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Solubilities Of Heavy Hydrocarbons In Supercritical Ethane

by

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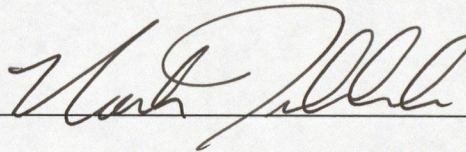
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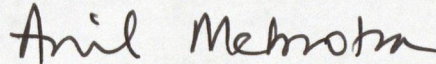
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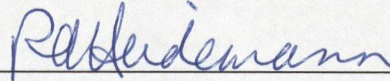
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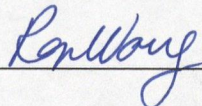
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Abstract

In this work, the solubilities of tetracosane, octacosane and dotriacontane in ethane were determined at a temperature of 308.15 K and at pressures ranging from 50 to 200 bar. A dynamic single-pass flow system was used for this purpose. The extracted solute was dissolved in toluene after depressurizing the supercritical mixture. This method of measuring the solubilities gives this experimental design the unique capability of obtaining dynamic solubility information by collecting and analyzing samples of toluene as the experiment proceeds. Dynamic sampling provides more reliable and accurate solubility information compared to the conventional methods based on the weight of solute extracted. The experimental solubilities measured in this work are in good agreement with previously published data.

The solubilities obtained in this work were modeled using the translated Trebble-Bishnoi-Salim (TBS) EOS which correlated the solubility data successfully to with an average error of about 6% for all the systems studied.

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Nomenclature

a	EOS attractive parameter ($\text{cm}^6 \text{mol}^{-2} \text{atm}$)
$\bar{a}$	TEOS attractive parameter evaluated at triple point ($\text{cm}^6 \text{mol}^{-2} \text{atm}$)
AAD	absolute average deviation
b	EOS covolume parameter ($\text{cm}^3 \text{mol}^{-1}$)
$\bar{b}$	TEOS covolume parameter evaluated at triple point ($\text{cm}^3 \text{mol}^{-1}$)
BFSL	best fit straight line
c	equation of state parameter ($\text{cm}^3 \text{mol}^{-1}$)
$\bar{c}$	TEOS parameter evaluated at triple point ($\text{cm}^3 \text{mol}^{-1}$)
$\bar{C}$	heat capacity at triple point (J/mol K)
d	equation of state parameter ($\text{cm}^3 \text{mol}^{-1}$)
$\bar{d}$	TEOS parameter evaluated at triple point ($\text{cm}^3 \text{mol}^{-1}$)
EOS	equation of state
f	fugacity (atm)
$\bar{f}$	fugacity at triple point (atm)
F-S	fluid-solid
G-S	gas-solid
G-L	gas-liquid
$\Delta\bar{H}$	latent heat at triple point (J/mol)
k_a	interaction parameter of the EOS attractive parameter
$\hat{k}_a$	interaction parameter for the TEOS attractive parameter
k_b	interaction parameter for the covolume parameter
k_c	interaction parameter for c
k_d	interaction parameter for d
LCEP	lower critical end point
LLV	liquid-liquid-vapor
L-G	liquid-gas
m	constant in equation 5.5

$\hat{m}$	constant in equation 5.12
p	constant in equation 5.5
$\hat{p}$	constant in equation 5.12
P	pressure (atm)
$\bar{P}$	triple point pressure (atm)
P-T	pressure-temperature
PVT	pressure-volume-temperature
R	universal gas constant (cc atm/mol K)
RMSE	root mean square error
s-l	solid-liquid
s-v	solid-vapor
SCF	supercritical fluid
SD	standard deviation
SFE	supercritical fluid extraction
SLV	solid-liquid-vapor
T	absolute temperature (K)
$\bar{T}$	triple point temperature (K)
TBS	Trebbles-Bishnoi-Salim
TEOS	translated equation of state
TTBS	translated TBS
UCEP	upper critical end point
v	molar volume (cc/mol)
$\bar{v}$	molar volume at triple point (cc/mol)
v-l	vapor-liquid
VLE	vapor-liquid equilibrium
x	mole fraction

Greek letters

α	temperature dependence in the v-l TBS EOS
$\hat{\alpha}$	temperature dependence in the translated TBS EOS
ξ	compressibility factor predicted by an equation of state

Subscripts

c	critical
i	component index
j	component index
l	liquid phase
p	pressure
r	reduced
s	solid phase
sat	saturation
subl	sublimation
v	vapor phase

Superscripts

EOS	equation of state
exp	experimental
*	ideal property

1.0 Introduction

In the past two decades, supercritical fluids (SCFs) have been the focus of active research and development programs. SCFs have the ability to separate a multicomponent mixture by capitalizing on the differences in component volatilities as well as the specific interactions between the components and the supercritical fluid. Thus, it utilizes the salient features of both distillation and liquid extraction. Supercritical fluid extraction (SFE, SCFE) offers considerable flexibility for an effective separation through controlling pressure, temperature and choice of solvents. At the center of this technology lies the enhanced solubility of the solute near the solvent's critical point. This significant increase in solvent strength is attributed to liquid like densities. In addition to these unique solubility characteristics, a supercritical fluid possesses other physico-chemical properties that add to its attractiveness. For example, though it possesses a liquid-like density over much of the region of industrial interest, it exhibits gas-like transport properties of diffusivity and viscosity. Additionally, SCFs have very low surface tension, which allows facile penetration into microporous materials. These properties of SCFs are compared to those of gases and liquids in Table 1.1.

Properties	Gas (1 atm)	SCF	Liquid
Density (Kg/m^3)	10	300	1000
Diffusivity (m^2/s)	10^{-5}	10^{-7} - 10^{-8}	$<10^{-9}$
Viscosity (Kg/m s)	10^{-6}	10^{-5} - 10^{-6}	10^{-4}

Table 1.1 Properties of Gas, Supercritical and Liquid phases

SCFE thus offers these advantages over extraction with conventional solvents:

- 1) combines gas like properties with liquid like solvent powers
- 2) offers moderate operating temperatures
- 3) utilizes non-toxic gases as solvents
- 4) dissolves non-volatiles

1.1 Applications

Most of the phenomena associated with SCFs are favorable to mass transfer and their ability to extract low volatility materials from various mixtures has led to their widespread applications in the specialty chemicals, pharmaceutical, food and petroleum industries. Some of the common applications include removing caffeine from coffee beans, extraction of oil from oil shales, removal of oil and cholesterol from food products, regeneration of carbon, decontamination of soil, removal of nicotine from tobacco, etc. Reviews of these applications of SFE are available elsewhere (Paulaitis, 1983; Eckert et al, 1986; McHugh and Krukoni, 1986). Some of the recent applications include supercritical water oxidation (SCWO), polymer fractionation processes, monomer purifications, supercritical fluid nucleation or rapid expansion from a supercritical solution (RESS), precipitation with a compressed fluid, gas antisolvent extraction or gas antisolvent recrystallization (GAS), heterogeneous catalysis, enzyme reactions etc. A brief overview of all these applications can be found in McHugh and Krukoni (1986).

1.1.1 Applications to petroleum processes

The ability of SCFs to separate high-boiling fractions from non-distillable materials and their capacity to extract low volatility materials has led researchers to investigate the effects of SCFs on petroleum recovery and processing applications. Propane deasphalting, one of the early industrial applications, is one such example utilizing the near critical property changes to improve the energy and phase separation efficiency of a lube-oil feedstock. Residuum oil supercritical extraction (ROSE) also takes clever advantage of the variable solvent power of a near-critical liquid for dissolving and precipitating high molecular weight compounds and causes the separation of desired oil from the solution. Other novel applications include de-ashing of coal liquids, regeneration of lubricating oil, fractionation of petroleum fractions (Jemison et al, 1995).

The potential SFE applications related to oil sands production, bitumen upgrading and bitumen analysis include upgrading bitumen and bitumen derived liquids by

techniques similar to the ROSE process, using SFE in surface mining recovery schemes, using SFE as an analytical tool for understanding the thermodynamic behavior of oil sands and using dense gases as additives in production of heavy oils by *in-situ* recovery methods. Recent discoveries have reservoir pressures and temperatures as high as 124 MPa and 188°C. Some shallow reservoirs have pressures as low as 0.8 MPa. These wide range of conditions make SFE a powerful technique for *in-situ* upgrading processes. Some recent studies (Deo et al, 1992; Hwang et al, 1995; Eisenbach et al, 1983; Yu et al, 1989; Huang and Radosz, 1990) have focused on the phase behavior and extraction of crude oils, oil sands, bitumen and bitumen derived liquids with supercritical solvents like propane, toluene and carbon dioxide.

1.2 Solubility determination

The enhanced solubility of solutes in supercritical solvents is perhaps the most important thermophysical property that must be determined and modeled for any SFE system. The potential applications of SFE resulted in the development of many new laboratory techniques for determining solubilities. The methods for determining solubility can be broadly classified as dynamic, static, chromatographic and spectroscopic. A review of the advantages and disadvantages of these methods can be found elsewhere (McHugh and Krukonis, 1986).

1.3 Scope of this work

Heavy molecular weight normal paraffins can be used as model compounds in the petroleum industry, as they comprise the majority of the compounds found in conventional crude oils. Experimental information on these selected model systems is required in order to properly represent the complex systems encountered in industrial applications. With respect to these applications the solubilities of some normal paraffins (C28-C36) in supercritical carbon dioxide, ethylene and ethane have been reported in the literature (McHugh et al, 1984; Moradinia and Teja, 1986; Suleiman and Eckert, 1995).

The critical properties of ethane and propane and their availability make them suitable for petroleum industry applications. Due to the lower critical temperature (32°C), ethane is chosen as the solvent for this work. To understand and appreciate the scope of this work it is necessary to study the phase behavior of ethane-hydrocarbon systems.

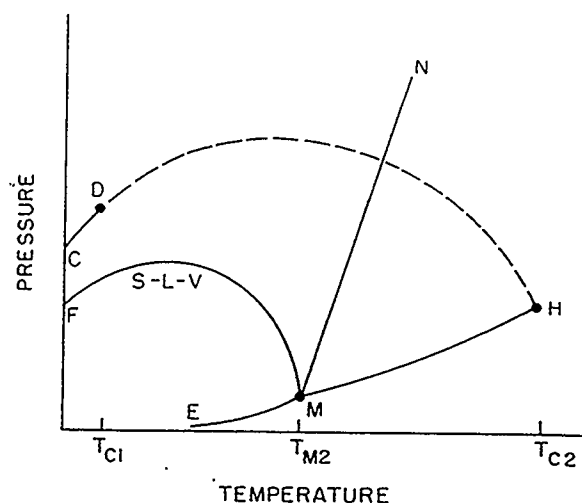
1.3.1 Phase behavior of SCF-Solid systems

Solid-SCF mixtures constitute a very large and important subset of binary mixtures. For this type of mixture the normal melting temperature of the solid is greater than the critical temperature of the SCF. Shown in Figure 1.1 is the simplest P-T diagram (McHugh and Krukoni, 1986) of a solid-SCF system.

Curves CD and MH are the pure component vapor pressure curves of the light (SCF) and heavy(solid) component, respectively. Curve MN is the pure heavy component melting curve, and curve EM the pure heavy component sublimation curve. Points D and H represent pure component critical points. The distinguishing trait for this type of system is that the critical mixture curve, representing different mixture compositions, runs continuously from the critical point of the heavy component to the critical point of the light component. Also a continuous three-phase solid-liquid-vapor (SLV) line is observed. The SLV line begins at the normal melting point of the heavy component, bends back toward lower temperatures as the pressure is increased, and finally ends at a temperature usually well below the critical temperature of the lighter component. For the binary mixture, the heavy component melting curve MN, exhibits a freezing point depression at elevated pressures due to the solubility of the light component in the heavy liquid phase. In Figure 1.1, this freezing point depression is depicted by the line MF, which represents the three-phase solid-liquid-gas equilibrium. If the solubility of the light component is large, the freezing point depression will be appreciable.

