that it is environmentally friendly because little solvent is lost due to vaporisation, foaming or degradation (Clare and Valentine, 1975).

Selexol has been used extensively and reliably for hydrogen sulphide and carbon dioxide removal. Applications have been for either bulk or selective acid gas removal. Good reviews on these techniques are available: Kohl and Riesenfeld (1985), Astarita et al. (1983) and Clare and Valentine (1975). Another benefit of this mixture of glymes is the option for Claus liquid phase reaction. The Claus reaction is:

where SO_2 and H_2S are absorbed in the solvent which benefits H_2S and SO_2 removal simultaneously, producing elemental sulphur. This advantage is further discussed in works on the subject of glymes, SO_2 , and the Claus liquid phase reaction: Hix and Lynn (1990), Neumann and Lynn (1986), and Sciamanna and Lynn (1988). Selexol is also recommended by Demyanovich (1984) and Demyanovich and Lynn (1985) for SO_2 removal by absorption by an organic solvent.

8. Thermodynamics of Phase Equilibrium

The solubility of pure or mixed gases in a liquid mixture is a result of equilibrium of the phases. The conditions for phase equilibrium in a closed system on a macroscopic basis are (Callen, 1985):

The equilibrium value of any unconstrained internal parameter is such as to maximise the entropy for the given value of the total internal energy

or

The equilibrium value of any unconstrained internal parameter is such as to minimise the energy for the given value of the total entropy

When the temperature and pressure are fixed in a closed system the total Gibbs function is minimum.

$$dG_{P,T} = 0 \quad d^2G_{P,T} > 0 \quad (8.1)$$

From this arises thermal, mechanical, and chemical equilibrium of the phases. In case of two phases, the criteria for phase equilibrium is:

$$T^L = T^V \quad (8.2)$$

$$P^L = P^V \quad (8.3)$$

$$\mu_n^L = \mu_n^V \quad n=1,2,\dots,N \quad (8.4)$$

Derivations are found in many standard thermodynamic text books: Callen (1985), Sandler (1989), Dodge (1944), and Prausnitz et al. (1986).

In 1901, Lewis (1901) introduced the fugacity and activity functions. These functions simplified evaluations of equilibrium when non-idealities are present. Using these functions, Equation (8.4) becomes:

$$f_n^L = f_n^V \quad n=1,2,\dots,N \quad (8.5)$$

The link between experimentally determined results (P,V,T) and chemical equilibrium can be expressed in Equation (8.5) by the use of fugacity coefficients and or activity coefficients where the fugacity coefficient is:

$$\phi_i = \frac{f_i}{y_i P} \quad (8.6)$$

for both phases. Alternatively, liquid phase fugacities are transformed to liquid phase activity coefficients where the activity coefficient is:

$$\gamma_i = \frac{f_i}{x_i f_i^L} \quad (8.7)$$

Therefore, the vapour phase fugacity, f_i^V , may be written as:

$$f_i^V = y_i \phi_i^V P \quad (8.8)$$

and the liquid phase fugacity, f_i^L , can be written equivalently as

$$f_i^L = x_i \phi_i^L P \quad (8.9)$$

$$f_i^L = x_i f_i^{\circ} \gamma_i \quad (8.10)$$

These three forms of the liquid and vapour phase fugacities are the underlying equations for vapour-liquid equilibrium (VLE) calculations. Equations (8.8) and (8.9) are the basis for calculations with equations of state, while (8.8) and (8.10) are the basis for calculations using activity coefficient models.

Equation of State Approach

Many equations have been developed since van der Waals proposed an equation of state to describe the volumetric data of vapours and liquids. These new formulations have either been cubic equations of state or modifications of the virial equation of state. Martin (1979), Kumar and Starling (1980), and Chao and Robinson (1979) offer excellent reviews on the subject of equations of state. These equations of state offer simplicity in calculation of VLE because no extra functions or variables are required. These equations of state are used to directly calculate the fugacity coefficients in the relationships below.

$$y_i \phi_i^V P = x_i \phi_i^L P \quad (8.11)$$

Activity Coefficient Model Approach

For systems containing polar components or polymers it is often difficult to find an equation of state that will allow for the correct calculation of the liquid phase fugacities (Rasmussen, 1982). For this situation, Equations (8.8) and (8.10) combine to give

$$y_i \phi_i^V P = x_i f_i^L \gamma_i^L \quad (8.12)$$

where f_i^L , the reference state fugacity is determined by

$$f_i^L = P_i^{SAT} \phi_i^{SAT} \exp \left\{ (1/RT) \int_{P(T)}^P v_i^L dP \right\} \quad (8.13)$$

The Poynting correction term (exponential portion) accounts for the increase in fugacity due to the fact that the system pressure is higher than the vapour pressure of the liquid (Sandler, 1989). The vapour phase mixture and pure component saturation fugacity coefficients are still determined by equations of state. Activity coefficient models have also been extensively used for VLE calculations. These equations are also reviewed by Rasmussen (1982) and Walas (1985).

The difficulty in vapour-liquid equilibrium modelling is which method to use; often the choice of approach is system dependent. A discussion on the applicability of these techniques to the (SO₂-glyme) system will be offered later.

9. Experimental Apparatus

The solubility apparatus is essentially the same as that used in this laboratory for solubility investigations of H_2S and CO_2 in pure and mixed solvents: Roberts and Mather (1988), MacGregor and Mather (1991), Henni and Mather (1995), and Jou et al. (1982). Vapour and liquid phases were brought to equilibrium in a windowed equilibrium cell consisting of a Jerguson liquid level gauge (model 19-T20 with a rating of 1723.7 kPa at 537.8 °C and 6894.8 kPa at 37.78 °C), and a tubular 250 cm³ gas reservoir mounted on top.

Vapour was circulated from the top of the reservoir by a magnetically driven pump similar to that devised by Ruska et al. (1970), to the bottom of the equilibrium cell as shown in Figure 9.1. The free piston within the pump was moved up or down by the coupled movement of the magnetic sleeve. This sleeve was driven by a Reliance 1/3 hp motor. All material in contact with the fluids was type 316 stainless steel. The equilibrium cell, reservoir and pump were housed in a 0.4 m³ air bath maintained at ± 0.1 °C of the set point temperature by a Hallikainen Instruments Thermocontrol. Refrigeration was supplied to the air bath by a Tecumseh Refrigeration Unit. Heat was supplied from electrically heated fins which allowed for a maximum temperature of 130°C. The air within the temperature bath was mixed with a blade fan powered by a Doerr Electrical Corporation 1/3 hp motor.

A type J iron-constantan thermocouple calibrated with a Leeds and Northup platinum resistance thermometer was used to measure the temperature of the phases within the cell. The output signal was displayed with a Hewlett-Packard Model 3468A multimeter.

Figure 9.1 Schematic of Equilibrium Solubility Apparatus Used in this Investigation, Modified from Roberts (1983)

Pressure measurements were made with two Heise Bourdon gauges. The high pressure gauge (400 psi) and the low pressure gauge (1000 kPa) had an accuracy of $\pm 0.1\%$ full span. These were previously calibrated with a Ruska 2400 HL dead weight tester. The pressure gauge lines were wrapped with heating tape to prevent condensation of the vapour phases.

Gas was delivered to the cell from external gas cylinders to the bottom of the equilibrium cell. Undesired gas was removed from the cell to the fume hood by purging the gas through either a sodium hydroxide absorption train or a Fisher Scientific vacuum pump (driven by a Leeson $\frac{1}{2}$ hp motor), depending on the total pressure and sulphur dioxide concentration. The absorption train consisted of a stainless steel absorption vessel with 2 M NaOH solution and an empty 500 mL Erlenmeyer flask.

Liquid was transferred to the bottom of the cell from the liquid inlet line located outside the air bath. All external lines were $\frac{1}{8}$ " stainless steel tubing with needle valves and were connected to the cell as illustrated by Figure 9.1. Liquid and gas phase samples were withdrawn from the cell through $\frac{1}{16}$ " stainless steel tubing and needle valve arrangements. The external section of the vapour sample line was heated to approximately 5°C above cell temperature with heating tape. The gas phase sample was withdrawn from the top of the vapour reservoir to a Hewlett Packard 5710A gas chromatograph. Liquid phase samples were withdrawn from near the bottom of the equilibrium cell.

10. Experimental Procedure

Start up:

Initially, the equilibrium apparatus was cleaned with both water and acetone, and allowed to dry overnight. Approximately 30-40 ml of the solvent was then used to rinse out the equilibrium cell. Nitrogen was used to purge the cell for about $\frac{1}{2}$ hour to remove any traces of oxygen. With the cell at the temperature of interest, vacuum was established. The solvent was then added to the cell through the liquid feed line. The amount of solvent added depended on the desired SO_2 loading. Nitrogen was then bubbled through the system for approximately 15 minutes to remove any traces of air from the solvent.

Sulphur dioxide was then added from the cylinder through the gas inlet valve to the desired partial pressure. When the partial pressure was below approximately 100 kPag, nitrogen gas was added to maintain a total pressure of about 100 kPag. At high partial pressures of SO_2 , (higher than its vapour pressure at room temperature) the refrigeration unit was used to condense the incoming gas. The amount required was estimated by the desired liquid mole fraction. The system temperature was then raised slowly to the temperature of interest.

Equilibrium:

Once the preferred conditions of liquid loading were set up, the pump was turned on and the vapour phase was then allowed to circulate through the liquid phase. During the circulation of the vapour, vapour phase samples were intermittently taken. Equilibrium was reached when the partial pressure of SO_2 remained constant after a few hours. After equilibrium was attained, the pump was turned off and both phases

were then analysed.

Vapour Phase Sampling:

The vapour phase analysis was performed with a Hewlett Packard model 5710A gas chromatograph. Gas chromatography has also been extensively used for many years as a tool for producing precise and accurate information on the qualitative and quantitative composition of a mixture. The operating conditions for the chromatograph used in this study were:

Injector Temp:	150°C
Detector Temp:	150°C
Oven Temp:	120°C
Column Dimensions:	2.13 m (7' 11") x 3.18 mm (1/8")
Column Packing:	Porapak QS mesh 50 - 80
Carrier Gas Flow:	≈ 40 cm ³ /min

Porapak QS column packing was chosen because of its successful experimental separation of nitrogen and sulphur dioxide in the vapour phase. Similarly other investigators have used Porapak porous polymer packings successfully for mixtures containing SO₂: Obermiller and Charlier (1968 and 1969) and Thornsby (1971). According to Waters Associates (1976) the Porapak support also has the advantage of containing no hydroxyl groups on the surface to contribute to excessive tailing of highly polar molecules.

The sample line was initially flushed with a small amount of the equilibrium vapour from the cell as illustrated in Figure 9.1. Samples were then injected into the chromatograph column from the sample line. The related amounts of the separated gases from the column were analysed using a thermal conductivity detector. The

response from the detector was analysed with a model 3380A Hewlett Packard integrator. Results were presented as percentages of the total peak area. These results along with a response factor between nitrogen and SO_2 were used to calculate the molar composition of the vapour phase of equilibrium. The response factor was determined by means of absolute calibration which can be found in many gas chromatograph textbooks: Schomburg (1990) and McNair and Bonelli (1968). Appendix A illustrates the procedure and presents the final results of the calibration. Sample calculations are presented in Appendix B.