For a binary mixture of fixed composition, varying types of phase behavior are possible depending on the mixture composition as the pressure is increased isothermally at a temperature greater than T_{c1} , but less than T_{m2} , to pressures above the three-phase pressure (McHugh and Krukoni, 1986). If the concentration of the heavy component in

Figure 1.1 Schematic P-T diagram for a heavy SCF-solid system (McHugh and Krukonis, 1986). The SLV curve is continuous.

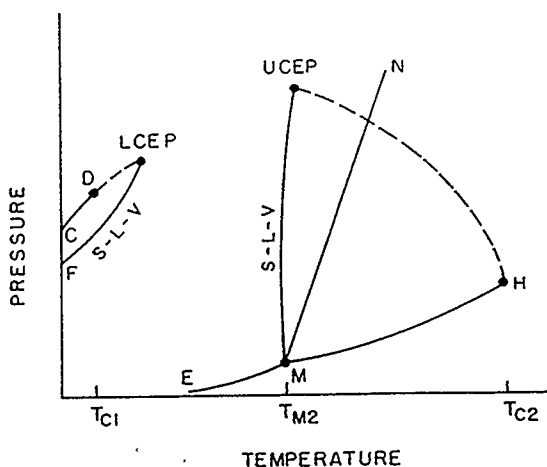


the mixture is slight, then liquid-gas equilibrium exists above the three-phase pressure until the vapor-liquid critical point is reached for the binary mixture (curve DH). Above this pressure a single fluid phase exists. However, if the concentration of the heavy component in the mixture is much greater, the solid-gas equilibrium would exist at all pressures above the three-phase pressure. Numerous examples of this type of phase behavior are reported in literature. Normally this type of behavior occurs for mixtures whose components are chemically similar such as the methane-carbon dioxide system.

The previously described solid-SCF phase behavior represents the simpler of two possible types. In a more complex type, the SLV line is no longer continuous and the critical mixture curve is also no longer a continuous curve. This type of behavior is found in systems where not only is the melting temperature of the heavier component greater than the critical temperature of the lighter component, but also the molecular size, shape, structure and critical conditions of the two components differ substantially. This is the case in the systems of carbon dioxide-hydrocarbon, ethylene-hydrocarbon and ethane-hydrocarbon. This work involves measuring the solubility of hydrocarbons in supercritical ethane and hence this type of phase behavior will be discussed in detail.

The phase behavior for this type of binary mixture, where the SLV line and the critical mixture curve are no longer continuous is depicted in the P-T diagram in Figure 1.2. The pure component equilibrium curves have the same notation as in Figure 1.1.

Figure 1.2 Schematic P-T diagram for a mixture of heavy non-volatile solid and a light SCF (McHugh and Krukonis, 1986). The SLV curve is not continuous.



In this case the melting curve MN, will exhibit a small freezing point depression at elevated pressures due to the limited solubility of the light component in the liquid phase. The branch of the three-phase SLV line starting at the normal melting point of the heavy solid does not bend toward lower temperatures with increasing pressure. Instead it rises steeply with increasing pressure and intersects the critical mixture curve at a UCEP (Upper critical end point). The lower temperature branch of the SLV line intersects the critical mixture curve at the LCEP (Lower critical end point).

The solubility of a heavy solid in a supercritical solvent will increase if the temperature is increased, but it is not possible to indefinitely raise the system temperature to increase the solubility of the solid, in the SCF phase. This is because the higher temperature branch of the SLV line will eventually be intersected and the solid will melt. The occurrence of this behavior will depend on the mixture composition and hence it is necessary to study the P-x diagrams of these systems.

Shown in Figure 1.3a is the P-T diagram for the ethylene-naphthalene system (McHugh 1981). The ethane-hydrocarbon system shows the same behavior as the ethylene-naphthalene system and hence the schematics 1.3a-1.3d also represent the P-T and P-x behavior of the ethane-hydrocarbon systems, which are the focus of this study.

Figure 1.3b depicts the solubility behavior of the heavy solid (hydrocarbon) in the supercritical solvent (ethane) at a temperature greater than the UCEP temperature. Solid-

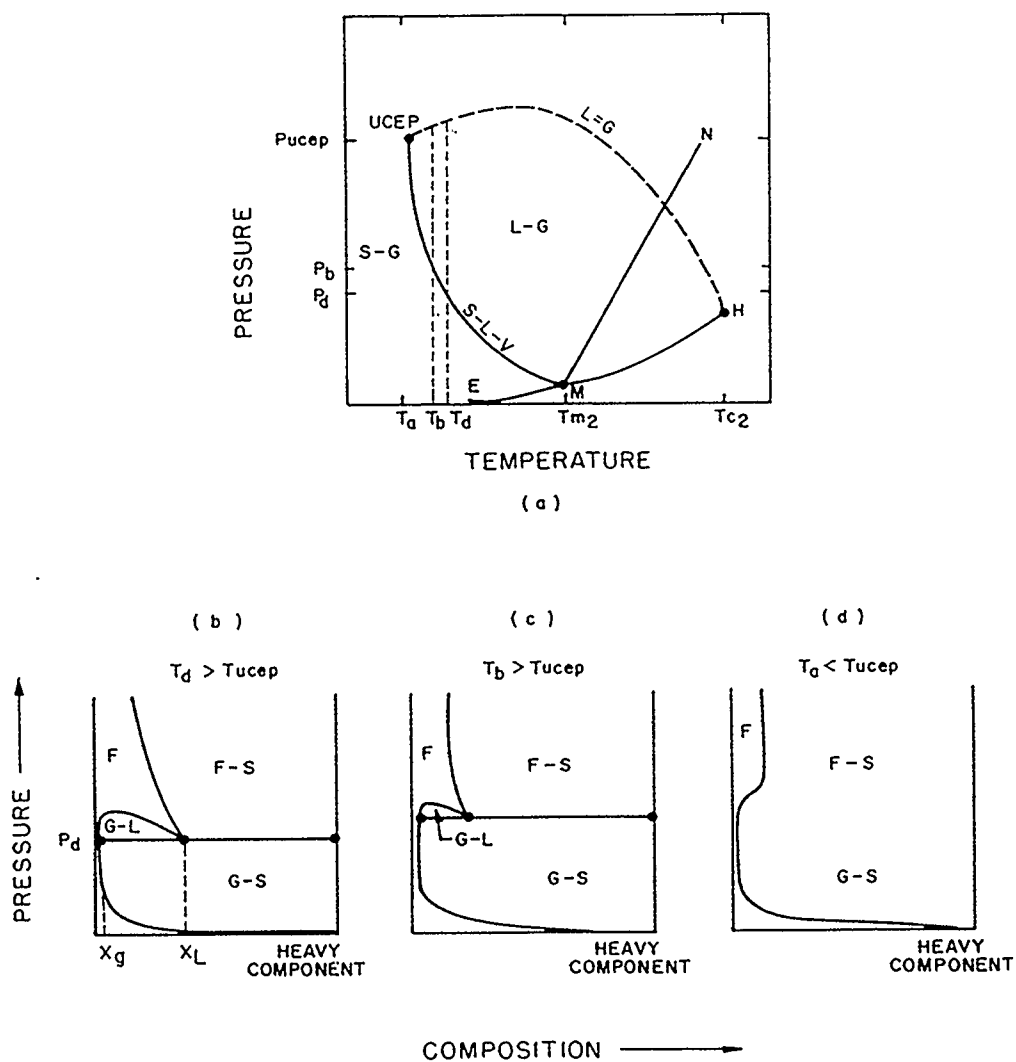


Figure 1.3 (a) Schematic P-T and (b,c,d) P-x diagrams for the ethylene - naphthalene system (McHugh, 1981)

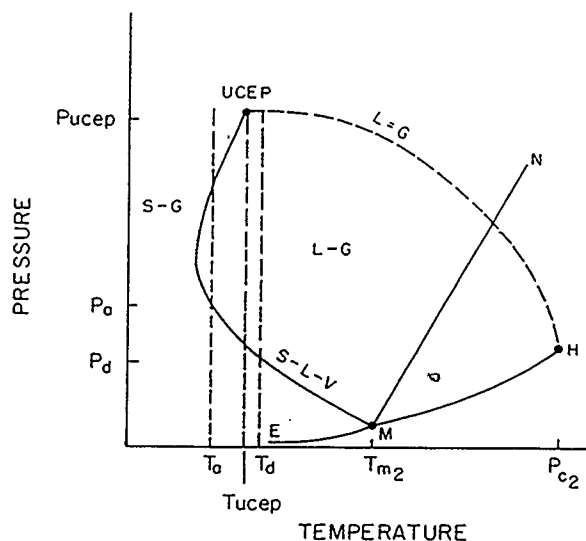
gas equilibria exist at low pressures until the three-phase SLV line is intersected. The equilibrium vapor, liquid and the solid phases are depicted as points on the horizontal tie line at pressure P_d . As the pressure is further increased a vapor-liquid envelope is observed for all mixture concentrations less than x_L . If the overall mixture composition is greater than x_L , then solid-gas equilibrium is observed as the pressure is increased above P_d .

Shown in Figure 1.3c is a solubility isotherm at a temperature, T_b , that is less than the previous temperature, T_d , but still higher than the UCEP temperature. The solubility behavior at T_b is similar to the behavior of Figure 1.3b. But at T_b the three-phase SLV line is intersected at a higher pressure, closer to the UCEP pressure. Hence the vapor-liquid envelope is diminished in size and the solid-gas equilibrium curve is shifted towards higher solvent concentrations. Shown in Figure 1.3d is a solubility isotherm at T_a , slightly less than the UCEP temperature. At this temperature, solid-gas equilibrium exists at all pressures, since the SLV line is never intersected.

It should also be mentioned that a slightly different type of solid-SCF phase behavior is also observed, in addition to the above mentioned two systems. Shown in Figure 1.4 is the P-T trace of a system with such behavior (carbon dioxide-biphenyl system). The distinguishing trait of this type of behavior is that the SLV line exhibits a temperature minimum with increasing pressure. This difference is a consequence of the extent of similarity between the components. Because of this there is a difference of solubility behavior near the UCEP, directly related to the mutual solubility of the mixture components. A more detailed discussion on the differences in behavior for the systems as shown in Figures 1.2 and 1.4 can be found elsewhere (McHugh and Krukoni, 1986).

In spite of the numerous solubility studies, in the literature very few deal with the solubilities of solid hydrocarbons in supercritical ethane. In one of the earlier works (McHugh and Yogan, 1984), the three-phase solid-liquid-gas equilibria was determined for the two systems of ethane-octacosane and ethane-biphenyl. They have observed that no large temperature minimum existed for the ethane-hydrocarbon systems, such as that found in the carbon dioxide systems. They have reported that the UCEP

Figure 1.4 Schematic P-T diagram for the carbondioxide-biphenyl system (McHugh, 1981)



for the ethane-octacosane system was at 38.9° C and 86.4 atm. The solubilities of C28-C33 paraffins in supercritical ethane have also been reported in the literature (Moradinia and Teja, 1986). The solubilities of C24-C36 in supercritical ethane were also determined later (Suleiman and Eckert, 1995) using a chromatographic technique.

The general operating conditions of the SFE process are above the critical point of the solvent. In the case of ethane the critical temperature is 32.2°C. The reported UCEP for octacosane is 38.9°C. As can be seen from Figure 1.3b, if the mixture composition is less than x_L , there is a possibility of melting the solute and solid-gas equilibria is not observed. The operating temperatures of most industrial processes involving SFE are close to the UCEP temperatures for these systems. Hence the operating temperature range is very limited. Similar behavior can happen in the case of tetracosane, though no UCEP temperature has been reported for tetracosane. The normal melting temperatures of tetracosane and octacosane are 50.6 °C and 61.2 °C respectively. Hence the possibility of melting of these solids at temperatures well below their normal melting temperatures is a serious issue, that can lead to erroneous solubility information. This kind of melting phenomenon would certainly take place in the case of static and chromatographic techniques, if the amount of solid is very small and the mixture composition is less than x_L . This could also happen in the case of dynamic techniques, if the concentration of the

solid in the mixture is low. For an accurate thermodynamic analysis of the phase behavior and solubility data, the phases in equilibrium at the time of measurement must be known.

Some of the reasons for the non-availability of solid solubilities of paraffins less than C28 in supercritical ethane are

- 1) These compounds can melt at temperatures well below their normal melting points, if the concentration of solid is low in the mixture.
- 3) Large amounts of solute would be required in the case of dynamic techniques.
- 4) Long times are required to obtain a measurement.

This problem of melting of the solute can be avoided if the concentration of the mixture is maintained above x_L . In the case of a dynamic method, one way of doing that would be to use a bigger extractor, packed with large amounts of pure solute and continuously contacted with the solvent. In this case there is an excess solid condition prevailing at all times in the extractor, which would prevent the melting of the solute. This method would provide accurate solid-SCF solubility data and would lead to an accurate thermodynamic analysis. This method was used in this work to obtain the solid solubilities of C24-C32 paraffins in supercritical ethane.

1.3.2 Modeling of solubility data

The design and evaluation of SCF processes relies heavily on the ability to predict phase behavior in these systems. The challenge to understand and predict phase behavior has led to the development of several thermodynamic models ranging from simple cubic equations to more complex perturbation theories and lattice models. A detailed description of these thermodynamic models is presented in Chapter 2.0. Most of these models rely on the assumption that the solid phase is pure and are incapable of predicting the thermophysical and thermodynamic properties of the solid phase itself. To overcome these limitations, a novel method was proposed (Salim and Trebble, 1994), by which a cubic equation of state (EOS) could be modified to allow calculations of equilibria involving solid phases as well as predict thermodynamic properties of the solid phase itself. This method is based on the principle of volume translation of a cubic EOS

at the triple point. This method is relatively simple and a standard flash algorithm can be used to calculate the phase equilibria involving the solid phase. The details of the algorithm of translation and prediction of phase equilibria involved in this method as applied to TBS(Trebbble-Bishnoi-Salim) EOS are described in Chapter 5. This method has been successfully applied to the SCF-solid systems (Salim and Trebbble, 1994; Salim, 1996) and was consequently used in this work, to model the solubility of hydrocarbons in supercritical ethane.

1.4 Objectives of this work

In view of the above mentioned scope and theoretical background, the following objectives were set for this work:

- 1) To design the experimental set-up required to measure the solid solubilities of hydrocarbons in supercritical solvents.
- 2) To validate the experimental method by measuring the solid solubilities of C28(octacosane) and C32(dotriacontane) paraffins in supercritical ethane and compare with existing data.
- 3) To determine the experimental solid solubilities of C24(tetracosane) in supercritical ethane.
- 4) To obtain the vapor-liquid TBS(Trebbble-Bishnoi-Salim) EOS parameters for these components as well as the vapor-solid parameters for the translated TBS equation (TTBS).
- 5) To model the solubility data obtained using the translated TBS EOS, by regressing the interaction parameters using a flash algorithm.

2.0 Review of Experimental and Modeling techniques in SCF phase behavior

2.1 Historical Perspective

Scientists and engineers have been aware of the enhanced solvency power of supercritical solvents for more than one hundred years, but it is only in the past two decades that such solvents have been the focus of active research and development programs. Some of the early experimental designs described in the literature attest to the creativity of the pioneers of high pressure behavior and serve as a guideline to the present studies.

The critical point of a substance was first discovered by Baron Cagniard de la Tour (1822). He used a piece of rifled cannon for his high pressure investigations and he used the discontinuities in the speed of sound to describe the critical point. He later carried out experiments in glass tubes. Among the notable earlier works, Dr. Thomas Andrews carried out an extensive investigation on the phase behavior of carbon dioxide (Andrews, 1875, 1876). He reported the critical point of carbon dioxide to be at 30.92 °C and 74 bar which is very close to the presently accepted value of 31.1°C and 73.8 bar. The ability of a supercritical fluid to dissolve low vapor pressure solids was first reported by Hanny and Hogarth at a meeting of the Royal Society of London in 1879 (Hanny and Hogarth, 1879, 1880). They carried out experiments in small glass tubes in which they observed that changes in pressure caused several inorganic salts (e.g., potassium iodide, potassium bromide) to dissolve or precipitate from ethanol at temperatures above the critical ($T_c=234^{\circ}\text{C}$).

In 1896, Villard published a review of supercritical fluid solubility phenomena (Villard, 1896). He described the ability of methane, ethylene, nitrous oxide and carbon dioxide to dissolve a number of liquid and solid hydrocarbons. Several years later, E.H.Buchner reviewed the literature and made significant additions to the experimental data base of high pressure SCF-solute mixtures (Buchner, 1906). He carried out his observations over a wide temperature range and used his observations of cloud points, freezing points and the number of phases present for his solubility determination.

Within the past ten years, a large number of authors have cited the solubility behavior of the naphthalene-ethylene system as the impetus for their own SCF studies. The features of the phase behavior of this system are evident in many other SCF-solute systems. One of the earliest works on this system was by Prins, who determined the three phase border curves and critical end points for naphthalene in both supercritical ethylene and carbon dioxide (Prins, 1915). Further investigations of naphthalene solubility slowed until the late 1940s, when Professor Scheffer began to publish extensively on ethylene-naphthalene phase behavior. In 1948, a study of the naphthalene solubility in supercritical ethylene was reported (Diepen and Scheffer, 1948 a, b). This was followed by several other papers on high pressure phase behavior by the two authors and their co-workers (van Welie and Diepen, 1961 a-e, 1963; van Hest and Diepen, 1963; Konningsveld and Diepen, 1963; de Swaan Aarons and Diepen, 1963; Konningsveld, Diepen and Chermin, 1966; Konningsveld and Diepen, 1983; Konningsveld, Kleintjens and Diepen, 1984).

In the early 1960s, the solubility of naphthalene in a variety of other gases was studied. Tsekhanskaya, Iomtev and Mushkina (1962, 1964) measured the solubilities in ethylene and carbon dioxide. Other investigators included McHugh and Paulaitis (1980), who studied the solubility of naphthalene in carbon dioxide, Kurnik, Holla and Reid (1981) who also studied naphthalene in carbon dioxide, Schmitt and Reid (1984) who studied the solubility of naphthalene in supercritical ethane, trifluoromethane and chlorotrifluoromethane and McHugh et al (1988), who studied the phase behavior of naphthalene with xenon as the solvent. Scores of other researchers investigated the solubility phenomena in supercritical solvents, but in its breadth the work of A.W. Francis surpasses his contemporaries. In a single paper in 1954, he presented an extensive quantitative study on solvent properties of liquid carbon dioxide with hundreds of compounds (Francis, 1954). He collected data for 464 ternary phase diagrams and determined the solubilities of 261 compounds in near critical carbon dioxide.

With the renewed interest in the late 1980s in SCF technology, numerous papers have been published on the phase behavior and solubility determination of SCF-solute

systems. These included both experimental and modeling methods. Some of these works will be discussed later in sections 2.3 and 2.3 specifically with reference to SCF-solid systems.

2.2 Experimental Techniques

Several experimental methods and techniques have been tried by scientists to investigate the phase behavior and to measure solubilities of a heavy liquid or solid in a SCF. Some of these are static and some are dynamic in nature. Solubilities have also been measured using spectroscopic and chromatographic techniques (Johnston, Kim and Combs, 1989; Brennecke and Eckert, 1990; Suleiman and Eckert, 1995). The most common among these is the dynamic method, in which a flow apparatus is used.

2.2.1 Dynamic Methods

The flow method described by Van Leer and Paulaitis (1980) is representative of most of the systems. A schematic of this flow apparatus is shown in Figure 2.1. This type of system contains a feed pump, an equilibrium cell, a metering valve and a solute trap. The solvent is continuously swept through the solute in the equilibrium cell and the solute leaving the extractor is collected in the solute trap after depressurising the mixture in the metering valve. There are certain other flow methods described in the literature for obtaining solubility information (Prausnitz and Benson, 1959; Kurnik, Holla and Reid, 1981; Johnston and Eckert, 1981; Krukonis and Kurnik 1985).

The flow method has certain disadvantages concerning the depressurization procedure. A precipitated solid can clog the metering valve and cause plugging in the system. To overcome this problem a simple modification was suggested by McHugh and Paulaitis (1980). They added a chromatographic switching valve to the system to obtain a sample of the SCF rich phase before it enters the heated metering valve. Another problem could arise from phase transitions occurring inside the equilibrium cell without the

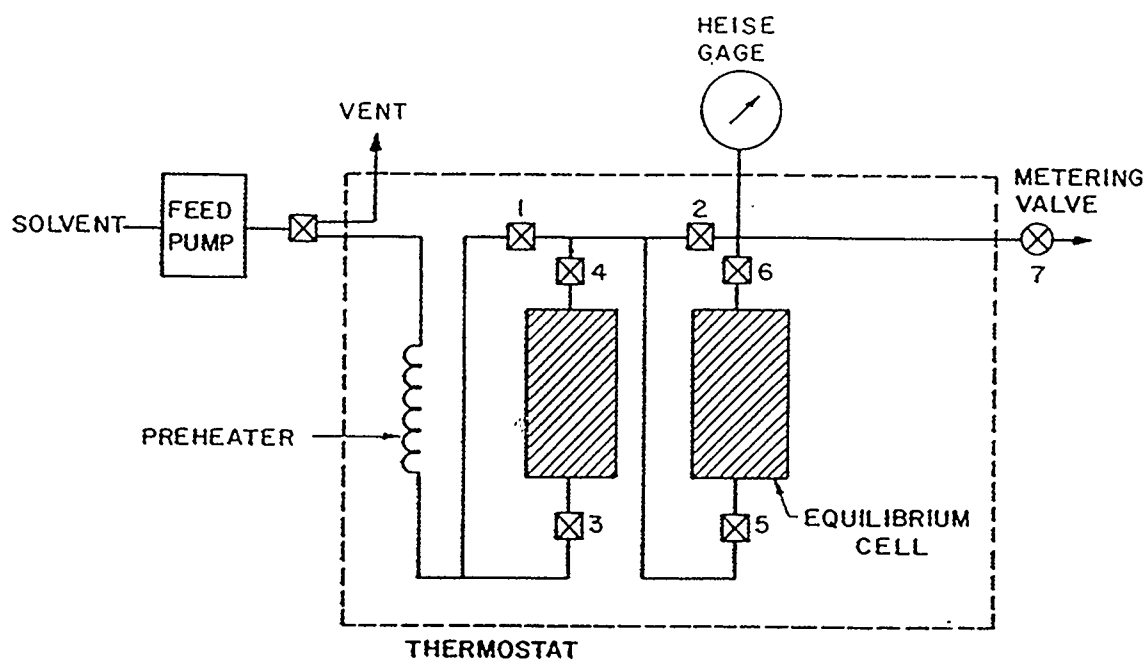


Figure 2.1 Schematic of a typical dynamic flow apparatus
(Van Leer and Paulaitis, 1980)

experimenter's knowledge. Chang and Morrell (1985) recommended using a high-pressure glass gauge packed with the heavy solute in parallel with the equilibrium cell. This would enable the visual observation of the phase transitions taking place in the equilibrium cell. A small variation of the flow technique that minimizes the residence times at high temperatures and enables the determination of tie lines for ternary mixtures was also suggested (Paulaitis, Gilbert and Nash, 1981; Hutcheson, Roebers and Thies, 1990). This apparatus is capable of operating up to 400°C and 350 bar.