Liquid Phase Sampling

After the vapour phase was sampled, a liquid phase sample was taken. Initially, ≈ 1 ml of liquid was withdrawn through the liquid sample line described earlier. Two collection vessels were used depending on the solvent loading. At low loading, below approximately 100 kPa, a 50 ml Erlenmeyer flask fitted with a rubber septum. Above 100 kPa, stainless steel bombs, with 40 ml and 50 ml internal volumes, fitted with a needle valve was used. In both cases the vessels were filled with 20 mL of 1-2 M (depending on loading) NaOH solution. The solution was used to break down the volatile liquid to non-volatile ionic components. The mass of the sample was calculated from the difference of the mass of the collection vessel before and after sampling. The mass was determined by using a Fisher Scientific Company Gramatic analytical balance to the nearest 10^{-4} g. Approximately 1-2 g of the liquid was extracted from the cell into the NaOH of the collection vessel. The amount of NaOH was determined in a similar manner to the amount of the sample.

The SO₂ content of the liquid sample was determined by iodometric titration. The iodometric method for the determination of SO₂ has been used extensively for both gas and liquid phase sample analysis. In this technique, the iodine solution oxidises the sulphur dioxide as follows:

Equal amounts of glacial acetic acid and 0.1 N standardised iodine solution were pipetted to a 250 mL Erlenmeyer flask containing 50 ml of distilled water. A small aliquot of the sample/caustic solution was pipetted into this iodine acid solution. For determination of the sulphur dioxide content of the sample, the amount of iodine was always in excess. The excess amount of iodine was then back-titrated with 0.1 N standardised thiosulphate solution. The thiosulphate solution reduces the iodine by:

Therefore, the amount of iodine used can be determined by simple stoichiometry. The burette had an accuracy of ± 0.025 ml at low concentrations and ± 0.05 ml at high concentrations of SO₂. The titration end point was determined when a change from a brownish-yellow colour to a pale yellow colour was observed. A starch solution was then added which turned the solution blue as shown by the reaction below.

Titration continued until this blue colour disappeared. The starch solution was added at the last moment of yellow colour to ensure reversibility as described by Roberts et al. (1984). From the amount of iodine consumed in the titrations, the amount of SO_2 in the liquid could be determined. The errors in the mole fraction are estimated to be two percent. All the raw experimental data are presented in Appendix E.

11. Laboratory Materials

Sodium hydroxide solutions were prepared from reagent grade sodium hydroxide, available from Fisher Scientific Co., and distilled water. Standard solutions of iodine and sodium thiosulphate were used in the titrations. Sulphur dioxide, min. 99.98% pure (liquid phase), and U.H.P. nitrogen was obtained from Linde Gas Co. and Praxair Gas Co. respectively. The tetraethylene glycol dimethyl ether, 99% pure, was obtained from Aldrich Chemical Co. The compositions of the glymes in Selexol was analyzed by gas chromatography in three independent laboratories. The average results for each polyethylene glycol dimethyl ether group based on weight percent were:

Component	Wt %
triethylene glycol dimethyl ether	6.1 ± 1.0
tetra "	19.6 ± 1.3
penta "	25.7 ± 0.5
hexa "	22.3 ± 0.8
hepta "	14.7 ± 0.7
octa "	7.3 ± 0.9
nona "	3.2 ± 0.3
deca "	1.2 ± 0.4
undeca "	0.2 ± 0.2

The moisture content and molecular weight of the Selexol were measured by the micro-analytical laboratory in the Department of Chemistry at the University of Alberta. The moisture content was measured by a Mitsubishi moisture meter and the molecular weight was measured by a Corona Wescan molecular weight apparatus. The molecular weight and moisture content were 277.5 (dry basis) and $506.4 \pm 9.0 \mu\text{g H}_2\text{O}/100\mu\text{l}$ solution respectively.

12. Experimental Results and Discussion

To ensure that proper laboratory and analytical techniques were performed, the solubility of sulphur dioxide in pure tetraethylene glycol (tetraglyme) was measured at 40°C . The solubility results are tabulated in Table 12.1 and are compared with the experimental results at 40°C of Härtel (1985) in Figure 12.1. The results obtained in this investigation compare well with the results of Härtel (1985). Included in Figure 12.1 are the results of Demyanovich (1984) and Albright et al. (1963) at a temperature of 37.8°C . As can be seen, the solubility data obtained in this investigation are consistent with the solubility trend exhibited at 37.8°C . The difference in the results is due to the 2.2°C temperature difference.

Activity Coefficient Calculations:

Activity coefficients, γ_i , of sulphur dioxide were calculated from Equation (12.1) using the experimentally determined solubility data; temperature (T), pressure (P), vapour mole fraction (y_i) and liquid mole fraction (x_i). It was assumed that the liquid phase was incompressible which resulted in the approximate form of the

Table 12.1 Mole Fraction Solubility and Calculated Activity Coefficients
of SO₂ in Tetraethylene Glycol Dimethyl Ether at 40°C

P_{SO_2} (kPa)	x_{SO_2}	γ_{SO_2}
0.7	0.018	0.064
1.18	0.032	0.061
4.32	0.085	0.084
10.5	0.160	0.108
14.1	0.230	0.101
16.4	0.247	0.109
35.6	0.381	0.153
80.2	0.531	0.249
92.5	0.559	0.260
140	0.607	0.351
147	0.647	0.372
167	0.628	0.374
280	0.739	0.545
393	0.822	0.762
393	0.821	0.763
529	0.900	0.920
650	1.000	1.000

Figure 12.1 Experimental Mole Fraction Solubility of SO_2 in Tetraethylene Glycol Dimethyl Ether at 40°C

Poynting correction factor, in Equation (8.13), shown in Equation (12.1)

$$y_i \phi_i^v P = x_i \gamma_i \phi_i^{SAT} P_i^{SAT} \exp \left\{ v_i (P - P_i^{SAT}) / RT \right\} \quad (12.1)$$

The vapour phase fugacity coefficients (ϕ_i^v) were calculated from the Redlich-Kwong-Soave equation of state (RK-EOS) with the predictive Wong-Sandler mixing rules found in the ASPEN PLUS release 9 program. The mixing rules were chosen because the calculated sulphur dioxide saturation fugacity coefficient (ϕ_i^{SAT}) and pressure (P_i^{SAT}) in the temperature range of interest compared very well with the ϕ_i^{SAT} (within 1%) values presented in Canjar and Manning (1967) and P_i^{SAT} (within 4 %) values calculated from Daubert and Danner (1989) correlation. Aspentech (1994) suggests this combination of mixing rules and equation of state makes accurate predictions, 3% in pressure and 2% in mole fraction, at a given temperature up to 150 bar for mixtures of non-polar and polar compounds in combination with light gases. The molar volume, v_i , was calculated from the modified Rackett equation of Spencer and Danner (1972). Saturation pressures of sulphur dioxide were calculated from the correlation as mentioned above.

The calculated sulphur dioxide activity coefficients in tetraglyme are presented in Figure 12.2 and Table 12.1. Figure 12.2 compares these results with the NRTL correlated of Demyanovich and Lynn (1987) at 40°C and with the calculated activity coefficients from the solubility data of Härtel (1985) and Albright et al. (1963) at 40°C and 37.8°C respectively. The non-random two liquid (NRTL) equation of Renon and Prausnitz (1968), presented in Appendix C, was used to correlate all the experimental results (as will be discussed later) obtained in this investigation.

Figure 12.2 Activity Coefficients of SO_2 in Tetraethylene Glycol Dimethyl Ether at 40°C

As seen in Figure 12.2 the calculated activity coefficients agree well with the previous investigations.

Correlation of the Experimental Results

Equation of State Approach

Initially, the equation of state approach was used to correlate the solubility data. In this case the Peng-Robinson (PR-EOS) equation of state with the original mixing rules, as shown in Appendix C, was used to correlate the solubility of SO₂ in tetraglyme with the data obtained by Albright et al. (1963). The fugacity coefficients of each phase in Equation (8.11) were calculated by PR-EOS represented by P in Equation 12.2.

$$\ln \phi_i^\alpha = -\frac{1}{RT} \int_{\infty}^{V^*} \left[\left(\frac{\partial P}{\partial n_i} \right)_{T, V, n_{i \neq j}} - \frac{RT}{V} \right] dV - \ln Z_m^\alpha \quad (12.2)$$

The one adjustable parameter, the optimum binary interaction parameter, k_{12} was determined at each temperature by minimising the objective function of Weiland et al. (1993).

$$F_i = \frac{[p_{SO_2}^{MEAS} - p_{SO_2}^{CALC}]^2}{[p_{SO_2}^{CALC} - p_{SO_2}^{MEAS}]} \quad (12.3)$$

$$F_{OBJ}(T) = \sum F_i \quad (12.4)$$

The fitted binary interaction parameters are presented in Table 12.2. It can be seen by Figures 12.3 and 12.4 that the PR-EOS does a fairly poor job of correlating

Table 12.2 Peng-Robinson Equation of State Binary Interaction Parameter
for the System (SO₂-Tetraethylene Glycol Dimethyl Ether)

k_{12}	F_{OBI}	Temperature (°C)
-0.30	0.327	25.0
-0.30	0.412	37.8
-0.28	0.271	65.6
-0.28	0.215	93.3

Figure 12.3 Solubility of SO_2 in Tetraethylene Glycol Dimethyl Ether
Using the Peng-Robinson (1976) Equation of State

Figure 12.4 Comparison of the Modelled Solubility of SO_2 in Tetraethylene Glycol Dimethyl Ether Using the Peng-Robinson (1976) Equation of State with the Experimentally Determined Solubility of Albright et al. (1963)

this system. This may be because the original PR-EOS is best suited for non-polar or mildly polar mixtures and cannot accurately predict liquid phase mixture fugacity coefficients of the strongly polar tetraglyme and sulphur dioxide mixture.

Activity Coefficients Approach

Because the PR-EOS was inadequate to correlate the (SO₂-glyme) system, activity coefficient models were used to correlate the solubility data. Originally the (sulphur dioxide-tetraglyme) system at 40°C was correlated with six activity coefficient models. These models along with the fitted parameters are presented in Appendix C and Table 12.3 respectively.

A Levenberg-Marquadt non-linear regression routine in SIGMAPLOT[®] was used to obtain the fitted parameters of the models. This routine minimises the sum of squares between the calculated and experimental activity coefficients. Included in Table 12.3 are the estimates of the error and CV% for each parameter. The CV% is a normalised version of the standard error and is defined as:

$$CV\% = \text{standard error} \left(\frac{100}{\text{parameter value}} \right) \quad (12.5)$$

These two values along with the norm, the coefficient of determination (R²) and the relative residual root mean square (RRMS) were used to gauge the accuracy of the fitted curve. In all cases except R² a lower value indicates a better fit.