2.2.2 Static Methods

Static view cells have also been used for obtaining solubility information by some researchers (McHugh, Seckner and Yogan, 1984; Seckner, McClellan and McHugh, 1988; McHugh and Guckes, 1985). A schematic of the apparatus used by McHugh, Seckner and Yogan is shown in Figure 2.2. The main component of this system is a high-pressure, variable volume view cell which allows visual determination of the phases present at equilibrium. Fixed amounts of solute and solvent are charged to the view cell and the pressure and temperature of the system are varied until phase changes are observed in the cell. A similar kind of apparatus has also been used for determining the three phase SLV line (McHugh and Yogan, 1984). Two other types of high-pressure experimental techniques involve spectroscopy and partial molar property measurements. Many researchers have begun using spectroscopic techniques to explore the strength of interactions and the local ordering, if any, in supercritical fluid mixtures (Johnston, Kim and Combs, 1989; Brennecke and Eckert, 1990; Knutson et al, 1992). Though a spectroscopic method is limited to infinitely dilute mixtures, it does provide information on intermolecular interactions in a solution. This technique is usually performed using conventional spectrophotometers interfaced with high-pressure, windowed cells. The crucial design consideration is choosing an appropriate window (Suppes and McHugh, 1989). The choice is dictated by two competing factors, the range of transmittance fixed by the window material and the amount of transmittance fixed by the window thickness. Eckert and co-workers (Eckert et al, 1986) provided a good

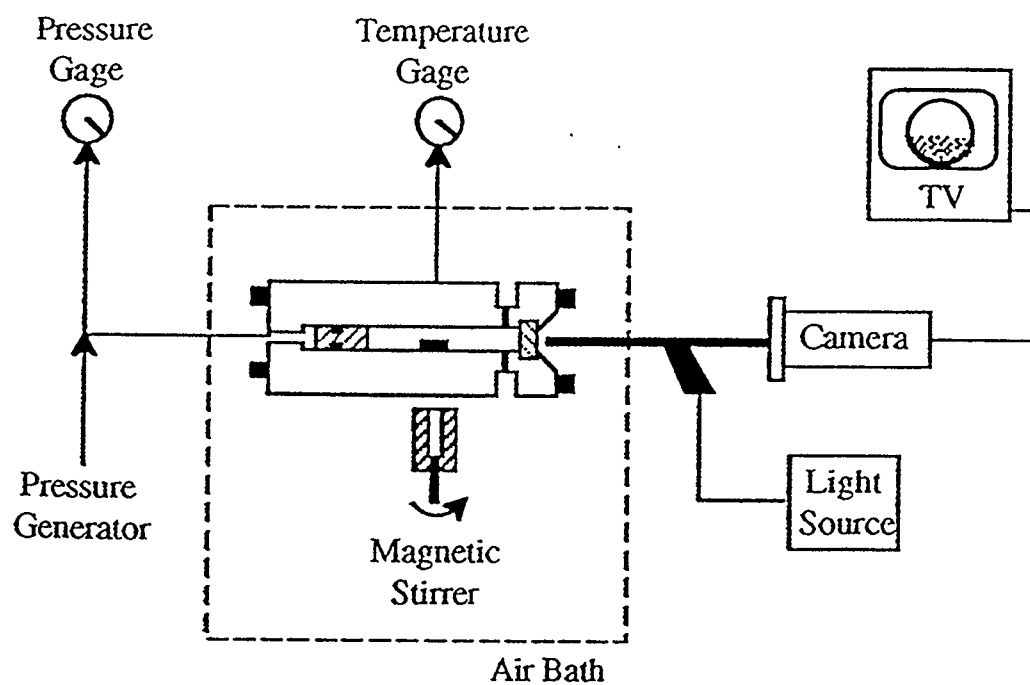


Figure 2.2 Schematic of a typical static view cell apparatus
(McHugh, Seckner and Yogan, 1984)

description of the method for obtaining partial molar property measurements. They facilitated the difficult measurement by using a vibrating tube densitometer. It is also possible to obtain partial molar volume information by using Supercritical Fluid Chromatography (SFC), if the stationary and mobile phases can be thermodynamically characterized (Shim and Johnston, 1991). Supercritical extraction was also coupled with mass spectroscopy to obtain solubility information. The solubility of solid CCl_4 in CF_4 was measured using an on-line quadrupole mass spectrometer for analyzing the mixture (Barber, Bienkowski and Cochran, 1990).

2.2.3 Miscellaneous systems studied

A new technique was proposed for measuring the solubilities of polychlorinated organics in SCF (Madras, Akgerman, and Erkey, 1993). This method was based on the principle of loading the solute from a SCF stream onto a bed of activated carbon and gravimetrically determining the amount adsorbed. However, this technique is only applicable for single component solubilities. Some recent studies focused on the solubility data of isomers in supercritical solvents using either the dynamic or static techniques with some minor modifications.. The solubility of hydroxybenzoic acid and dihydroxybenzene isomers in supercritical carbon dioxide were studied (Krukoniš and Kurnik, 1985). The solubilities of 2-3, 2-6 and 2-7 dimethylnaphthalene isomers and 2-5, 2-6 and 3-4 xlenols in supercritical carbon dioxide have also been reported (Kurnik et al, 1981; Mori et al, 1992). The solubilities of ethyllinolenate and naphthol isomers in supercritical carbon dioxide have also been studied (Tan and Weng, 1987; Lee and Kim, 1994). More recently, a flow apparatus was used to measure the solubilities of 2,3,4 methoxybenzoic acids in supercritical carbon dioxide (Chen and Tsai, 1995).

For applications in the extraction of vegetable and other oils the solubilities of heavy alkanes have also been studied. The solubilities of C_{28} and C_{30} n-alkanes in supercritical carbon dioxide were determined (McHugh et al, 1984). The solubility of nC_{28} in supercritical carbon dioxide was further investigated by several researchers (Swaid et al, 1985; Reverchon, Russo and Stassi, 1993). Some recent studies investigated

the use of hydrocarbons as supercritical solvents for extracting heavy hydrocarbons which would find applications in the petroleum industry. Most common among these are propane and ethane. Solubility data for octadecane and phenanthrene and their mixtures in supercritical propane were obtained in a flow apparatus (Dimitrelis and Prausnitz, 1989). The gas samples were analyzed using a gas chromatograph equipped with a Flame Ionization Detector (FID). The solubilities of the n-alkane series C28-C33 in supercritical ethane were studied (Moradinia and Teja, 1986,1988). They outlined the different behavior of the even and odd numbered molecules of the homologous series. They correlated the enhancement factor in the supercritical region against the carbon number in their studies. Their studies ranged from temperatures of 308.15 to 319.15 K and pressures up to 20 MPa. They have concluded that ethane is a more efficient solvent for the n-alkanes compared to carbon dioxide and that the solubilities in ethane were an order of magnitude higher.

With the renewed interest and the broadened usefulness of the supercritical fluid extraction, numerous studies have been done to study the phase behavior and solubilities of solutes in supercritical fluid solvents. Although it would be impossible to discuss details of all these works in this study it is useful to include a table of systems studied to date. Table 2.1 classifies the data on the basis of the type of solute and solvent used, the range of temperatures and pressures studied and provides the source of these data. Part of Table 2.1 has been taken from an earlier review (Foster et al, 1991). Another review paper (Bartle et al, 1991) contains the list of all the papers dealing with the solubility of low volatility solids and liquids in supercritical carbon dioxide.

Table 2.1 Solubility Data of Solutes in Supercritical Solvents**Solvent; Ethane: T_c = 305.4 K; P_c = 48.8 bar**

Solute	T (K)	P (bar)	Reference
acridine	308-343	56.1-364	Schmitt and Reid, 1986
2-aminofluorene	318-343	65.9-364	Schmitt and Reid, 1986
5-aminoindole	308	70.6-183.3	Nakatani et al., 1989
anthracene	303-343	104.4-483.5	Johnston et al., 1982
benzoic acid	308-343	54.8-363.5	Schmitt and Reid, 1986
biphenyl	308-318	70.5-281	Schmitt and Reid, 1986
cholesterol	313.1-333.1	70-190	Foster et al, 1993
n-dotriacontane	308-319	65.7-202	Moradinia and Teja, 1986
n-dotriacontane	308.2-348.2	80-240	Suleiman and Eckert, 1995
n-hexatriacontane	308.2-348.2	80-240	Suleiman and Eckert, 1995
5-hydroxyindole	308	58.6-189.8	Nakatani et al, 1989
indole	308	45.8-204.8	Sako et al., 1988
indole-3-aldehyde	308	65.9-169.5	Nakatani et al., 1989
indole-3-carboxylic acid	308	74.3-192.6	Nakatani et al., 1989
5-methoxyindole	308	52-192	Sako et al., 1989
naphthalene	293-318	35.4-276.7	Johnston et al., 1982
naphthalene	308-328	50.9-364	Schmitt and Reid, 1986
naphthalene	308	48.1-215.6	Sako et al., 1988
2-naphthol	308-343	61-364	Schmitt and Reid, 1986
1,4-naphthoquinone	308-343	63-364	Schmitt and Reid, 1986
n-nonacosane	308	64.7-202	Moradinia and Teja, 1988
n-nonacosane	308.2-348.2	80-240	Suleiman and Eckert, 1995
n-octacosane	308	65.7-202	Moradinia and Teja, 1988
n-octacosane	308.2-348.2	80-240	Suleiman and Eckert, 1995
oxindole	308	49.3-196.3	Nakatani et al., 1989
pentacosane	308.2-348.2	80-240	Suleiman and Eckert, 1995
phenanthrene	303-333	69.9-414.5	Johnston et al., 1982
phenanthrene	318-328	71-355	Schmitt and Reid, 1986
phenanthrene	313	138-551	Eisenbeiss, 1964
polystyrene	323-453	35-670	Pradhan et al, 1994
skatole	308	49.3-185	Sako et al., 1989
n-tetracosane	308.2-348.2	80-240	Suleiman and Eckert, 1995
n-triacontane	308-313	65.7-200.2	Moradinia and Teja, 1986
n-tritriacontane	308-318	64.7-202	Moradinia and Teja, 1988
n-tritriacontane	308.2-348.2	80-240	Suleiman and Eckert, 1995
triphenylmethane	303-323	69.9-380	Johnston et al., 1982

Table 2.1 (Contd..) Solubility Data of Solutes in Supercritical Solvents**Solvent; Ethylene: T_c = 282.4 K; P_c = 50.4 bar**

Solute	T (K)	P (bar)	Reference
5-aminoindole	308	65.9-191.7	Nakatani et al.,1989
anthracene	323-358	104-483.6	Johnston and Eckert, 1981
benzoic acid	318-338	120-280	Kurnik et al., 1981
2,3-dimethyl naphthalene	308-328	77-280	Kurnik et al., 1981
2,6-dimethyl naphthalene	308-328	78-280	Kurnik et al., 1981
fluorene	298-343	69.9-483.5	Johnston et al., 1982
hexa methyl benzene	298-343	63-483.4	Johnston et al., 1982
5-hydroxyindole	308	90-198.1	Nakatani et al.,1989
indole	308	57.2-204.5	Sako et al., 1988
indole-3-aldehyde	308	80.7-194.4	Nakatani et al.,1989
indole-3-carboxylic acid	308	80.7-185.2	Nakatani et al.,1989
5-methoxyindole	308	72.4-185	Sako et al., 1989
naphthalene	285-308	38.5-114.3	Diepen and Scheffer, 1948
naphthalene	285-333	41.1-274	Diepen and Scheffer, 1948
naphthalene	285-318	50.7-304	Tsekhanskaya et al., 1964
naphthalene	298-323	56.1-173.4	Johnston and Eckert, 1981
naphthalene	308	59-197.5	Sako et al., 1988
oxindole	308	75.2-192.6	Nakatani et al.,1989
phenanthrene	318-338	120-280	Kurnik et al., 1981
phenanthrene	298-343	56.1-276.7	Johnston and Eckert, 1981
phenanthrene	298-343	276.7-311.3	Johnston et al., 1982
phenanthrene	313	138-551	Eisenbeiss, 1964
pyrene	318-348	83.7-483.5	Johnston et al., 1982
skatole	308	71.4-191	Sako et al., 1989

Table 2.1 (Contd..) Solubility Data of Solutes in Supercritical Solvents**Solvent; Carbon Dioxide: T_c = 304.2 K; P_c = 73.8 bar**