Table 12.3 Fitted Parameters for the Various Vapour-Liquid Equilibria Models

Model	$P_1 \pm \text{std.terr}$	$P_2 \pm \text{std.terr}$	CV ₁ %	CV ₂ %	Norm	R ²	RRMS
Margules	-2.58 ± 0.09	-5.69 ± 0.20	3.61	3.60	0.528	0.9899	0.3931
Wilson	9.57 ± 0.61	1.58 ± 0.16	6.47	7.37	0.460	0.9680	0.5930
TK Wilson	12.76 ± 0.92	2.00 ± 0.14	7.22	7.18	0.594	0.9446	0.7609
van Laar	-2.77 ± 0.04	-7.19 ± 0.23	1.55	3.83	0.313	0.9917	0.3290
UNIQUAC	2.73 ± 0.17	0.67 ± 0.10	6.55	14.64	0.328	0.9891	0.3689
NRTL	0.269 ± 0.12	-3.00 ± 0.07	45.2	2.39	0.308	0.9926	0.3127

P_1 and P_2 for each associated model are presented in Appendix C

The RRMS is defined as:

$$RRMS = \sum ([\gamma_{SO_2}^{MEAS} - \gamma_{SO_2}^{CALC}]^2)^{1/2} \quad (12.6)$$

As seen in Table 12.3 and Figure 12.5 the NRTL model does the best job correlating the sulphur dioxide activity coefficients. The NRTL equation of Renon and Prausnitz (1968) has three adjustable parameters: non randomness parameter (α_{12}), and two energy parameters (τ_{12} , and τ_{21}). When all three parameters were used to fit the data, the value of α_{12} became unreasonably large compared with the recommended values of Prausnitz et al. (1986). Prausnitz et al. (1986) showed that α_{12} varied from about 0.2 to 0.47 when a large number of binary experimental data were reduced using the NRTL equation. Walas (1985) and Prausnitz et al. (1986) recommend an estimate for α_{12} should be about 0.3 for non-aqueous mixtures.

The non-randomness parameter was varied from 0.1 to 0.5 to determine the best value for correlating the data. The LEMF equation ($\alpha_{12} = -1$) of Tassios and Marina (1973) and $\alpha_{12} = 1$, as used by Demyanovich (1984) and Demyanovich and Lynn (1987), were also tried in the data reduction. It was found that $\alpha_{12} = 0.3$ correlated the data the best. When the NRTL equation was used to correlate the data, Tassios' criteria (Walas, 1985) was followed.

$$|\tau_{12}| + |\tau_{21}| \rightarrow \text{minimum} \quad (12.7)$$

Tassios showed that the best fit was obtained when Equation (12.7) was satisfied.

Figure 12.5 Comparison of the Modelled SO_2 Activity Coefficients in Tetraethylene Glycol Dimethyl Ether with the Experimentally Determined Activity Coefficients

As seen in Table 12.3 the van Laar model parameters have a lower parameter error but according to Smith et al. (1996), the Margules and van Laar equations have a scant theoretical foundation and they do not incorporate an explicit temperature dependence for the parameters and were therefore rejected. The UNIQUAC model was also rejected because the model is algebraically complex and does not offer a superior fit. The Wilson equation (Wilson, 1966) and its modifications (Tsuboka and Katayama, 1975) were also rejected because of their poor goodness of fit. Therefore the NRTL equation with $\alpha_{12} = 0.3$ was used to fit all the solubility data.

Selexol Results

The solubility of sulphur dioxide was measured in Selexol at 25, 40, 70 and 100°C. The results at each temperature seem to follow smooth curves shown in Figure 12.6 and tabulated in Tables 12.4 to 12.7. As illustrated in Figure 12.6, there is a significant decrease in the solubility as the temperature increases. The experimental results also indicate there are significant negative deviations from Raoult's Law.

Activity coefficients of SO_2 were calculated from Equation (12.1) using the same method described earlier. The results are presented in Tables 12.4 to 12.7. Located in Figure 12.7 are the calculated activity coefficients at each temperature along with the best fit curves obtained from the NRTL equation with $\alpha_{12} = 0.3$. Calculated values for these fitted curves are presented in Appendix D. The NRTL does a good job of fitting the data except at lower liquid mole fractions where there are some scatter in the data. On average, as shown in Figure 12.8, the fit is good with an average error of about 10%.

Figure 12.6 Experimental Mole Fraction Solubility of SO_2 in Selexol at 25, 40, 70 and 100°C

Table 12.4 Mole Fraction Solubility and Calculated Activity Coefficients
of SO₂ in Selexol at 25°C

P_{SO_2} (kPa)	x_{SO_2}	γ_{SO_2}
0.268	0.019	0.037
0.357	0.023	0.040
0.675	0.043	0.041
0.799	0.046	0.045
0.808	0.044	0.047
1.26	0.064	0.050
1.36	0.074	0.047
1.85	0.083	0.057
1.89	0.094	0.052
2.52	0.105	0.062
2.53	0.110	0.055
4.46	0.173	0.064
6.87	0.236	0.076
11.7	0.323	0.092
25.8	0.480	0.140
26.2	0.452	0.151
51.5	0.593	0.222
52.3	0.591	0.226
70.5	0.679	0.269
102	0.688	0.386
153	0.752	0.528
198	0.793	0.644
286	0.867	0.836
287	0.870	0.834
400	1.000	1.000

Table 12.5 Mole Fraction Solubility and Calculated Activity Coefficients
of SO₂ in Selexol at 40°C

P_{SO_2} (kPa)	x_{SO_2}	γ_{SO_2}
0.944	0.025	0.061
0.983	0.024	0.067
1.02	0.032	0.053
2.11	0.049	0.070
2.42	0.065	0.060
2.59	0.074	0.058
5.67	0.127	0.074
13.2	0.206	0.104
19.2	0.294	0.108
41.5	0.410	0.168
63.5	0.517	0.204
148	0.668	0.365
255	0.765	0.540
256	0.768	0.540
303	0.802	0.610
430	0.857	0.791
584	0.945	0.959
650	1.000	1.000

Table 12.6 Mole Fraction Solubility and Calculated Activity Coefficients
of SO₂ in Selexol at 70°C

P_{SO_2} (kPa)	x_{SO_2}	γ_{SO_2}
4.09	0.031	0.104
5.64	0.042	0.105
11.8	0.074	0.125
23.3	0.146	0.125
70.2	0.310	0.176
113	0.397	0.223
144	0.458	0.246
197	0.517	0.297
310	0.620	0.384
312	0.605	0.396
614	0.758	0.602
996	0.862	0.823
1303	0.937	0.956
1483	1.000	1.000

Table 12.7 Mole Fraction Solubility and Calculated Activity Coefficients
of SO₂ in Selexol at 100°C

P_{SO_2} (kPa)	x_{SO_2}	γ_{SO_2}
8.02	0.021	0.168
14.4	0.036	0.176
23.6	0.063	0.165
34.8	0.083	0.185
62.3	0.139	0.198
106	0.189	0.247
161	0.297	0.241
188	0.316	0.264
263	0.370	0.313
504	0.538	0.404
726	0.627	0.489
727	0.630	0.488
2905	1.000	1.000

Figure 12.7 Activity Coefficients of SO_2 in Selexol at 25, 40, 70 and 100 °C

Figure 12.8 Comparison of the Modelled and Calculated Activity Coefficients of SO₂ in Selexol at 25, 40, 70 and 100 °C

As discussed earlier, $\alpha_{12} = 0.3$ was used to correlate the data. All the fitted parameters at each temperature are presented in Table 12.8. Figure 12.7 also illustrates the large non-ideality of the (sulphur dioxide-Selexol) system. Again, it can be seen from Figure 12.7 and Figure 12.6 with Equation (12.1) that the solubility decreases significantly with increasing temperature.

Infinite Dilution

Because flue gas desulphurisation usually involves dilute streams of sulphur dioxide, it is of interest to look at the infinitely dilute range of sulphur dioxide concentration in tetraglyme and Selexol. Infinite dilution activity coefficient (γ^∞) and Henry's constant (H_{12}) for SO_2 in tetraglyme were calculated at 40°C from the fitted parameters τ_{12} , τ_{21} and α_{12} , which are presented in Table 12.3. These results are presented and compared to previous investigations in Table 12.9. The infinite dilution activity coefficient of SO_2 from this study fits in between the two previous investigations.

The infinite dilution activity coefficient and Henry's constant of sulphur dioxide in Selexol are presented in Table 12.10 as a function of temperature. Again the values of γ^∞ and H_{12} were calculated from the NRTL equation at infinite dilution. At 40°C the γ^∞ of sulphur dioxide in Selexol is consistent with the value calculated for the other glymes.

The variation of γ^∞ as a function temperature was correlated using the Henry's law correlation, presented in Appendix C. This temperature dependence is shown in Figure 12.9. Variation of the Henry's constant with temperature is illustrated in Figure 12.10.

Table 12.8 Fitted Parameters for the NRTL ($\alpha_{12} = 0.3$) and Henry's Law Activity Coefficient Models

T(°C)	$P_1 \pm \text{std.err}$	$P_2 \pm \text{std.err}$	CV ₁ %	CV ₂ %	Norm	R ²	RRMS
25	0.22 ± 0.12	-3.39 ± 0.08	52.1	2.27	0.515	0.9832	0.5367
40	0.37 ± 0.14	-3.19 ± 0.08	35.2	2.68	0.327	0.9984	0.1712
70	0.80 ± 0.19	-2.95 ± 0.05	13.2	1.81	0.280	0.9993	0.0894
100	2.33 ± 0.80	-2.96 ± 0.15	34.1	5.01	0.192	0.9853	0.1262
Henry's	3.71 ± 0.02	-2056 ± 7.32	0.62	0.36	0.005	0.9996	0.0019

P_1 and P_2 for each associated model are presented in Appendix C

Table 12.9 Comparison of the Infinite Dilution Activity Coefficient of SO₂ in Tetraethylene Glycol Dimethyl Ether at 40°C

Investigator	γ^∞	H ₁₂ (kPa)
This study	0.064	41.46
Demyanovich and Lynn (1987)	0.071	45.96
Sciamanna and Lynn (1988)	0.052	33.77

Table 12.10 Infinite Dilute Activity Coefficient and Henry's Constant for SO₂ in Selexol at 25, 40, 70 and 100°C

Temperature (°C)	γ^∞	H ₁₂ (kPa)
25	0.041	16.5
40	0.057	37.3
70	0.102	151.8
100	0.165	478.6

Figure 12.9 Variation of the Infinite Dilution Activity Coefficient of SO_2 in Selexol With Temperature

Figure 12.10 Variation of the Henry's Constant of SO_2 in Selexol With Temperature

The Henry's constant and the infinite dilution activity coefficient temperature dependence are similar to that with the pure glymes. The correlation parameters for the Henry's law model are presented in Table 12.8. As shown in Figure 12.9, Figure 12.10 and by the statistics in Table 12.8, the fit of the dilute properties with respect to temperature is very good using the Henry's law correlation.

Heat Effects Accompanying SO₂ Absorption

There are two associated heat effects when a gas is absorbed into a liquid with no chemical reaction: the heat of solution and the heat of mixing. The heat of solution is an enthalpy change associated with the dissolution of 1 mole of solute combining with a solvent to form a solution. The heat of solution, the sum of the heats of mixing and heats of condensation, is determined by the variation of Henry's constant with temperature (in the dilute region only). When considering a non-volatile solvent and a dissolved solute at low pressures, according to Sciamanna (1986), the relationship is:

$$\Delta H_{SO_2}^{SOLN} = R \left(\frac{\partial \ln H_{12}}{\partial (1/T)} \right)_{x_{SO_2}} \quad (12.8)$$

The calculated results for Selexol are compared with the other glymes investigated by Sciamanna and Lynn (1988) and Demyanovich and Lynn (1987) in Table 12.11. The heat of solution for SO₂ in Selexol is negative which indicates an exothermic process. This results in the solubility decreasing with increasing temperature. The heat of solution of SO₂ in Selexol is consistent, within experimental error, to the heat of

Table 12.11 Heat of Solution for SO₂ in Organic Solvents in the Henry's Law Region

Investigator	Solvent	ΔH^{SOLN} (kJ/mol SO ₂)
Present Study	Selexol	-41.5
Demyanovich and Lynn (1987)	diglyme	-37.3
Sciamanna and Lynn (1988)	diglyme	-39.4
Demyanovich and Lynn (1987)	triglyme	-36.5
Sciamanna and Lynn (1988)	triglyme	-38.2
Demyanovich and Lynn (1987)	tetraglyme	-35.3
Sciamanna and Lynn (1988)	tetraglyme	-35.7

solution in the pure glymes as shown in Table 12.11 indicating a similar solubility trend.

The heat of solution of SO_2 in dimethyl-aniline was determined calorimetrically by Balej and Regner (1956) to be -62 kJ/mol SO_2 at 25°C . According to Balej and Regner (1956) this high value supports the assumption that an addition compound was formed. The heat of solution of SO_2 in Selexol is 20 kJ/mol lower than the reported value for SO_2 in dimethyl-aniline. This lower value indicates that the bond between the sulphur dioxide-glyme mixture is weaker than the sulphur dioxide-amine bond resulting in lower energy requirements for solvent regeneration.

Heat of Mixing

The second heat effect of gas absorption is the heat of mixing. This heat, or enthalpy, of mixing is the enthalpy change due to solute and solvent interactions in the liquid phase and is defined as the enthalpy change when pure species are mixed to form 1 mole of solution.

In systems of strong solute solvent interactions the heat of mixing is negative (exothermic). Hanks et al. (1971) concluded that in most cases, for six binary systems, excellent agreement between the calculated and experimental equilibrium data was obtained when the NRTL parameters were determined from H^E data. Therefore the heat of mixing for the (SO_2 - Selexol) system was calculated from the NRTL equation using the fitted vapour liquid equilibrium parameters.

The excess enthalpy is obtained via the Gibbs-Helmholtz relation:

$$\frac{H^E}{RT} = - \left\{ \frac{(T \partial(G^E/RT))}{\partial T} \right\}_{P,x} \quad (12.9)$$

The excess Gibbs energy, excess enthalpy, and excess entropy are all related by:

$$H^E = G^E + TS^E \quad (12.10)$$

The respective forms of excess Gibbs energy, excess entropy and excess enthalpy are presented in Appendix C. The fitted parameters, from the vapour liquid equilibrium data, were used to calculate G^E , TS^E , and H^E at each temperature. The calculated excess properties (G^E , H^E , and TS^E) are presented in Figure 12.11 for the (SO₂-tetraglyme) system. Figures 12.12 to 12.14 show the calculated G^E , TS^E , and H^E respectively for the (SO₂-Selexol) system.

The minimum excess enthalpy for the mixing of SO₂ in tetraglyme, at 40°C, is at $x_{\text{SO}_2} = 0.7$ with a value of -3.9 kJ/mol solution. The minimum is shifted to the sulphur dioxide side because sulphur dioxide is relatively small compared to the tetraglyme (CH₃O(CH₂CH₂O)₄-CH₃) molecule. The minimum values for the (SO₂ - Selexol) system, occur at $x_{\text{SO}_2} = 0.7$ with a value of -4.4 kJ/mol, -4.3 kJ/mol, -4.1 kJ/mol and -4.0 kJ/mol at 25, 40, 70 and 100°C respectively. The value of H^E at 40°C for sulphur dioxide-Selexol mixing is consistent with the value calculated for sulphur dioxide-tetraglyme. The difference is due to a slightly stronger interaction between the Selexol and SO₂ than with tetraethylene glycol dimethyl ether.

Figure 12.11 Calculated Excess Gibbs Energy, Enthalpy and Entropy of SO_2 in Tetraethylene Glycol Dimethyl Ether at 40°C

Figure 12.12 Calculated Excess Gibbs Energy of SO_2 in Selexol

Figure 12.13 Calculated Excess Entropy of SO_2 in Selexol

Figure 12.14 Calculated Excess Enthalpy of SO₂ in Selexol

It can be seen by the TS^E curves for both systems that mixing of the liquids is non-ideal. To assess whether the calculated excess properties are reasonable, a comparison was made with the published data other (polar compound-glyme) systems. The system 2,2,2-trifluoroethanol and polyethylene glycol dimethyl ether 250, studied by Lopez et al. (1997) has a minimum H^E of -4.267 kJ/mol solution at $x_{SO_2} = 0.6965$ and 25°C which is in the same region of the Selexol minimum at 25°C. The negative values of H^E indicate that SO_2 and Selexol are two dissimilar compounds. Because the heat of mixing is large and exothermic, it can be concluded that Selexol is a good absorbent for SO_2 .

Another calorimetric determination of excess enthalpies for SO_2 mixtures was determined by Tsvetkov et al. (1977). Minimum excess enthalpies at 25°C for tributyl phosphate and pyridine (some other popular SO_2 removal solvents) are -2.93 kJ/mol and -10.46 kJ/mol respectively. The results for Selexol indicate that the electron donor power of Selexol is greater than tributyl phosphate but lower than pyridine which was also indicated in the solubility data.

Because insufficient data were obtained at 100°C, the temperature dependent form of the NRTL energy parameters Δg_{12} and Δg_{21} were used to accurately calculate the excess properties at 100°C. These were calculated from the fitted parameters τ_{12} and τ_{21} at each temperature as shown in Equation (12.11) and presented in Table 12.12.

$$\tau_{12} = \frac{\Delta g_{12}}{RT} \quad \tau_{21} = \frac{\Delta g_{21}}{RT} \quad (12.11)$$

Table 12.12 Calculated Temperature Dependent Parameters of the NRTL Equation for the System (SO₂-Selexol)

T (°C)	$\Delta g_{12}(\text{J/mol})$	$\Delta g_{21}(\text{J/mol})$
25	545.34	-8410.6
40	973.98	-8313.1
70	2464.95	-8404.8
100	7228.53	-9189.2

As illustrated in Figure 12.15, Δg_{21} and Δg_{12} are linearly dependent with temperature; however, the value of Δg_{12} at 100°C appears to be too high. This results because not enough solubility data were taken at 100°C. If this value were used, the H^E , TS^E , G^E calculated at 100°C would not be valid or consistent with the other temperatures over the full composition range. Therefore, a linear temperature dependence model, as suggested by Hanks et al. (1978) and Demirel (1990), for Δg_{12} and Δg_{21} was used to calculate the excess properties. The linear form used was:

$$\Delta g_{12} = a + b(T - 298.15) \quad (12.12)$$

$$\Delta g_{21} = c + d(T - 298.15) \quad (12.13)$$

The correlated results are presented in Figure 12.15. It can be seen, the linear form of the temperature dependence fits the data well except for Δg_{12} at 100°C. At 100°C, Δg_{12} was extrapolated from Equation (12.12) which was fitted from the data at 25, 50, and 70°C. The parameters for the Equations (12.12) and (12.13) are:

$$a = -8235 \pm 214.8 \quad b = -10.21 \pm 4.84$$

$$c = 454.6 \pm 143.0 \quad d = 43.67 \pm 5.221$$

As illustrated in Figures 12.12 to 12.14, the value used for Δg_{12} at 100°C, the predicted values of the excess properties at 100°C are consistent with the other temperatures over the full composition range. Equations (12.12) and (12.13) can be used, with the NRTL equation, to interpolate the excess properties and activity coefficients between 25°C and 100°C. Extrapolations can be made with caution and are suggested not to exceed 10°C in either direction.

Figure 12.15 Variation of the NRTL Temperature Dependent Parameters With Temperature

At infinite dilution the heat of mixing was determined with Equation (12.14).

$$\Delta H_{SO_2}^{MX} = R \left(\frac{\partial \ln \bar{\gamma}_{SO_2}}{\partial (1/T)} \right)_{x_{SO_2}} \quad (12.14)$$

The results for the SO₂-Selexol system are presented and compared in Table 12.13.

Table 12.13 illustrates that the mixing effects of SO₂ and Selexol are somewhat less at higher temperatures than with the other glymes. However within experimental errors the results are consistent.

The Effect of Water

The solubility of sulphur dioxide is lower in water than in pure glymes. Sometimes, water inadvertently enters in the recycled solvent during the regeneration process. One such process is the Linde Solinox process, which uses the tetraglyme for SO₂ removal agent (Becker and Linde, 1985), which uses a water wash and steam in the solvent regeneration stage. Because of this, the effect of water on the solubility of SO₂ in water-enriched Selexol was studied. As shown earlier, the weight percentage of H₂O in the Selexol used was 0.4 % by weight (wt). The effect of water was studied with a 6.04 wt % water solution. Figure 12.16 illustrates the effect of the solubility with this mixture at 25°C. At a constant pressure, the mass fraction of SO₂ decreases, indicating a decrease in the solubility of SO₂. The average moisture content in the regenerated solvent runs about 5 wt % (Becker and Linde, 1985). Therefore, the 6.04 wt % is an over-estimate of the solubility decrease in an industrial situation. Using a best fit line between the data, it can be seen within experimental error that the

addition of water to the solution decreases the solubility of SO_2 in Selexol. The mass fraction solubility of the pure Selexol and the 6.04 wt % are compared in Table 12.14. The solubility of the water solution was only investigated in the dilute region, of SO_2 concentration, and fitted with empirical equations presented in Table 12.14. As can be seen in Figure 12.16 the empirical equations fit the data well.

Table 12.13 Heat of Mixing for SO₂ in Organic Solvents in the Henry's Law Region

Investigator	Solvent	ΔH_{mix} (kJ/mol SO ₂)
Present Study	Selexol	-17.1
Demyanovich and Lynn (1987)	diglyme	-13.1
Sciamanna and Lynn (1988)	diglyme	-15.2
Demyanovich and Lynn (1987)	triglyme	-12.3
Sciamanna and Lynn (1988)	triglyme	-14.0
Demyanovich and Lynn (1987)	tetraglyme	-11.1
Sciamanna and Lynn (1988)	tetraglyme	-11.5

Table 12.14 Mass fraction Solubility of SO₂ in Selexol and 6.04 wt% Water Solution

Selexol		6 wt.% water	
w _{SO2}	p _{SO2} (kPa)	w _{SO2}	p _{SO2} (kPa)
0.0049	0.268	0.0046	0.357
0.0058	0.357	0.0109	1.116
0.0107	0.675	0.0210	2.281
0.0118	0.808	0.0403	4.280
0.0118	0.799	0.0612	7.578
0.0166	1.262	0.1055	15.68
0.0191	1.360		
0.0218	1.858		
0.0249	1.890		
0.0281	2.520		
0.0312	2.530		
0.0491	4.460		
0.0708	6.870		
0.1051	11.70		
Selexol		$\log(p_{\text{SO}_2})=1.21309\log(w_{\text{SO}_2})+5.16926$	
6.04 wt% water solution		$\log(p_{\text{SO}_2})=1.1757\log(w_{\text{SO}_2})+5.33769$

Figure 12.16 Effect of Water on the Mass Fraction Solubility of SO_2 in Selexol at 25°C

13. Conclusions

Increased sulphur dioxide in the atmosphere is detrimental to the health and well-being of humans and the environment. Man-made emissions account for most of the increased SO_2 in the atmosphere. Organic solvents have been recommended for removing sulphur dioxide from post processing gas streams. The best solvents for sulphur dioxide absorption are those with a good electron donor ability. The absorption capacity, on a mole fraction basis, at 101.3 kPa decreases with respect to the following groups

glycol ether > amine > sulphoxide > phosphate

The solvent Selexol has many advantageous properties and satisfies the criteria for a good SO_2 removal solvent.