Solute	T (K)	P (bar)	Reference
acridine	308-343	101.6-364.1	Schmitt and Reid, 1986
acridine	308	119.5-349.5	Dobbs et al., 1987
adamantane	340-400	100.3-1000	Swaid et al., 1985
2-aminobenzoic acid	308	119.5-349.5	Dobbs et al., 1987
2-aminofluorene	318-343	116-364	Schmitt and Reid, 1986
2-aminoindole	308	82.6-184.3	Nakatani et al., 1989
2-aminopyrazine	308.15	63-195	Nakatani, 1991
anthracene	303-343	90.6-414.5	Johnston et al., 1982
anthracene	294-473	52-900	Robling and Franck, 1983
anthracene	313	100-200	Kwiatowski et al., 1984
anthracene	293-368	69-1156	Zerda et al., 1986
anthracene	308	120-350	Dobbs and Johnston, 1987
anthracene	313-473	150-400	Miller and Hawthorne, 1995
anthracene	308-318	104-277	Kosal and Holder, 1987
arachidyl alcohol	308.15	9-237	Iwai et al, 1993
behenic acid	313-333	81-253	Chrastil 1982
benzoic acid	318-338	120-280	Kurnik et al., 1981
benzoic acid	308-343	101-364.1	Schmitt and Reid, 1986
benzoic acid	308	120-280	Dobbs et al., 1987
benzoic acid	313-323	60.8-106	Sunol et al, 1995
biphenyl	308.8-330.5	106-490	McHugh and Paulaitis, 1980
biphenyl	328	510-538	Paulaitis et al., 1983
caffeine	323-433	50-250	Ebeling and Franck, 1984
caffeine	313-353	200-350	Johannsen and Brunner, 1994
caffeine	323-368	80-300	Varadarajan and Hartland, 1991
carbazole	313	100-200	Kwiatkowski et al., 1984
b-carotene	313-343	212-439	Cygnarowicz et al., 1990
p-chlorophenol	309	81-240	Van Leer and Paulaitis, 1980
2-chloropyrimidine	308.15	63-195	Nakatani, 1991
cholesterol	313-353	101-202.6	Chrastil, 1982
cholesterol	308-333	100.9-278.9	Wong und Johnston, 1986
cholesterol	313.4-333	100-250	Yun et al., 1991
DDT	313-333	104-207.9	Foster and Macnaughton, 1994
n-decane	293-343	10-150	Peng et al, 1992
diacetoxyscirpenol	334.6	80-138	Smith et al., 1987
dibenzothiophene	309-338	76.8-276.8	Mitra and Chen, 1988
4,4-dichlorobiphenyl	308.1-323.1	90-480	Enping Yu et al., 1995

Table 2.1 (Contd..) Solubility Data of Solutes in Supercritical Solvents

Solvent; Carbon Dioxide: $T_c = 304.2$ K; $P_c = 73.8$ bar

Solute	T (K)	P (bar)	Reference
2,4-dichlorophenol	309	80.3-206	Van Leer and Paulaitis, 1980
o-dihydroxybenzene	328	310	Krukoni and Kurnik, 1985
m-dihydroxybenzene	328	310	Krukoni and Kurnik, 1985
p-dihydroxybenzene	328	310	Krukoni and Kurnik, 1985
2,3-dimethyl naphthalene	308-328	99-280	Kurnik et al., 1981
2,6-dimethyl naphthalene	308-328	96-280	Kurnik et al., 1981
diphenylamine	305.2-310	40.5-203	Tsekhanskaya and Mushkina, 1962
n-dotriacontane	308	91.6-161	King et al., 1983
n-dotriacontane	308.2-338.2	50.3-208.9	Yau and Tsai, 1993
eicosanoic acid	308.2-328.2	37.5-212.6	Yau and Tsai, 1994
1-eicosanol	308.2-328.2	37.5-212.6	Yau and Tsai, 1994
ergosterol	308	250.8-276.7	Wong and Johnston, 1986
fluorene	303-343	69.9-483.5	Johnston et al., 1982
fluorene	313	100-200	Kwiatowski et al., 1984
fluorene	308-328	78.3-254	Bartle et al., 1990
hexachlorobenzene	298-318	111.5	Madras et al., 1993
hexachloroethane	308-328	97-280	Kurnik et al., 1981
2,2,3,3,4,4,-hexachlorobiphenyl	308.1-323.1	90-480	Enping Yu et al., 1995
1-hexadecanol	318-338	141.8-415.9	Kramer and Thodos, 1988
hexadecanol	308	81-218	Iwai et al, 1991
hexamethylbenzene	303-343	69.9-483.5	Johnston et al., 1982
hexamethylbenzene	308	150-350	Dobbs et al., 1986
hexatriacontane	308.2-338.2	50.3-208.9	Yau and Tsai, 1993
o-hydroxybenzoic acid	373	204-409	Krukoni and Kurnik, 1985
o-hydroxybenzoic acid	308-328	81-202.6	Gurdial and Foster, 1985
m-hydroxybenzoic acid	373	204-409	Krukoni and Kurnik, 1985
m-hydroxybenzoic acid	308-328	81-202.6	Gurdial and Foster, 1991
p-hydroxybenzoic acid	373	204-409	Krukoni and Kurnik, 1985
p-hydroxybenzoic acid	308-328	81-409	Gurdial and Foster, 1991
5-hydroxyindole	308	88.2-185.2	Nakatani et al., 1989
4-hydroxypyrimidine	308.15	63-195	Nakatani, 1991
indole-3-aldehyde	308	78.9-158.4	Nakatani et al., 1989
indole-3-carboxylic acid	308	91.8-193.5	Nakatani et al., 1989
menthol	308-328	67-116	Sovova and Jez, 1994
2-mercaptopyrimidine	308.15	63-195	Nakatani, 1991
2-methoxybenzoic acid	308.2-328.2	99.6-246.9	Chen and Tsai, 1995
3-methoxybenzoic acid	308.2-328.2	99.6-246.9	Chen and Tsai, 1995

Table 2.1 (Contd..) Solubility Data of Solutes in Supercritical Solvents

Solvent; Carbon Dioxide: Tc = 304.2 K; Pc = 73.8 bar

Solute	T (K)	P (bar)	Reference
4-methoxybenzoic acid	308.2-328.2	99.6-246.9	Chen and Tsai, 1995
5-methoxyindole	308	79.8-184	Sako et al., 1989
2-methoxynaphthalene	313-323	60.8-106	Sunol et al, 1995
m-methoxyphenylacetic acid	308.2	110-340	Lee and Kim, 1994
o-methoxyphenylacetic acid	308.2	110-340	Lee and Kim, 1994
p-methoxyphenylacetic acid	308.2	110-340	Lee and Kim, 1994
5-methoxy-1-tetralone	308	83-275	Chang and Morrell, 1985
6-methoxy-1-tetralone	308	83-277	Chang and Morrell, 1985
7-methoxy-1-tetralone	308	85-276	Chang and Morrell, 1985
methyl m-nitrobenzoate	308	83-277	Chang and Morrell, 1985
methyl p-nitrobenzoate	308	83-272	Chang and Morrell, 1985
methyl oleate	323-333	172-309	Nilsson et al, 1991
monocrotaline	308-328	88.6-274.1	Schaeffer et al., 1988
myristic acid	308	81-218	Iwai et al, 1991
naphthalene	307-318	40.5-209	Tsekhanskaya and Mushkina, 1962
naphthalene	308-328	60.8-334	Tsekhanskaya et al., 1964
naphthalene	297-346	1-132	Najour and King, 1966
naphthalene	308-337.9	82.2-291.4	McHugh and Paulaitis, 1980
naphthalene	308	81-125.1	King et al., 1983
naphthalene	309-328	75-277	Mitra and Chen, 1988
naphthalene	308	121.8-204	Sako et al., 1988
naphthalene	308-328	105	Madras et al., 1993
naphthalene	293-343	10-150	Peng et al, 1992
naphthalene	313-323	60.8-106	Sunol et al, 1995
1-naphthol	308-328	92.2-172.2	Tan and Weng, 1987
2-naphthol	308-343	102.8-363.6	Schmitt and Reid, 1986
2-naphthol	308-328	92.2-172.2	Tan and Weng, 1987
2-naphthol	308	120-350	Dobbs et al., 1987
1,4-naphthoquinone	318-343	100.8-364	Schmitt and Reid, 1986
neopentane	310-313.5	62.9-104.4	Rowley et al, 1990
nitrendipine	333-373	100-300	Knez et al, 1995
octacosane	323-362	204.5-810	Swaid et al., 1985
octacosane	35-45	80-275	Reverchon et al., 1993
octacosane	308.2-338.2	50.3-208.9	Yau and Tsai, 1993
1-octadecanol	318-338	139.9-452.8	Kramer and Thodos, 1989
oleic acid	323-333	172-309	Nilsson et al, 1991
mono-olylglycerol	323-333	172-309	Nilsson et al, 1991

Table 2.1 (Contd..) Solubility Data of Solutes in Supercritical Solvents

Solvent; Carbon Dioxide: Tc = 304.2 K; Pc = 73.8 bar

Solute	T (K)	P (bar)	Reference
di-olylglycerol	323-333	172-309	Nilsson et al, 1991
tri-olylglycerol	323-333	172-309	Nilsson et al, 1991
oxindole	308	85.4-188.9	Nakatani et al., 1989
palmitic acid	318-338	142.1-574.8	Kramer and Thodos, 1988
palmitic acid	308	81-218	Iwai et al, 1991
pentachlorophenol	298-318	111.5	Madras et al., 1993
phenanthrene	313	138-551	Eisenbeiss, 1964
phenanthrene	318-338	120-280	Kurnik et al., 1981
phenanthrene	303-343	80.9-414.5	Johnston et al., 1982
phenanthrene	313	100-200	Kwiatowski et al., 1984
phenanthrene	308	100-350	Dobbs et al., 1986
phenanthrene	308-328	78.3-254	Bartle et al., 1990
phenanthrene	313-323	60.8-106	Sunol et al, 1995
phenol	309	79.3-249.4	Van Leer and Paulaitis, 1980
phenylacetic acid	308-318	83.5-191	Wells et al., 1990
α -pinene	313-328	50-120	Richter and Sovova, 1993
pyrene	308-343	83.6-483.4	Johnston et al., 1982
pyrene	308-328	80.4-254	Bartle et al., 1990
skatole	308	75.2-190	Sako et al., 1989
stearic acid	318-338	145.4-467.5	Kramer and Thodos, 1989
stearic acid	308.15	9-237	Iwai et al, 1993
stearyl alcohol	308.15	9-237	Iwai et al, 1993
steroids	308-373	84-231	Dean et al, 1995
stigmasterol	308-333	91.1-304	Wong and Johnston, 1986
2,3,4,5-tetrachlorobiphenyl	308.1-323.1	90-480	Enping Yu et al., 1995
tetracosane	308.2-338.2	50.3-208.9	Yau and Tsai, 1993
theobromine	313-353	200-350	Johannsen and Brunner, 1994
theobromine	323-368	80-300	Varadarajan and Hartland, 1991
theophylline	313-353	200-350	Johannsen and Brunner, 1994
triacontane	35-45	80-275	Reverchon et al., 1993
tripalmitin	313-473	150-400	Miller and Hawthorne, 1995
triphenyl-methane	303-323	69.9-414.5	Johnston et al., 1982
vanillin	315-329	80-200	Billoni et al., 1988
vanillin	308-318	83-195	Wells et al., 1990
cis-verbanol	313-328	50-120	Richter and Sovova, 1993
2,5-xilenols	308	74-267	Iwai et al. 1990
2,6-xilenols	308	103-207	Iwai et al. 1990

Table 2.1 (Contd..) Solubility Data of Solutes in Supercritical Solvents**Solvent; Chlorotrifluoromethane: T_c = 301.9 K; P_c = 39.2 bar**

Solute	T (K)	P (bar)	Reference
acridine	318-328	67-341	Schmitt and Reid, 1986
2- aminofluorene	328-343	79.5-241	Schmitt and Reid, 1986
benzoic add	318-323	60.5-357.9	Schmitt and Reid, 1986
naphthalene	308-328	50.1-360.3	Schmitt and Reid, 1986
2-naphthol	323-343	73-364	Schmitt and Reid, 1986
1,4-naphthoquinone	318-328	56.3-364	Schmitt and Reid, 1986
phenanthrene	318-328	75.5-301	Schmitt and Reid, 1986