The vapour-liquid equilibrium apparatus and analytical technique used in this investigation reproduced the literature data well for the solubility of SO_2 in tetraethylene glycol dimethyl ether at 40°C. The solubility of sulphur dioxide in Selexol was measured at 25, 40, 70 and 100 °C. The NRTL equation fitted the activity coefficients well with an average error of about 10%. The calculated excess Gibbs energy, entropy and enthalpy indicate that there are strong interactions between the sulphur dioxide and Selexol. This results in a highly non-ideal system, that gives large SO_2 solubilities.

As expected an increased amount of water in the Selexol lowers the solubility. Data are available in the dilute region at 25°C for an 6.04 wt % solution of water in Selexol. The solubility difference can be determined from empirically fitted equations.

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Appendix A Response Factor Determination

The response factor of sulphur dioxide relative to nitrogen was determined by the absolute calibration technique. Exact amounts of pure samples, SO₂ and N₂, were injected independently into the gas chromatograph and analysed. The peak areas were plotted against the amount injected for each gas. The calibration curves from these injections are presented in Figure A.1. and Table A.1. It can be seen that the calibration curves are linear and pass through the origin. The slopes of the fitted curves were used in Equation A.1 to calculate the response factor.

$$RF = \frac{A_{SO_2}}{A_{N_2}} \quad (A.1)$$

From the linear regression the slopes were 252.8 and 199.0 (area units/μl gas) for sulphur dioxide and nitrogen respectively. From this a response factor of 1.27 was determined.

Figure A.1 Gas Chromatograph Calibration Curves

Table A.1 Variation of the N₂ and SO₂ Response Area With Volume Injected

Volume (μL)	Area N ₂	Area SO ₂
10	2189	2826
20	4156	5504
30	5977	7985
40	7952	10842
60	11849	14641
80	15898	19850
100	19912	25370

Appendix B Calculation of the Solubility of SO₂ from Measured Quantities

This appendix illustrates the calculations involved in the determination of the solubility of sulphur dioxide in the solvents studied. Typical values of the experimentally determined quantities were used in the sample calculations.

SO₂ content in the liquid sample

Data:

Temperature	25°C
total mass of NaOH	23.4863 g
mass of the sample	2.5749 g
volume of sample aliquot	1 mL
density of aliquot	1.0708 g/mL
volume 0.1N iodine solution	10 mL
volume 0.1N thiosulphate solution	0.3 mL

moles of SO₂ in sample aliquot

$$0.1 * \frac{(10-0.3)}{2000} = 4.85 \times 10^{-4} \text{ moles}$$

moles of SO₂ in sample

$$(4.85 \times 10^{-4}) * \frac{23.4863}{1.0708 * 1} = 1.06377 \times 10^{-2} \text{ moles}$$

mass of SO₂ in sample

$$1.06377 \times 10^{-2} * 64.063 = 0.68148 \text{ grams}$$

mass of solvent in sample

$$2.5749 - 0.68148 = 1.8934 \text{ grams}$$

mass of water in solvent

$$0.00479 * (1.8934) = 9.0695 \times 10^{-3} \text{ grams}$$

mass of Selexol

$$1.8934 - 9.0695 \times 10^{-3} = 1.8843 \text{ grams}$$

mole fraction SO₂

$$\frac{1.06377 \times 10^{-2}}{\left\{ 1.06377 \times 10^{-2} + \frac{9.0695 \times 10^{-3}}{18.0152} + \frac{1.8843}{277.51} \right\}}$$

$$x = 0.5933$$

mass fraction SO₂

$$\frac{0.68148}{\left\{ 0.68148 + 9.0695 \times 10^{-3} + 1.8843 \right\}}$$

$$w = 0.2647$$

Calculation of the SO₂ liquid mole fraction in the pure tetraethylene glycol dimethyl ether is analogous. The mass of water in the system is zero and is therefore dropped in the subsequent calculations. In case of the 6.04 wt% water in the Selexol the mass fraction was calculated from

$$\frac{\text{mass } SO_2}{\{\text{mass } SO_2 + \text{mass solvent}\}} \quad (\text{B.1})$$

SO₂ content in the vapour sample

Data:

Temperature	25°C
cell pressure	267.36 kPa
area percent SO ₂	23.273
response factor	1.27
(1/response factor)	0.787

mole fraction SO₂

$$\left\{ \frac{23.273 * (0.787)}{23.273 * (0.787) + (100 - 23.273)} \right\}$$

$$y = 0.1927$$

SO₂ partial pressure

$$267.36 * \left\{ \frac{23.273 * (0.787)}{23.273 * (0.787) + (100 - 23.273)} \right\}$$

$$= 51.52 \text{ kPa}$$

Appendix C Pertinent Equations of Vapour-Liquid Equilibrium

Cubic Equations of State

Peng Robinson Equation of State (Peng and Robinson, (1976))

$$P = \frac{RT}{v-b} - \frac{a\alpha}{v(v+b)+b(v-b)} \quad (C.1)$$

where

$$b=0.07780\frac{RT_c}{P_c} \quad a=0.45724\frac{R^2T_c^2}{P_c} \quad (C.2)$$

$$\alpha=((1+(1-T_r^{0.5})(0.37464+1.5422\omega-0.26992\omega^2))^2 \quad (C.3)$$

mixtures

$$a\alpha = \sum \sum y_i y_j (a\alpha)_{ij} \quad b = \sum y_i b_i \quad (C.4)$$

$$(a\alpha)_{ij} = (1-k_{ij})(a\alpha_i a\alpha_j)^{1/2} \quad (C.5)$$

where k_{12} is an adjustable parameter

Redlich-Kwong-Soave Equation of State (Soave, (1972))

$$P = \frac{RT}{v-b} - \frac{a\alpha}{v(v+b)} \quad (C.6)$$

$$b=0.08664 \frac{RT_c}{P_c} \quad a=0.42747 \frac{R^2 T_c^2}{P_c} \quad (C.7)$$

$$\alpha = ((1 + (1 - T_r^{0.5})(0.48508 + 1.55171\omega - 0.15613\omega^2))^2 \quad (C.8)$$

$$a\alpha = \sum \sum y_i y_j (a\alpha)_{ij} \quad b = \sum y_i b_i \quad (C.9)$$

$$(a\alpha)_{ij} = (1 - k_{ij})(a\alpha_i a\alpha_j)^{1/2} \quad (C.10)$$

Wong-Sandler mixing rules are described in detail in Wong and Sandler (1992)

where k_{12} is an adjustable parameter

Activity Coefficient Models:

P_1 and P_2 are the fitted parameters in Table 12.3 and 12.8

Non Random Two Liquid (NRTL) Equation (Renon and Prausnitz, (1968))

$$\ln \gamma_1 = x_2^2 \left\{ \tau_{21} \left(\frac{G_{21}}{x_1 + x_2 G_{21}} \right)^2 - \frac{\tau_{12} G_{12}}{(x_2 + x_1 G_{12})^2} \right\} \quad (C.11)$$

$$G_{12} = \exp(-\alpha \tau_{12}) \quad G_{21} = \exp(-\alpha \tau_{21}) \quad (C.12)$$

$$\tau_{12} = \frac{\Delta g_{12}}{RT} \quad \tau_{21} = \frac{\Delta g_{21}}{RT} \quad (C.13)$$

where α , τ_{12} (P_1), and τ_{21} (P_2) are the adjustable parameters and Δg_{12} , Δg_{21} are the temperature dependent adjustable parameters

Wilson Equation (Wilson, (1964))

$$\ln \gamma_1 = \left\{ -\ln(x_1 + \Lambda_{12} x_2) + \left(\frac{\Lambda_{12}}{x_1 + x_2 \Lambda_{12}} \right) - \frac{\Lambda_{21} x_2}{x_2 + x_1 \Lambda_{21}} \right\} \quad (C.14)$$

$$\Lambda_{21} = \frac{v_1}{v_2} \exp(-\Delta \lambda_{21}/RT) \quad \Lambda_{12} = \frac{v_2}{v_1} \exp(-\Delta \lambda_{12}/RT) \quad (C.15)$$

where Λ_{12} (P_1) and Λ_{21} (P_2) are the adjustable parameters and $\Delta \lambda_{21}$ and $\Delta \lambda_{12}$ are the temperature dependent adjustable parameters

T-K-Wilson Equation (Tsuboka and Katayama, (1975))

$$\ln \gamma_1 = \ln \frac{x_1 + V_2 x_2 / V_1}{x_1 + \Lambda_{12} x_2} + (\beta - \beta_v) x_2 \quad (C.16)$$

$$\beta_v = \frac{V_2/V_1}{x_1 + V_2 x_2 / V_1} - \frac{V_1/V_2}{V_1 x_1 / V_2 + x_1} \quad \beta = \frac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} - \frac{\Lambda_{21}}{x_2 + \Lambda_{21} x_1} \quad (C.17)$$

$$\Lambda_{21} = \frac{v_1}{v_2} \exp\left(\frac{\Delta \lambda_{21}}{RT}\right) \quad \Lambda_{12} = \frac{v_2}{v_1} \exp\left(\frac{\Delta \lambda_{12}}{RT}\right) \quad (C.18)$$

where Λ_{12} (P_1) and Λ_{21} (P_2) are the adjustable parameters and $\Delta \lambda_{21}$ and $\Delta \lambda_{12}$ are the temperature dependent adjustable parameters

van Laar

$$\ln \gamma_1 = A_{12} \left\{ \frac{x_2 A_{21}}{x_1 A_{12} + x_2 A_{21}} \right\}^2 \quad (C.19)$$

where A_{12} (P_1), and A_{21} (P_2) are the adjustable parameters

Margules

$$\ln \gamma_1 = [A_{12} + 2(A_{21} - A_{12})x_1]x_2^2 \quad (C.20)$$

where A_{12} (P_1), and A_{21} (P_2) are the adjustable parameters

UNIQUAC Equation (Abrams and Prausnitz, (1975))

$$\ln \gamma_1 = \ln \frac{\phi_1}{x_1} + \frac{z}{2} q_1 \ln \frac{\theta_1}{\phi_1} + \phi_2 \left(l_1 - \frac{r_1}{r_2} l_2 \right) + q'_1 \left[-[\ln(\theta'_1 + \theta'_2 \tau_{21})] + \frac{\theta'_2 \tau_{21}}{\theta'_1 + \theta'_2 \tau_{21}} + \frac{\theta'_1 \tau_{12}}{\theta'_2 + \theta'_1 \tau_{12}} \right] \quad (\text{C.21})$$

$$\phi_1 = \frac{x_1 r_1}{x_1 r_1 + x_2 r_2} \quad \phi_2 = \frac{x_2 r_2}{x_1 r_1 + x_2 r_2} \quad (\text{C.22})$$

$$\theta_1 = \frac{x_1 q_1}{x_1 q_1 + x_2 q_2} \quad \theta_2 = \frac{x_2 q_2}{x_1 q_1 + x_2 q_2} \quad (\text{C.23})$$

$$\theta'_1 = \frac{x_1 q'_1}{x_1 q'_1 + x_2 q'_2} \quad \theta'_2 = \frac{x_2 q'_2}{x_1 q'_1 + x_2 q'_2} \quad (\text{C.24})$$

$$l_1 = \frac{z}{2} (r_1 - q_1) - (r_1 - 1) \quad l_2 = \frac{z}{2} (r_2 - q_2) - (r_2 - 1) \quad (\text{C.25})$$

$$\tau_{12} = \exp\left(-\frac{\Delta u_{12}}{RT}\right) \quad \tau_{21} = \exp\left(-\frac{\Delta u_{21}}{RT}\right) \quad (\text{C.26})$$