Solvent; Fluoroform: T_c = 299.2 K; P_c = 49.5 bar

Solute	T (K)	P (bar)	Reference
acridine	318-328	65.5-353	Schmitt and Reid, 1986
2-aminofluorene	328-343	91.03-364	Schmitt and Reid, 1986
5- aminoindole	308	65.9-189.8	Nakatani et al., 1989
anthracene	328-343	91.8-299	Schmitt and Reid, 1986
benzoic acid	318-328	65.5-341	Schmitt and Reid, 1986
5-hydroxyindole	308	48.3-189.8	Nakatani et al., 1989
indole	308	54.2-174	Sako et al., 1989
indole-3-aldehyde	308	85.4-184.3	Nakatani et al., 1989
indole-3 carboxylic acid	308	82.6-174.1	Nakatani et al., 1989
5-methoxyindole	308	58.5-191	Sako et al., 1989
naphthalene	308-328	60.5-351.4	Schmitt and Reid, 1986
2-naphthol	328-343	79-364	Schmitt and Reid, 1986
1,4-naphthoquinone	318-328	66-356	Schmitt and Reid, 1986
oxindole	308	80.7-181.5	Nakatani et al., 1989
phenanthrene	318-328	80-364	Schmitt and Reid, 1986
skatole	308	54.1-181	Sako et al., 1989

Table 2.1 (Contd..) Solubility Data of Solutes in Supercritical Solvents**Solvent; Methane: $T_c = 190.4$ K; $P_c = 46.0$ bar**

Solute	T (K)	P (bar)	Reference
n-dotriacontane	293.2-423.2	120-240	Suleiman and Eckert, 1995
n-eicosane	293.2-423.2	120-240	Suleiman and Eckert, 1995
n-hexatriacontane	293.2-423.2	120-240	Suleiman and Eckert, 1995
n-nonacosane	293.2-423.2	120-240	Suleiman and Eckert, 1995
n-octacosane	293.2-423.2	120-240	Suleiman and Eckert, 1995
n-pentacosane	293.2-423.2	120-240	Suleiman and Eckert, 1995
n-tetracosane	293.2-423.2	120-240	Suleiman and Eckert, 1995
n-tritriacontane	293.2-423.2	120-240	Suleiman and Eckert, 1995

Solvent; Propane: $T_c = 369.85$ K; $P_c = 42.5$ bar

Solute	T (K)	P (bar)	Reference
phenanthrene	390-420	35-60	Prausnitz and Dimitrelis, 1989
polystyrene	323-453	35-670	Pradhan et al, 1994
octadecane	390-420	35-60	Prausnitz and Dimitrelis, 1989

Solvent; Trifluoromethane: $T_c = 299.9$ K; $P_c = 48.3$ bar

Solute	T (K)	P (bar)	Reference
griseofulvin	313-333	120-330	Reverchon et al, 1995

Solvent; Tetrafluoromethane: $T_c = 227.6$ K; $P_c = 37.4$ bar

Solute	T (K)	P (bar)	Reference
tetrachloromethane	226-250	15-315	Barber and Bienkowski, 1990

2.3 Applications to EOR processes

The strong ability of SCFs to extract low volatility materials from various mixtures has led researchers to investigate the effects of SCFs on Enhanced Oil Recovery (EOR) processes. Experimental methods have been developed to study the solubilities of narrow-boiling, heavy fossil-fuel fractions in a compressed methane+water mixture (Monge and Prausnitz, 1983). The use of supercritical propane and toluene in the extraction of oil from Athabasca oil sands has also been investigated (Eisenbach et al, 1983). More recently, supercritical cyclohexane and pentane were also used for fractionation of asphalt materials (Jemison et al, 1995). Three different asphalts were fractionated into ten fractions and characterised by a variety of analyses. They found that reblending of these fractions showed improved aging characteristics. Several other studies have been carried out on the fractionation ability of supercritical solvents (Stegeman et al, 1991; 1992). Being relatively easier to handle and generally more economical to use than other solvents at supercritical conditions, carbon dioxide has been widely used as a solvent for EOR processes. Orr et al. (1981) have studied the phase behavior of mixtures of carbon dioxide with a synthetic oil composed of C5, C10, C16 and C30 at 37.8°C and pressures ranging from the bubble point of the oil to about 13 MPa (Orr et al, 1981). Orr et al. (1983) subsequently used both continuous multiple contact and slim-tube displacement tests to study the phase behavior and pressure-volume-temperature relation of carbon dioxide+crude oil mixtures at 32°C, which is slightly above the critical temperature of carbon dioxide. Experimental studies of phase equilibria of a number of carbon dioxide+bitumen systems have been reported by different researchers (Svrcek and Mehrotra, 1982; Mehrotra and Svrcek, 1984, 1985a, b, 1988; Yu et al, 1989; Xu and Hepler, 1990; Huang and Radosz, 1990). However there are only few isolated measurements in the SCF carbon dioxide region. Moreover, as the emphasis has generally been laid upon the bitumen-rich phase, the vapor-rich phase composition data are sparse and hydrocarbon contents of the vapors are usually assumed to be negligible. Recently an apparatus for measuring the phase equilibrium of heavy hydrocarbons in carbon dioxide has been developed (Han et al, 1992). The apparatus can be used to measure the solubility

of gas in a liquid and that of liquid in a gas at temperatures ranging from 20°C to 70°C and system pressures up to 150 bar. The solubilities of n-decane and naphthalene in carbon dioxide were measured. Among the later studies, the phase behavior of carbon dioxide and crude oil mixtures has been reported (Hwang et al, 1995). They used a continuous multiple-contact SCF extraction system to study the predominantly paraffin crude oil. They have found that the earlier extracts contained lighter compounds. Also as the extraction proceeds relatively greater amounts of paraffinics and lesser amounts of aromatics and naphthenics are extracted. In an earlier study involving bitumen and bitumen derived liquids (Deo, Hwang and Hanson, 1992) supercritical propane was used as the solvent. They found that higher oil yields were obtained at lower solvent reduced densities when the extraction temperatures were in the vicinity of the pure solvent critical temperatures.

Among the more recent studies (Suleiman and Eckert, 1995a, 1995b) the phase equilibria of alkanes in natural gas systems (methane and ethane) were studied. They have used a new chromatographic technique to measure solubilities for several n-alkanes C7-C34 in methane in the range 293.2°C to 423.2°C and 120-240 bar and for C24-C36 in ethane from 308.2°C to 348.2°C and 80-240 bar. The chromatographic system used in this investigation works best for low solubilities (10^{-2} mole fraction).

2.4 Modeling the SCF-Solid Phase Equilibria

The ability to understand and ultimately predict the phase behavior of SCF-solid systems is challenging and important due to the complexity in their molecular behavior. There are primarily four challenges in predicting the phase behavior in the SCF state (Johnston et al, 1989b). (1) The vapor pressure is the most important indicator of solubility; however it is often unavailable for relatively non-volatile solids. (2) The EOS must predict densities accurately in the critical region. (3) SCF solutions are often highly asymmetric in that there are huge differences in the sizes and energies of the components (4) The solutions are highly compressible, which leads to solvent condensation or clustering about the solute even in non-polar systems. This section introduces a number of theoretically based and empirical models which attempt to address these difficulties.

The phase equilibria between a SCF and the solute is obtained by equating the fugacities of the two phases.

$$f_i^{SCF} = f_i^S \quad (2.1)$$

In case of a solid compound in equilibrium with a supercritical solvent, the solubility of the fluid in the solid phase is generally considered negligible. The solid phase is considered to be incompressible in normal working conditions. In this instance, the fugacity of component *i* as a pure solid phase (denoted by superscript S) is given by

$$f_i^S(T, P) = P_i^{sat}(T) \phi_i^{sat}(T) \exp\left(\frac{1}{RT} \int_{P_i^{sat}}^P v_i^S dP\right) \quad (2.2)$$

The exponential term in equation (2.2) is the poynting factor and the fugacity coefficient ϕ_i^{sat} is a correction term for high saturation pressures. It can be set equal to unity in solid-SCF systems since the saturation pressure of a crystalline solid is much less than 1 bar.

The molar volume of the crystalline solid usually remains constant up to high pressures so that the exponential term in equation (2.2) can be simplified to

$$\exp\left[\frac{(P - P_i^{sat}) v_i^S}{RT}\right] \quad \text{which leads to}$$

$$f_i^S(T, P) = P_i^{sat}(T) \exp \left[\frac{(P - P_i^{sat}) v_i^S}{RT} \right] \quad (2.3)$$

The fugacity of a solute in the fluid phase can be described by a ‘compressed gas’ or an ‘expanded liquid’ model. The compressed gas model uses the fugacity coefficient (denoted by the superscript SCF) to model the fugacity of the solute in the fluid phase.

$$f_i^{SCF}(T, P, y_i) = y_i \phi_i^{SCF} P \quad (2.4)$$

The expression for the solubility of a heavy non-volatile solid in the supercritical fluid solvent phase is obtained by setting equations (2.3) and (2.4) equal.

$$y_i = \frac{P_i^{sat}(T) \exp \left[\frac{(P - P_i^{sat}) v_i^S}{RT} \right]}{\phi_i^{SCF} P} \quad (2.5)$$

In the expanded liquid model (Mackay and Paulaitis, 1979), the fugacity is given by :

$$f_i^L = x_i \gamma_i(P^0, x_i) f_i^{OL}(P^0) \exp \left(\int_0^P \frac{v_i}{RT} dP \right) \quad (2.6)$$

where $\gamma_i(P^0, x_i)$ is the activity coefficient at the reference pressure, and $f_i^{OL}(P^0)$ is the reference liquid fugacity. Although the models are similar, the expanded liquid has a practical advantage. Since the reference state can be chosen to give exact results at a pressure in the dense near-critical region the equation of state can be calibrated in this region. For the compressed gas model, the reference state is at zero pressure, requiring the equation of state to be accurate from zero pressure through the critical region- a stringent requirement. A limitation in the expanded liquid model is that few techniques have been developed to calculate the reference activity coefficient. The compressed gas model does not require this type of additional parameter and therefore has been adopted predominantly in the literature.

2.4.1 Cubic Equations Of State and Mixing rules:

The fugacity coefficient of the solute in the supercritical phase is usually determined by a suitable equation of state. Cubic equations of state along with mixing rules are commonly used for correlating the experimental data (Mackay and Paulaitis, 1979, Kurnik and Reid, 1982, Debenedetti and Kumar, 1986). The most commonly used cubic EOS is the Peng-Robinson EOS with quadratic mixing rules. The ratio of the actual solubilities in a SCF phase reaches several orders of magnitude compared to ideal solubilities. There are several limitations to this approach. First, cubic equations of this type do not represent the behavior of the pure fluid near the critical point (Levelt-Sengers et al, 1986). Also the unlike pair interaction parameter, k_{ij} must be correlated from experimental data. It has been found that the unlike pair interaction parameter K_{ij} which is used in the following quadratic mixing rules, does not follow trends based on physical properties (Wong et al, 1985). The reason for this is that the pure component critical temperatures are so far apart that k_{ij} is required to account for a large correction to the geometric mean.

Quadratic mixing rules:

$$a = \sum_i \sum_j y_i y_j a_{ij} \quad (2.7)$$

$$b = \sum_i \sum_j y_i y_j b_{ij} \quad (2.8)$$

and the combining rules are

$$a_{ij} = (a_i a_j)^{1/2} (1 - k_{ij}) \quad (2.9)$$

$$b_{ij} = \frac{(b_i + b_j)}{2} (1 - l_{ij}) \quad (2.10)$$

where a_i , b_i are calculated from pure component parameters and k_{ij} and l_{ij} are adjustable interaction parameters. If $l_{ij} = 0$

$$b = \sum y_i b_i \quad (2.11)$$

A review of the thermodynamic modeling of supercritical mixtures by equations of state (EOS) of the cubic type is available (Johnston et al, 1989b). In another work, nine

different equations of state have been tested for supercritical extraction calculations (Haselow et al, 1986). They concluded that the traditional van der Waals mixing rules cannot yield good predictions and there is a need for the development of better mixing rules.