SO₂ and tetraglyme parameters are presented in Demyanovich and Lynn (1987)

where τ_{12} (P_1), and τ_{21} (P_2) are the adjustable parameters and Δu_{12} , Δu_{21} are the temperature dependent adjustable parameters

Henry's law (Prausnitz et al., (1980))

$$H_{1,2} = \gamma_{1,2}^{\infty} f_1^{\circ} L \quad (\text{C.27})$$

$$\ln \gamma_{1,2}^{\infty} = \delta_{1,2} + \frac{\delta_{2,1}}{T} \quad (\text{C.28})$$

where $\delta_{1,2}$ (P_1), and $\delta_{2,1}$ (P_2) are the adjustable parameters

Excess Free Energy, Enthalpy and Entropy Forms of the NRTL Equation

All forms taken from Gennaro de Chialvo and Chialvo (1994)

The excess Gibbs energy form of the NRTL equation is

$$G^E = -\frac{RT}{\alpha} x_1 x_2 \left(\frac{G_{21} \ln G_{21}}{(x_1 + G_{21} x_2)} + \frac{G_{12} \ln G_{12}}{(x_2 + G_{12} x_1)} \right) \quad (C.29)$$

The excess entropy form is

$$S^E = -\frac{R}{\alpha} x_1 x_2 \left(\frac{x_1 G_{21} (\ln G_{21})^2}{(x_1 + G_{21} x_2)^2} + \frac{x_2 G_{12} (\ln G_{12})^2}{(x_2 + G_{12} x_1)^2} \right) \quad (C.30)$$

The excess enthalpy is then calculated from

$$H^E = G^E + TS^E \quad (C.31)$$

$$G_{ij} = \exp[-\alpha(\Delta g_{ij})/RT] \quad i=1,2 \quad j=1,2 \quad (C.32)$$

Appendix D Calculated Values From the NRTL Equation**Table D.1 Calculated Activity Coefficient of SO₂ in Tetraethylene Glycol Dimethyl Ether at 40°C**

x_{SO_2}	γ
0.01	0.065
0.02	0.066
0.03	0.068
0.04	0.069
0.05	0.071
0.06	0.072
0.07	0.074
0.08	0.075
0.09	0.077
0.1	0.079
0.2	0.099
0.3	0.129
0.4	0.172
0.5	0.235
0.6	0.328
0.7	0.465
0.8	0.654
0.9	0.873
0.91	0.893
0.92	0.913
0.93	0.931
0.94	0.947
0.95	0.962
0.96	0.975
0.97	0.985
0.98	0.993
0.99	0.998
1	1.000

Table D.2 Calculated Activity Coefficient of SO₂ in Selexol

x_{SO_2}	γ_{25}	γ_{40}	γ_{70}	γ_{100}
0.010	0.042	0.058	0.104	0.167
0.020	0.043	0.060	0.105	0.169
0.030	0.044	0.061	0.107	0.171
0.040	0.045	0.062	0.108	0.174
0.050	0.046	0.063	0.110	0.176
0.060	0.047	0.064	0.112	0.178
0.070	0.048	0.066	0.114	0.181
0.080	0.049	0.067	0.115	0.183
0.090	0.050	0.068	0.117	0.186
0.100	0.051	0.070	0.119	0.189
0.200	0.066	0.088	0.142	0.219
0.300	0.087	0.113	0.174	0.258
0.400	0.119	0.151	0.219	0.310
0.500	0.169	0.207	0.283	0.379
0.600	0.249	0.294	0.375	0.471
0.700	0.376	0.426	0.507	0.593
0.800	0.572	0.618	0.685	0.745
0.900	0.831	0.855	0.885	0.909
0.910	0.857	0.877	0.904	0.924
0.920	0.881	0.899	0.921	0.937
0.930	0.905	0.920	0.937	0.950
0.940	0.927	0.939	0.952	0.962
0.950	0.947	0.956	0.966	0.973
0.960	0.965	0.970	0.977	0.982
0.970	0.979	0.983	0.987	0.990
0.980	0.990	0.992	0.994	0.995
0.990	0.998	0.998	0.998	0.999
1.000	1.000	1.000	1.000	1.000

Table D.3 Calculated Excess Properties of SO₂ in Tetraethylene Glycol Dimethyl Ether at 40°C

x_{SO_2}	G^E (kJ/mol)	TS^E (kJ/mol)	H^E (kJ/mol)
0	0	0	0
0.01	-7.14E-2	-7.99E-4	-7.22E-2
0.02	-0.142	-2.15E-3	-0.144
0.03	-0.213	-4.07E-3	-0.217
0.04	-0.282	-6.54E-3	-0.289
0.05	-0.352	-9.59E-3	-0.361
0.06	-0.42	-1.32E-2	-0.434
0.07	-0.488	-1.74E-2	-0.506
0.08	-0.556	-2.21E-2	-0.578
0.09	-0.623	-2.75E-2	-0.65
0.1	-0.689	-3.34E-2	-0.722
0.2	-1.31	-0.125	-1.44
0.3	-1.86	-0.275	-2.13
0.4	-2.3	-0.48	-2.78
0.5	-2.61	-0.73	-3.34
0.6	-2.75	-0.999	-3.75
0.7	-2.66	-1.23	-3.9
0.8	-2.27	-1.33	-3.6
0.9	-1.45	-1.07	-2.52
0.91	-1.33	-1.01	-2.34
0.92	-1.22	-0.94	-2.16
0.93	-1.09	-0.863	-1.95
0.94	-0.958	-0.776	-1.73
0.95	-0.818	-0.678	-1.5
0.96	-0.671	-0.57	-1.24
0.97	-0.516	-0.448	-0.964
0.98	-0.352	-0.314	-0.666
0.99	-0.181	-0.165	-0.345
1	0	0	0

Table D.4 Calculated Excess Properties of SO₂ in Selexol at 25°C

x_{SO_2}	G^E (kJ/mol)	TS^E (kJ/mol)	H^E (kJ/mol)
0	0	0	0
0.01	-7.78E-2	-5.36E-4	-7.83E-2
0.02	-0.155	-1.67E-3	-0.157
0.03	-0.232	-3.42E-3	-0.235
0.04	-0.308	-5.77E-3	-0.314
0.05	-0.383	-8.75E-3	-0.392
0.06	-0.458	-1.23E-2	-0.471
0.07	-0.533	-1.66E-2	-0.549
0.08	-0.607	-2.14E-2	-0.628
0.09	-0.68	-2.69E-2	-0.707
0.1	-0.752	-0.033	-0.785
0.2	-1.44	-0.13	-1.57
0.3	-2.04	-0.294	-2.34
0.4	-2.54	-0.524	-3.06
0.5	-2.9	-0.811	-3.71
0.6	-3.07	-1.13	-4.21
0.7	-3	-1.43	-4.43
0.8	-2.59	-1.58	-4.17
0.9	-1.67	-1.31	-2.99
0.91	-1.55	-1.25	-2.79
0.92	-1.41	-1.17	-2.58
0.93	-1.27	-1.07	-2.34
0.94	-1.12	-0.97	-2.09
0.95	-0.955	-0.852	-1.81
0.96	-0.784	-0.718	-1.5
0.97	-0.604	-0.568	-1.17
0.98	-0.414	-0.399	-0.813
0.99	-0.213	-0.211	-0.423
1	0	0	0

Table D.5 Calculated Excess Properties of SO₂ in Selexol at 40°C

x_{SO_2}	G^E (kJ/mol)	TS^E (kJ/mol)	H^E (kJ/mol)
0	0	0	0
0.01	-7.39E-2	-1.54E-3	-7.54E-2
0.02	-0.147	-3.65E-3	-0.151
0.03	-0.22	-6.35E-3	-0.227
0.04	-0.293	-9.63E-3	-0.302
0.05	-0.365	-1.35E-2	-0.378
0.06	-0.436	-0.018	-0.454
0.07	-0.507	-0.023	-0.53
0.08	-0.577	-2.87E-2	-0.606
0.09	-0.647	-0.035	-0.682
0.1	-0.716	-4.19E-2	-0.758
0.2	-1.37	-0.145	-1.52
0.3	-1.95	-0.313	-2.26
0.4	-2.43	-0.543	-2.97
0.5	-2.78	-0.827	-3.61
0.6	-2.95	-1.14	-4.09
0.7	-2.89	-1.42	-4.31
0.8	-2.49	-1.56	-4.05
0.9	-1.61	-1.28	-2.89
0.91	-1.49	-1.21	-2.69
0.92	-1.36	-1.13	-2.49
0.93	-1.22	-1.04	-2.26
0.94	-1.07	-0.938	-2.01
0.95	-0.916	-0.823	-1.74
0.96	-0.753	-0.693	-1.45
0.97	-0.58	-0.547	-1.13
0.98	-0.397	-0.384	-0.781
0.99	-0.204	-0.202	-0.406
1	0	0	0

Table D.6 Calculated Excess Properties of SO₂ in Selexol at 70°C

x_{SO_2}	G^E (kJ/mol)	TS^E (kJ/mol)	H^E (kJ/mol)
0	0	0	0
0.01	-0.068	-5.02E-3	-0.073
0.02	-0.136	-1.05E-2	-0.146
0.03	-0.203	-1.65E-2	-0.219
0.04	-0.269	-2.31E-2	-0.292
0.05	-0.336	-3.01E-2	-0.366
0.06	-0.401	-3.76E-2	-0.439
0.07	-0.467	-4.57E-2	-0.512
0.08	-0.532	-5.42E-2	-0.586
0.09	-0.596	-6.33E-2	-0.659
0.1	-0.66	-7.29E-2	-0.733
0.2	-1.27	-0.199	-1.46
0.3	-1.8	-0.379	-2.18
0.4	-2.25	-0.612	-2.86
0.5	-2.58	-0.888	-3.46
0.6	-2.74	-1.18	-3.92
0.7	-2.68	-1.43	-4.11
0.8	-2.31	-1.53	-3.83
0.9	-1.49	-1.22	-2.71
0.91	-1.37	-1.15	-2.53
0.92	-1.25	-1.08	-2.33
0.93	-1.12	-0.987	-2.11
0.94	-0.989	-0.888	-1.88
0.95	-0.845	-0.777	-1.62
0.96	-0.694	-0.652	-1.35
0.97	-0.534	-0.513	-1.05
0.98	-0.366	-0.359	-0.725
0.99	-0.188	-0.189	-0.376
1	0	0	0