Other mixing rules, such as conformal solution mixing rules, have been developed for these equations of state and applied to solid fluid equilibria (Park et al, 1987). With these improved mixing rules it was found that the solubility data were correlated very accurately in the dense region above the critical point and that the interaction parameters were independent of temperature. This model requires three parameters per binary. Recently, the energy parameter has been determined by equating the excess free energy calculated from the EOS to that from a UNIFAC group contribution liquid model (Sheng et al, 1992). These mixing rules were found to correlate the solubilities of five organics in carbon dioxide satisfactorily. Recently, an 'excess function - equation of state' model was applied to the solubility of hydrocarbon solids in carbon dioxide (Barna et al, 1994). This model is based on the relations which exist between the Helmholtz energy of pure components and the excess Helmholtz energy in a mixing process at constant packing fraction. The expression of Van Laar was used for the residual term of the excess function. They used several cubic equations of state and volume corrected cubic equations of state and concluded that the best results for calculations of solubility were obtained by using precise equations of state for each compound. Another recent study (Spiliotis et al, 1994) involved the prediction of solubility of aromatic hydrocarbons in supercritical carbon dioxide with EOS/ G^E (excess function - equation of state) models. The solubilities of liquid and solid aromatic hydrocarbons were predicted using the recently proposed LCVM model (Boukouvalas, 1994) and the MHV2 (Dahl and Michelsen, 1990; Dahl et al. 1991) models. Satisfactory results were obtained using the LCVM model. With regard to sensitivity of solubility predictions, they concluded that the uncertainty in the critical properties of the heavy compounds can cause erroneous results.

A 'covolume dependent' mixing rule was developed by Rao and Mukhopadhyay (1988) for the attraction parameter given by

$$a = b^{3/2} \sum_i \sum_j y_i y_j \frac{a_{ij}}{b_{ij}^{3/2}} \quad (2.12)$$

which was applied to the Peng-Robinson equation of state. The rationale behind this mixing rule is that the calculated solubilities are less sensitive with respect to the binary interaction parameters, which improves the predictive capability of the model. The inability of conventional mixing rules to represent certain phase behavior has led to the concept of combining the mixing rules with ideality deviation. It can be said that there is a correlation between the two methodologies at infinite pressure (Vidal, 1978) as shown by the following equation for a modified van der Waals equation (SRK or PR):

$$g^E(T, P \rightarrow \infty) = - \left(\frac{a}{b} - \sum_i x_i \frac{a_{ii}}{b_i} \right) \lambda \quad (2.13)$$

where λ is a numerical constant based on the equation of state used. Therefore, in the field of equations of state, advantage can be taken of proven models for conventional liquid phases. For example, local compositions take into consideration the heterogeneity inside a homogeneous liquid phase. In the vicinity of a center of attraction, the composition may be different from the mean value. Such local composition mixing rules, will be expressed as a function of energies of molecular interaction, and a mixing rule was deduced (Huron and Vidal, 1979) for systems containing polar constituents.

$$a = b \sum_i x_i \left[\frac{a_{ii}}{b_{ii}} - \sum_j \frac{x_j b_j \exp\left(\frac{-\alpha_{ij} c_{ji}}{RT}\right) c_{ij}}{\sum_k x_k \exp\left(\frac{-\alpha_{ik} c_{ki}}{RT}\right)} \frac{1}{\lambda} \right] \quad (2.14)$$

It was shown that this mixing rule represents the solubility of naphthalene in ethylene accurately (Won, 1983). One problem with this model is that it risks predicting false liquid-liquid insolubilities in the critical zone (Vidal, 1984).

It has been quite logically proposed (Mollerup, 1981; Whiting and Prausnitz, 1982) that consideration be given to the influence of density on local compositions;

$$x_{ji} = \frac{x_j \exp\left(-\frac{\alpha v_{ji}}{RT}\right)}{\sum_k x_k \exp\left(-\frac{\alpha v_{ki}}{RT}\right)} \quad (2.15)$$

with

$$v_{ji} = -\frac{a_{ji} b_{ii}}{b_{ji} v} \quad (2.16)$$

which leads to an EOS containing an exponential density term. The theories discussed earlier do not consider the fact that local compositions of polar solvents near polar solutes will deviate from the bulk compositions more so than in nonpolar systems, especially in regions where there are large compressibilities. To account for this effect, these mixing rules have been applied to several supercritical systems (Johnston et al, 1987). The local composition concept is that the concentration of the molecules in the first coordination shell about a central molecule may deviate from the bulk values because of the differences in the interaction energies and the sizes of the constituents. The model treats the polar and non-polar components of the pair attraction energies in the short and long range terms in a new way so that the local composition effects on the free energy are not overpredicted. As a result, the model has been used to correlate phase equilibria of both non-polar and polar systems more effectively. The VDW1 mixing rule, which describes long range interactions has been used successfully to correlate solid-fluid equilibria data of polar and non-polar binary systems (Kurnik et al, 1981; Johnston, 1984) and to predict such data for non-polar systems using no adjustable pair parameters (Johnston et al, 1982; Wong et al, 1985). In order to use this concept the chemical potential is separated into the relevant terms so that

$$RT \ln(\phi_i z) = \mu_i^{rep} - \mu_i^{ig} + \mu_i^{sr} + \mu_i^{lr} \quad (2.17)$$

where $z = Pv/RT$ and rep, ig, sr and lr stand for repulsive, ideal gas, short range and long range respectively. In the work of Johnston et al (1987) the long range attractive part of the chemical potential was obtained from a modified augmented Van der Waals (AVDW) equation of state along with the VDW1 mixing rule for the attraction parameter. This model uses the best features of the two models. Several solutes were studied with carbon

dioxide and ethylene as solvents. The solubility data in carbon dioxide was correlated with an average AAD of 18.6% and 15.0% for the polar and non-polar solutes respectively. A more recent work (Chen et al, 1995), used the PR EOS with a modified mixing model to calculate the solubilities of solids in carbon dioxide and cosolvents. The mixture parameters of the equation of state are determined from a modified Huron-Vidal (HV) mixing model with a volume correction term. They have correlated the volume correction term with the solid volume. Satisfactory results were obtained in the binary systems and the ternary systems with cosolvents.

A cubic equation of state was proposed for polar fluids that is potentially superior to the P-R and RK equations (Patel and Teja, 1982). It was applied to a series of solid n-alkanes in supercritical ethane (Moradinia and Teja, 1987).

2.4.2 Empirical and Semi-empirical Correlations:

Empirical correlations are used to minimize the experimental effort required for determination of solubility at high pressure by methods of correlation and prediction. There are several simple expressions available in the literature for calculating concentration of solutes in supercritical fluids. The virial equation of state, limited to the second virial coefficient was used to arrive at the following equation (Robin and Vodar 1953).

$$\log m = A + B\rho \quad (2.18)$$

where m is the mass of the solute in g/cc of the compressed gas and ρ is the density of the gas. A and B are constants.

Regular solution theory was applied (Czubryt et al, 1970) to arrive at the following correlation

$$\log y = a + b\delta + c\delta^2 \quad (2.19)$$

where y is the mole fraction of the solute and δ is the solubility parameter of the solute.

A direct relationship between the concentration of a solute in a compressed gas (denoted by c), and the gas density (denoted by ρ), was later proposed (Stahl et al, 1978).

$$\ln c = m \ln \rho + \text{constant} \quad (2.20)$$

The factor m and the constant of the equation (2.20) vary with the properties of the solute. They found that equation (2.20) was valid for a wide variety of substances in a pressure range of about 80 to 2000 bars. Later, another correlation was developed (Chrastil, 1982) from the association laws and/or from the entropies of the components for relating solubility and density

$$c = \rho^k \exp\left(\frac{a}{T} + b\right) \quad (2.21)$$

where c is the concentration of the solute, ρ is the density of the gas, and a and b are solubility constants with some physical meaning attached to each. On rearranging

$$\ln \rho = \left(\frac{1}{k}\right) \left[\ln c - \left(\frac{a}{T} + b\right) \right] \quad (2.22)$$

The log-log relationship between density and solubility was found to be linear up to high concentrations of solute. This equation was able to correlate the solubilities of several solutes in supercritical ethylene to within an AAD of 10%.

Later, this equation was modified (Adachi and Lu, 1983) by considering the quantity k in equation (2.22) to be density dependent as given by equation 2.23. This modification reduced the errors by over 50% for some systems.

$$k = e_1 + e_2 \rho + e_3 \rho^2 \quad (2.23)$$

A linear correlation was later developed (Jonah, 1989) for solid solubilities in supercritical gases based on an expression for molar residual Gibbs free energy for a binary mixture in terms of certain thermodynamic properties of the pure solvent. They correlated the solubilities of six solutes in supercritical ethylene and carbon dioxide with a maximum error of 17%. Simple correlative models have been developed for enhancement factors of solutes in supercritical solvents (Schmitt and Reid, 1985; Kumar and Johnston, 1988) which can minimize the number of required parameters and experimental data. Because of simplicity, these models are recommended for correlating solubility isotherms, however they are not predictive.

2.4.3 Perturbed Hard Sphere Equations of state

The repulsive term in cubic equations may be improved by replacing the van der Waals expression with an accurate expression for hard spheres (Carnahan and Starling, 1972). There is increased physical meaning of the repulsive term in a model based on a hard sphere reference fluid compared to a cubic where b commonly appears in both the attractive and repulsive terms. This model was applied to predict the solubilities of nonvolatile solids in supercritical ethylene and carbon dioxide (Johnston and Eckert, 1981). They used an analytical Carnahan-Starling van der Waals (CSVDW) model, whose main feature is that it does not use the principle of corresponding states based on the critical properties but instead uses the heat of vaporization of the solute to determine the attraction parameter, a_{12} for a given fluid. Another advantage of this method is that it is not necessary to know the critical properties of the solute. The repulsive term of the EOS can be improved further by using the model for a mixture of hard spheres (Mansoori et al, 1971), that is superior to the CS expression with linear mixing rules (Dimitrelis and Prausnitz, 1986). A mixed hard sphere van der Waals (HSVDW) model was used to predict the solubility of relatively nonpolar solutes in ethylene in carbon dioxide and ethylene, more accurately than the CSVDW model (Wong et al, 1985). The other important advantage of the HSVDW model is that it includes the solute-solute attraction parameter; which was observed to be necessary (Brennecke and Eckert, 1990). In the HSVDW model, a_{12} is related directly to a parameter q , which is defined as a function of the solute and solvent molecular volumes and the solute atomic number that is,

$$a_{12} = C_1 \theta + C_0 \quad (2.24)$$

and

$$\theta = \frac{A_2 b_2^{2/3}}{(b_1^{1/3} + b_2^{1/3})^3} \quad (2.25)$$

where C_1 and C_0 are the constants for each solvent and A_2 is the solute atomic number. By using the linear relation of a_{12} versus q , the solubilities of solutes for 44 isotherms have been predictive (Wong et al, 1985). This model is predictive but needs refinement in the near critical region (Johnston et al, 1989b).

The augmented van der Waals EOS (AVDW) model (Johnston et al, 1982) , uses a second order perturbation term based on the molecular dynamics results for square-well fluids. This model includes the influence of clustering of solvent molecules about the solute which increases the solubility in the highly compressible near critical region. This model illustrates the importance of clustering of the solvent about the solute and provided the impetus for experimental and theoretical techniques to explore these clusters.

2.4.4 Perturbed Hard Chain Theory

The perturbed hard chain theory (PHCT) (Beret and Prausnitz, 1975; Donohue and Prausnitz, 1978) has also been applied to supercritical mixtures. The PHCT equation of state uses theoretical considerations to include important molecular effects that were included in previous models through empiricism. Because of its perturbation theory basis, the PHCT utilizes coefficients regressed from pure component PVT data rather than utilizing a corresponding states theory to determine these parameters. This model was extended to mixtures by introducing one binary interaction coefficient and was applied to the binary systems of naphthalene and anthracene in supercritical carbon dioxide (Mart et al, 1986). The binary interaction parameter is obtained from the subcritical K factor and Henry's constant data. They have found that since the PHCT was designed primarily for linear chain molecules, it does not provide accurate results with different structures.