Table D.7 Calculated Excess Properties of SO₂ in Selexol at 100°C

x_{SO_2}	G^E (kJ/mol)	TS^E (kJ/mol)	H^E (kJ/mol)
0	0	0	0
0.01	-6.38E-2	-9.58E-3	-7.34E-2
0.02	-0.127	-1.96E-2	-0.147
0.03	-0.19	-2.99E-2	-0.22
0.04	-0.253	-4.07E-2	-0.293
0.05	-0.315	-5.19E-2	-0.367
0.06	-0.377	-6.35E-2	-0.44
0.07	-0.438	-7.55E-2	-0.513
0.08	-0.499	-8.79E-2	-0.587
0.09	-0.559	-0.101	-0.66
0.1	-0.619	-0.114	-0.733
0.2	-1.19	-0.27	-1.46
0.3	-1.69	-0.47	-2.16
0.4	-2.1	-0.71	-2.81
0.5	-2.41	-0.978	-3.38
0.6	-2.55	-1.25	-3.8
0.7	-2.49	-1.47	-3.96
0.8	-2.14	-1.52	-3.66
0.9	-1.38	-1.18	-2.56
0.91	-1.27	-1.11	-2.39
0.92	-1.16	-1.04	-2.2
0.93	-1.04	-0.949	-1.99
0.94	-0.914	-0.851	-1.77
0.95	-0.781	-0.743	-1.52
0.96	-0.641	-0.622	-1.26
0.97	-0.493	-0.488	-0.982
0.98	-0.337	-0.341	-0.678
0.99	-0.173	-0.179	-0.352
1	0	0	0

Appendix E Experimental Data

Solubility of SO₂ in Tetraethylene Glycol Dimethyl Ether @ 40C

Total P (kPa)	Partial P (kPa)	y SO ₂	Mass Sample (g)	mmol SO ₂	mass SO ₂ (g)	Mass Ether (g)	moles Ether	x SO ₂	w SO ₂
1.242E+02	7.036E-01	5.667E-03	2.931E+00	2.342E-01	1.501E-02	2.916E+00	1.312E-02	1.754E-02	5.121E-03
9.914E+01	1.177E+00	1.187E-02	1.223E+00	1.824E-01	1.169E-02	1.212E+00	5.451E-03	3.238E-02	9.552E-03
1.591E+02	4.325E+00	2.718E-02	2.715E+00	1.111E+00	7.119E-02	2.644E+00	1.189E-02	8.545E-02	2.622E-02
1.415E+02	1.051E+01	7.428E-02	8.675E-01	7.069E-01	4.529E-02	8.222E-01	3.699E-03	1.604E-01	5.221E-02
1.622E+02	1.413E+01	8.714E-02	1.529E+00	1.885E+00	1.208E-01	1.408E+00	6.335E-03	2.293E-01	7.899E-02
1.578E+02	1.642E+01	1.041E-01	1.951E+00	2.636E+00	1.689E-01	1.783E+00	8.019E-03	2.474E-01	8.655E-02
2.017E+02	3.558E+01	1.764E-01	3.977E+00	9.368E+00	6.001E-01	3.377E+00	1.519E-02	3.814E-01	1.509E-01
1.559E+02	8.020E+01	5.144E-01	3.954E+00	1.517E+01	9.719E-01	2.982E+00	1.341E-02	5.307E-01	2.458E-01
5.077E+02	9.253E+01	1.822E-01	2.132E+00	8.909E+00	5.707E-01	1.562E+00	7.026E-03	5.591E-01	2.677E-01
7.515E+02	1.402E+02	1.866E-01	3.411E+00	1.641E+01	1.051E+00	2.360E+00	1.062E-02	6.072E-01	3.082E-01
2.068E+02	1.488E+02	7.099E-01	2.308E+00	1.244E+01	7.988E-01	1.512E+00	6.800E-03	6.465E-01	3.451E-01
1.327E+03	1.669E+02	1.258E-01	1.913E+00	9.762E+00	6.254E-01	1.287E+00	5.791E-03	6.277E-01	3.270E-01
1.150E+03	2.801E+02	2.436E-01	5.362E+00	3.755E+01	2.406E+00	2.956E+00	1.330E-02	7.385E-01	4.487E-01
3.930E+02	3.930E+02	1.000E+00	1.965E+00	1.749E+01	1.120E+00	8.445E-01	3.799E-03	8.215E-01	5.702E-01
3.931E+02	3.931E+02	1.000E+00	1.919E+00	1.707E+01	1.094E+00	8.250E-01	3.712E-03	8.214E-01	5.700E-01
5.286E+02	5.286E+02	1.000E+00	1.395E+00	1.570E+01	1.006E+00	3.889E-01	1.750E-03	8.997E-01	7.212E-01

Solubility of SO2 In Selexol @ 25C

Total P (kPa)	Partial P (kPa)	y SO2	Mass Sample (g)	mmol SO2	mass SO2 (g)	Mass Solvent (g)	mass Water (g)	mass Ether (g)	mmoles Water	mmoles Ether	x SO2	w SO2
1.663E+02	2.683E-01	1.613E-03	1.815E+00	1.376E-01	8.812E-03	1.806E+00	8.649E-03	1.797E+00	4.801E-01	6.476E+00	1.939E-02	4.857E-03
2.522E+02	3.572E-01	1.416E-03	1.203E+00	1.089E-01	6.975E-03	1.196E+00	5.727E-03	1.190E+00	3.179E-01	4.287E+00	2.310E-02	5.801E-03
1.808E+02	6.752E-01	3.734E-03	1.180E+00	2.039E-01	1.306E-02	1.167E+00	5.589E-03	1.161E+00	3.102E-01	4.184E+00	4.339E-02	1.107E-02
1.839E+02	7.989E-01	4.344E-03	1.728E+00	3.184E-01	2.040E-02	1.708E+00	8.180E-03	1.700E+00	4.541E-01	6.125E+00	4.617E-02	1.180E-02
2.548E+02	8.083E-01	3.173E-03	1.354E+00	2.362E-01	1.513E-02	1.339E+00	6.412E-03	1.332E+00	3.559E-01	4.800E+00	4.380E-02	1.118E-02
2.398E+02	1.262E+00	5.263E-03	1.780E+00	4.624E-01	2.963E-02	1.750E+00	8.384E-03	1.742E+00	4.654E-01	6.277E+00	6.418E-02	1.664E-02
1.932E+02	1.359E+00	7.036E-03	1.122E+00	3.367E-01	2.157E-02	1.101E+00	5.272E-03	1.095E+00	2.928E-01	3.947E+00	7.357E-02	1.922E-02
2.418E+02	1.858E+00	7.684E-03	1.744E+00	5.945E-01	3.809E-02	1.706E+00	8.169E-03	1.697E+00	4.535E-01	6.116E+00	8.298E-02	2.184E-02
1.725E+02	1.892E+00	1.097E-02	1.895E+00	7.362E-01	4.716E-02	1.848E+00	8.853E-03	1.839E+00	4.914E-01	6.628E+00	9.372E-02	2.488E-02
1.589E+02	2.516E+00	1.584E-02	1.183E+00	5.189E-01	3.324E-02	1.150E+00	5.506E-03	1.144E+00	3.057E-01	4.123E+00	1.049E-01	2.811E-02
1.638E+02	2.533E+00	1.547E-02	1.197E+00	5.528E-01	3.540E-02	1.162E+00	5.565E-03	1.156E+00	3.089E-01	4.166E+00	1.099E-01	2.957E-02
2.084E+02	4.464E+00	2.142E-02	2.159E+00	1.654E+00	1.060E-01	2.053E+00	9.835E-03	2.043E+00	5.460E-01	7.364E+00	1.730E-01	4.908E-02
1.596E+02	6.874E+00	4.308E-02	1.660E+00	1.834E+00	1.175E-01	1.543E+00	7.390E-03	1.535E+00	4.102E-01	5.533E+00	2.358E-01	7.076E-02
3.110E+02	1.171E+01	3.765E-02	1.748E+00	2.869E+00	1.838E-01	1.564E+00	7.494E-03	1.557E+00	4.160E-01	5.610E+00	3.225E-01	1.051E-01
1.298E+02	2.583E+01	1.991E-01	1.151E+00	3.335E+00	2.138E-01	9.372E-01	4.489E-03	9.327E-01	2.492E-01	3.361E+00	4.802E-01	1.856E-01
1.314E+02	2.646E+01	2.013E-01	1.679E+00	4.490E+00	2.876E-01	1.391E+00	6.863E-03	1.384E+00	3.698E-01	4.988E+00	4.559E-01	1.713E-01
2.674E+02	5.152E+01	1.927E-01	2.575E+00	1.064E+01	6.815E-01	1.893E+00	9.069E-03	1.884E+00	5.034E-01	6.790E+00	5.933E-01	2.647E-01
2.564E+02	5.230E+01	2.039E-01	2.264E+00	9.279E+00	5.944E-01	1.669E+00	7.996E-03	1.661E+00	4.438E-01	5.986E+00	5.907E-01	2.626E-01
1.778E+02	7.048E+01	3.964E-01	1.415E+00	7.579E+00	4.855E-01	9.298E-01	4.454E-03	9.253E-01	2.472E-01	3.334E+00	6.791E-01	3.431E-01
1.288E+02	1.021E+02	7.923E-01	1.801E+00	9.916E+00	6.352E-01	1.168E+00	5.585E-03	1.160E+00	3.100E-01	4.181E+00	6.882E-01	3.527E-01
1.539E+02	1.532E+02	9.954E-01	3.903E-01	2.607E+00	1.670E-01	2.233E-01	1.070E-03	2.222E-01	5.937E-02	8.008E-01	7.519E-01	4.279E-01
1.983E+02	1.978E+02	9.978E-01	8.447E-01	6.404E+00	4.102E-01	4.345E-01	2.081E-03	4.324E-01	1.155E-01	1.558E+00	7.928E-01	4.856E-01
3.266E+02	2.864E+02	8.768E-01	1.452E+00	1.399E+01	8.962E-01	5.561E-01	2.864E-03	5.534E-01	1.478E-01	1.994E+00	8.672E-01	6.171E-01
3.294E+02	2.868E+02	8.709E-01	1.472E+00	1.432E+01	9.174E-01	5.547E-01	2.857E-03	5.521E-01	1.475E-01	1.989E+00	8.702E-01	6.232E-01

Solubility of SO₂ In Selexol @ 40C

Total P (kPa)	Partial P (kPa)	y SO ₂	Mass Sample (g)	mmol SO ₂	mass SO ₂ (g)	Mass Solvent (g)	mass Water (g)	mass Ether (g)	mmoles Water	mmoles Ether	x SO ₂	w SO ₂
2.475E+02	9.437E-01	3.812E-03	1.237E+00	1.237E-01	7.926E-03	1.229E+00	5.889E-03	1.224E+00	3.269E-01	4.409E+00	2.546E-02	6.405E-03
2.517E+02	9.830E-01	3.906E-03	1.563E+00	1.460E-01	9.355E-03	1.554E+00	7.442E-03	1.546E+00	4.131E-01	5.572E+00	2.382E-02	5.985E-03
9.772E+01	1.327E+00	1.358E-02	1.015E+00	1.275E-01	8.167E-03	1.007E+00	4.825E-03	1.002E+00	2.878E-01	3.612E+00	3.181E-02	8.043E-03
2.411E+02	2.110E+00	8.751E-03	1.294E+00	2.554E-01	1.636E-02	1.277E+00	6.118E-03	1.271E+00	3.396E-01	4.580E+00	4.935E-02	1.265E-02
2.725E+02	2.418E+00	8.875E-03	1.258E+00	3.312E-01	2.122E-02	1.236E+00	5.923E-03	1.231E+00	3.288E-01	4.434E+00	6.502E-02	1.687E-02
1.001E+02	2.591E+00	2.589E-02	1.034E+00	3.132E-01	2.006E-02	1.014E+00	4.856E-03	1.009E+00	2.695E-01	3.635E+00	7.425E-02	1.941E-02
1.041E+02	5.673E+00	5.450E-02	1.833E+00	9.876E-01	6.327E-02	1.769E+00	8.476E-03	1.761E+00	4.705E-01	6.346E+00	1.266E-01	3.452E-02
2.554E+02	1.317E+01	5.156E-02	1.614E+00	1.518E+00	9.728E-02	1.517E+00	7.267E-03	1.510E+00	4.034E-01	5.441E+00	2.062E-01	6.026E-02
1.041E+02	1.919E+01	1.843E-01	9.948E-01	1.448E+00	9.273E-02	9.021E-01	4.321E-03	8.977E-01	2.398E-01	3.235E+00	2.941E-01	9.322E-02
1.076E+02	4.152E+01	3.860E-01	1.684E+00	3.849E+00	2.466E-01	1.438E+00	6.886E-03	1.431E+00	3.823E-01	5.156E+00	4.100E-01	1.464E-01
1.006E+02	6.346E+01	6.306E-01	3.331E+00	1.086E+01	6.958E-01	2.635E+00	1.262E-02	2.623E+00	7.007E-01	9.451E+00	5.169E-01	2.089E-01
1.486E+02	1.484E+02	9.984E-01	9.886E-01	5.124E+00	3.282E-01	6.604E-01	3.163E-03	6.572E-01	1.756E-01	2.368E+00	6.682E-01	3.320E-01
2.709E+02	2.553E+02	9.422E-01	5.370E+00	3.736E+01	2.394E+00	2.976E+00	1.426E-02	2.962E+00	7.914E-01	1.067E+01	7.652E-01	4.457E-01
2.725E+02	2.561E+02	9.397E-01	2.961E+00	2.080E+01	1.332E+00	1.629E+00	7.801E-03	1.621E+00	4.330E-01	5.840E+00	7.683E-01	4.500E-01
3.030E+02	3.030E+02	1.000E+00	1.643E+00	1.282E+01	8.211E-01	8.220E-01	3.937E-03	8.181E-01	2.186E-01	2.948E+00	8.019E-01	4.997E-01
4.305E+02	4.305E+02	1.000E+00	2.144E+00	1.996E+01	1.279E+00	8.647E-01	4.142E-03	8.606E-01	2.299E-01	3.101E+00	8.570E-01	5.966E-01
5.836E+02	5.836E+02	1.000E+00	1.921E+00	2.424E+01	1.553E+00	3.684E-01	1.765E-03	3.666E-01	9.796E-02	1.321E+00	9.447E-01	8.082E-01

Solubility of SO₂ In Selexol @ 70C

Total P (kPa)	Partial P (kPa)	y SO ₂	Mass Sample (g)	mmol SO ₂	mass SO ₂ (g)	Mass Solvent (g)	mass Water (g)	mass Ether (g)	mmoles Water	mmoles Ether	x SO ₂	w SO ₂
1.129E+02	4.094E+00	3.628E-02	1.297E+00	1.574E-01	1.008E-02	1.287E+00	6.165E-03	1.281E+00	3.422E-01	4.616E+00	3.077E-02	7.774E-03
1.391E+02	5.644E+00	4.057E-02	1.572E+00	2.610E-01	1.672E-02	1.555E+00	7.451E-03	1.548E+00	4.136E-01	5.578E+00	4.174E-02	1.064E-02
9.998E+01	1.184E+01	1.184E-01	6.812E-01	2.062E-01	1.321E-02	6.680E-01	3.200E-03	6.648E-01	1.776E-01	2.396E+00	7.418E-02	1.939E-02
1.021E+02	2.326E+01	2.279E-01	1.509E+00	9.512E-01	6.093E-02	1.448E+00	6.934E-03	1.441E+00	3.849E-01	5.192E+00	1.457E-01	4.039E-02
1.323E+02	7.025E+01	5.309E-01	1.515E+00	2.358E+00	1.511E-01	1.364E+00	6.535E-03	1.358E+00	3.627E-01	4.892E+00	3.097E-01	9.969E-02
1.286E+02	1.129E+02	8.784E-01	1.658E+00	3.614E+00	2.315E-01	1.427E+00	6.833E-03	1.420E+00	3.793E-01	5.116E+00	3.968E-01	1.396E-01
1.475E+02	1.443E+02	9.784E-01	1.922E+00	5.174E+00	3.314E-01	1.591E+00	7.620E-03	1.583E+00	4.230E-01	5.705E+00	4.578E-01	1.724E-01
1.970E+02	1.970E+02	1.000E+00	1.754E+00	5.731E+00	3.671E-01	1.387E+00	6.645E-03	1.381E+00	3.689E-01	4.975E+00	5.175E-01	2.093E-01
3.133E+02	3.098E+02	9.890E-01	2.045E+00	9.167E+00	5.872E-01	1.457E+00	6.980E-03	1.450E+00	3.875E-01	5.226E+00	6.202E-01	2.872E-01
3.153E+02	3.124E+02	9.910E-01	9.539E-01	4.084E+00	2.616E-01	6.923E-01	3.316E-03	6.889E-01	1.841E-01	2.483E+00	6.050E-01	2.743E-01
6.137E+02	6.137E+02	1.000E+00	8.652E-01	5.884E+00	3.769E-01	4.883E-01	2.339E-03	4.859E-01	1.298E-01	1.751E+00	7.578E-01	4.357E-01
9.964E+02	9.984E+02	1.000E+00	1.871E+00	1.770E+01	1.134E+00	7.367E-01	3.529E-03	7.332E-01	1.959E-01	2.642E+00	8.618E-01	6.062E-01
1.303E+03	1.303E+03	1.000E+00	1.358E+00	1.666E+01	1.068E+00	2.909E-01	1.393E-03	2.895E-01	7.734E-02	1.043E+00	9.370E-01	7.859E-01

Solubility of SO₂ In Selexol @ 100C

Total P (kPa)	Partial P (kPa)	y SO ₂	Mass Sample (g)	mmol SO ₂	mass SO ₂ (g)	Mass Solvent (g)	mass Water (g)	mass Ether (g)	mmoles Water	mmoles Ether	x SO ₂	w SO ₂
2.923E+02	8.022E+00	2.744E-02	1.554E+00	1.293E-01	8.280E-03	1.545E+00	7.402E-03	1.538E+00	4.109E-01	5.541E+00	2.125E-02	5.330E-03
2.895E+02	1.437E+01	4.963E-02	1.279E+00	1.847E-01	1.183E-02	1.267E+00	6.069E-03	1.261E+00	3.369E-01	4.544E+00	3.647E-02	9.253E-03
2.864E+02	2.359E+01	8.236E-02	1.413E+00	3.600E-01	2.306E-02	1.389E+00	6.855E-03	1.383E+00	3.694E-01	4.983E+00	6.302E-02	1.633E-02
2.443E+02	3.476E+01	1.423E-01	1.029E+00	3.492E-01	2.237E-02	1.007E+00	4.822E-03	1.002E+00	2.677E-01	3.610E+00	8.260E-02	2.174E-02
2.486E+02	6.232E+01	2.507E-01	1.160E+00	6.952E-01	4.454E-02	1.116E+00	5.344E-03	1.110E+00	2.966E-01	4.001E+00	1.392E-01	3.839E-02
2.793E+02	1.063E+02	3.807E-01	6.538E-01	5.566E-01	3.566E-02	6.181E-01	2.961E-03	6.152E-01	1.844E-01	2.217E+00	1.895E-01	5.454E-02
1.761E+02	1.608E+02	9.133E-01	2.347E+00	3.461E+00	2.217E-01	2.125E+00	1.018E-02	2.115E+00	5.650E-01	7.621E+00	2.972E-01	9.449E-02
1.893E+02	1.879E+02	9.927E-01	1.852E+00	2.954E+00	1.892E-01	1.663E+00	7.965E-03	1.655E+00	4.421E-01	5.963E+00	3.156E-01	1.022E-01
2.660E+02	2.631E+02	9.893E-01	4.019E-01	7.934E-01	5.083E-02	3.511E-01	1.682E-03	3.494E-01	9.335E-02	1.259E+00	3.698E-01	1.265E-01
5.087E+02	5.039E+02	9.907E-01	1.721E+00	5.993E+00	3.839E-01	1.337E+00	6.406E-03	1.331E+00	3.556E-01	4.796E+00	5.378E-01	2.231E-01
7.293E+02	7.261E+02	9.957E-01	1.791E+00	8.194E+00	5.249E-01	1.266E+00	6.062E-03	1.259E+00	3.365E-01	4.539E+00	6.270E-01	2.932E-01
7.293E+02	7.266E+02	9.964E-01	3.579E+00	1.655E+01	1.060E+00	2.519E+00	1.207E-02	2.507E+00	6.698E-01	9.035E+00	6.304E-01	2.962E-01

Solubility of SO₂ in 6.04%wt Water in Selexol @ 25C

Total P (kPa)	Partial P (kPa)	y SO ₂	Mass Sample (g)	mmol SO ₂	mass SO ₂ (g)	Mass Solvent (g)	mass Water (g)	mass Ether (g)	mmoles Water	mmoles Ether	x SO ₂	w SO ₂
1.531E+02	3.567E-01	2.329E-03	1.868E+00	1.354E-01	8.673E-03	1.859E+00						4.644E-03
2.400E+02	1.116E+00	4.649E-03	1.743E+00	2.960E-01	1.896E-02	1.724E+00						1.088E-02
2.272E+02	2.281E+00	1.004E-02	1.934E+00	6.324E-01	4.051E-02	1.894E+00						2.095E-02
2.437E+02	4.282E+00	1.757E-02	1.351E+00	8.510E-01	5.452E-02	1.297E+00						4.034E-02
2.466E+02	7.578E+00	3.073E-02	1.903E+00	1.818E+00	1.164E-01	1.786E+00						6.120E-02
2.554E+02	1.568E+01	6.139E-02	3.016E+00	5.118E+00	3.279E-01	2.689E+00						1.087E-01