A method for estimating the binary interaction parameter for PHCT based equations of state, from molecular structure information was later proposed (Fermeglia and Kikic, 1993). The model has been developed in terms of the Helmholtz function by considering an attractive and repulsive contribution. The former is made up of two terms, one for the low density region, the latter being based on a generalized form of the Carnahan-Starling equation. They have studied several binary systems with carbon dioxide, propane and ethane as solvents. They have compared the results from PHCT with other models using PR EOS and found that the deviations are lower for the PHCT especially, for systems with components very different in size. Comparisons were also made with the MHV2 model for some systems containing carbon dioxide and the

pressure deviations were found to be lower for the PHCT based EOS. The main advantages of using this model is that the pure component parameters are completely predicted and that it gives very good predictions of the volumetric properties of both the liquid and vapor phases. The only disadvantage of using the PHCT is that the critical region is not described accurately and the model cannot be used with confidence in the critical region (Gregorowicz et al, 1991).

2.4.5 Lattice Models

Statistical mechanics based lattice models have the ability to account for mixtures with large size differences. A mean field lattice model which contains the Flory-Huggins term was used to model the ethylene-naphthalene system with two mixture parameters, one temperature independent and the other strongly temperature dependent (van der Haegen et al, 1988). Another lattice fluid model was developed (Kumar et al, 1987), which extended the pure component model of Panayiotou and Vera, to mixtures by accounting for the nonrandom distribution of molecular segments. The model was applied to several binary systems with supercritical carbon dioxide as the solvent. The model correlated the data within experimental accuracy with only one temperature independent binary interaction parameter. Another recent work (Balbuena et al, 1991) used the method of approximation of Taylor's series truncated after the second term, for the numbers of contact pairs between segments of molecules. The objective of the model was to correlate the effect of adding a solute to a binary solute-solvent system. They have presented the results for four ternary systems along with some binary systems. The results were fairly good and the parameters extracted from correlating the experimental data were in agreement with a simple mechanistic explanation of the different solubility behaviors in ternary systems.

2.4.6 Decorated Lattice Models

The accuracy of the lattice models can be improved further in the near critical region by using a decorated lattice model, which is a superposition of two lattices, one

for the solute and one for the solvent (Gilbert and Eckert, 1986; Nielson and Levelt-Sengers, 1987). The primary lattice is a cubic array of cells not filling the entire volume. The secondary lattice is an array of cells superimposed onto the primary lattice such that exactly one secondary cell lies on each bond between nearest-neighbor primary cells. Only solvent molecules are allowed to populate the cells of the primary lattice and only solid molecules are allowed to populate the cells of the secondary lattice. The main advantage of this model is its high accuracy in the critical region. It requires two adjustable parameters which are not constant when used to model different sets of data for the same system (e.g., partial molar volume and solubility data). The earlier work (Gilbert and Eckert, 1986) used the Mermin lattice because it is very good for mixtures of different size molecules since the cell volumes of both superimposed lattices can be varied independently. They then developed a parametric scaling EOS to model the thermodynamic functions of the solvent lattice near the pure solvent critical point. Although the solubility data was fitted with two parameters, the partial molar volume data was fitted with only one parameter. The later work (Nielson and Levelt-Sengers, 1987) makes use of two decorated lattice gas models. The pure solvent was described by Mermin's decorated lattice gas model. The supercritical solution was described by a second decorated lattice gas system. Since, the two lattice systems are mathematically isomorphic, properties of the mixture were derived from those of the pure solvent. They studied three different binary systems and the model provides a semiquantitative representation of experimental solubility data.

2.4.7 Kirkwood-Buff Solution Theory

The Kirkwood-Buff theory is a general theory for mixtures, valid in the bulk phases as well as near critical points. The Kirkwood-Buff factor gives the number of fluctuations in a grand canonical ensemble

$$G_{mn} = \int_0^{\infty} 4\pi R^2 [g_{mn}(R) - 1] dR \quad (2.26)$$

where R is the distance between the molecules m and n and g_{mn} is the spatial pair correlation function for an m - n interaction. The G_{mn} integral represents the excess of m molecules and is sometimes called the affinity of m for n . The factor diverges near the critical loci, being a good indicator of criticality. The Kirkwood-Buff formalism is general for systems where the fluctuation integral of equation (2.26) makes sense. These should include spherical and nonspherical molecules as well as polar and nonpolar species. This theory has been used to treat non-idealities in a supercritical fluid phase. These fluctuation integrals are related to concentration fluctuations (Cochran et al, 1987; Pfund et al, 1988).

At constant temperature, the solubility of a solid (2) in a fluid (1) is

$$\ln y_2 = \ln \left[\frac{P_2^{sat}}{P} \right] + \frac{v^s (P - P_2^{sat})}{kT} + \ln z^0 + \int_P^{P_2^{sat}} \left(\frac{G_{12}}{kT} \right) dP \quad (2.27)$$

where z^0 is the compressibility factor of the pure solvent. In order to evaluate the integral, two methods were developed for estimating G_{12} at infinite dilution: the excluded volume (Cochran et al, 1987) and local composition models. The latter was recommended (Pfund et al, 1988). The local composition model separates the fluctuation integral into short range and long range contributions at the first peak in the pair correlation function and assumes that the pair energies are conformal to one another. Solvent properties were obtained either from critical properties (Cochran et al, 1987) independent of state, or from an accurate empirical EOS (Pfund et al, 1988). The excluded volume model caused overprediction of the solubilities at high pressures for the naphthalene-carbon dioxide system. Thus the simplistic excluded volume model with no adjustable parameters is only qualitative. The local composition model correlated the data with an average absolute deviation of 18% with three adjustable parameters for 19 binary systems in carbon dioxide and ethylene.

2.4.8 Integral Equation Theory

In the integral equation method, the structural and thermodynamic properties, which are free from statistical errors, are easily determined from various intermolecular

interaction parameters (Tanaka and Nakanishi, 1994). In addition, the free energy can also be obtained from the hyper netted chain (HNC) approximation and therefore the solubility can be estimated in terms of the intermolecular interactions. The integral equation theory was used (Cochran and Lee, 1989) to determine the radial distribution functions for the Lennard-Jones mixtures. The fluctuation integral in equation (2.27) can also be calculated more accurately with the use of these radial distribution functions. Some other publications discuss the application of the integral equation to supercritical fluid mixtures (Ekart et al, 1989; Lee et al, 1989).

A more recent work (Tanaka and Nakanishi, 1994) investigated the solubilities in supercritical fluid mixtures with and without co-solvents using an integral equation approach. In this study, the intermolecular interactions were assumed to be additive and the shape of all solvent, co-solvent and solute molecules was approximated to that of a sphere described by the Lennard-Jones (LJ) potential

$$\phi_{ij}(r) = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r} \right)^{12} - \left(\frac{\sigma_{ij}}{r} \right)^6 \right] \quad (2.28)$$

The integral equations were solved with the HNC closure for the solvent. The properties of the solute were obtained from the infinite dilution data. The solubility of the solute y was calculated in terms of the residual chemical potential of the solute and the saturated vapor pressure of the pure solute species P^0 as

$$y = \frac{P^0}{\rho kT} \exp \left\{ -\beta \left[\mu^c + v(P^0 - P) \right] \right\} \quad (2.29)$$

where v is the molecular volume of the pure solute and the pressure P is the hydrostatic pressure of the system. The results were compared to those of molecular dynamics simulation and were found to be in good agreement.

2.4.9 Mean Field Theory

Another method used to model the solid-fluid binary mixtures is the mean field theory which is similar to the van der Waals theory but includes higher order perturbation

terms. The perturbing potential has a stronger effect on the fluid structure (Jonah et al, 1983)

$$\frac{v_2 - v_1}{RT} - \left[\frac{\partial \ln y_2}{\partial P} \right]_T - \frac{v_1}{RT} \ln \left[\frac{P_2^{sat} z_1}{P y_2 f_1} + \frac{v_2^s P}{RT} \right] = \frac{k}{T^2} \quad (2.30)$$

At high pressures k is assumed to be constant - the mean field assumption. If a few high pressure solubility data are known at constant temperature, equation (2.30) can be used to estimate the solubility of a solute near the critical point. This was done for the ethylene-naphthalene system. These results are comparable to those of using the PR EOS with quadratic mixing rules.

2.4.10 SAFT Equation of State

Statistical associating fluid theory (SAFT) has been used for modeling solubilities in supercritical solvents, especially for polymer and multicomponent systems. This model was used for describing the bitumen-carbon dioxide systems (Huang and Radosz, 1991). The reference part of SAFT includes the hard sphere (hs) as well as the chain and association (assoc) terms. The perturbation part of SAFT accounts for relatively weaker mean field effects. The detailed description of SAFT is described elsewhere (Huang and Radosz, 1990). The general expression for the residual Helmholtz energy can be expressed as the sum of the reference (ref) and dispersion (disp) parts .

$$a^{res} = a^{ref} + a^{disp} \quad (2.31)$$

where

$$a^{ref} = a^{hs} + a^{chain} + a^{assoc} \quad (2.32)$$

Each of the above contributions can be expressed as a function of known quantities and three molecular parameters: the number of segments, m , per molecule; the segment volume, v^{00} , per mole of segments; and the segment energy, u^0/k . In addition, one adjustable interaction parameter k_{ij} is necessary to fit the experimental data. One of the advantages of SAFT is that the major reference part a^{ref} has been extended to mixtures on the basis of rigorous statistical mechanics. For the bitumen-carbon dioxide system (Huang and Radosz, 1991) the pseudo-component approach and generalised correlations

were used to estimate the molecular parameters of SAFT model. They have found that at temperatures close to the critical the cubic equations of state are better, but at higher temperatures SAFT predictions are more accurate. Also SAFT can account for molecular self-association and cross-association that are key to understanding the phase behavior of reservoir fluids. In a more recent work (Pradhan et al, 1994) SAFT simulations were used to model the solubilities of polystyrene in supercritical ethane and propane. In their work the pseudo-components were chosen in such a way that they have the same chemical structure, irrespective of their molecular weight distribution.

2.4.11 Monte Carlo Simulation

Monte Carlo simulation uses intermolecular potentials to provide a means to calculate phase behavior. It does not use the kind of assumptions required in EOS models. It is a powerful technique for testing theories with known potential functions and for testing potential functions. It has been used to predict solubilities in supercritical solvents (Shing and Chung, 1987). They chose the isothermal-isobaric ensemble, to allow for significant density fluctuations, characteristic of near critical systems. The Lennard-Jones potential plus quadruple interactions was used as the pair potential, producing a qualitative representation of the naphthalene-carbon dioxide system. The objective of the study was to validate the test-particle method. They have also used an extension of the Kirkwood potential equation, implemented in the isothermal-isobaric ensemble. The first method is useful at low to moderate densities where the solute is not too large compared to the solvent and the second method is useful at high densities where the solute is considerably larger in size compared to the solvent. The qualitative trends were well represented. By optimizing the potential parameters the quantitative agreement can be improved.

2.4.12 Translation of a cubic EOS

Most of the above mentioned models are based on the assumption that the solid phase is pure meaning that the solubility of the fluid in the solid phase is negligible.

Moreover, they lack the ability to predict the thermodynamic and thermophysical properties of the solid phase itself. To overcome these shortcomings, a simple methodology was described (Salim and Trebble, 1994) by which a cubic EOS can be modified to allow calculation of equilibria involving solid phases as well as thermodynamic properties of the solid phase itself. This is achieved by the volume translation of the cubic EOS at the triple point using the experimental value of solid density.

The temperature dependent parameters of the translated equation of state (TEOS) are then obtained either from regressing the vapour pressure data below the triple point or by using generalised parameters based on the derivation of heat capacities. The TEOS can then be utilized to describe solid phases at temperatures above and below the triple point by extrapolation. The TEOS then becomes an operative solid phase model and can be applied for the prediction of S-V, S-L and S-L-V phase behaviour. This methodology is successfully applied to the Trebble-Bishnoi-Salim (TBS) EOS (Salim and Tebble, 1994).

This novel approach of modeling solid phases in equilibrium was demonstrated for the supercritical systems of carbon dioxide-benzoic acid and ethylene-benzoic acid. The model uses two adjustable binary interaction parameters and the solubility data (Kurnik et al, 1981) for these systems was fit to within a RMSE of about 10%. It is also notable that the above model was able to match the experimentally observed crossover in benzoic acid solubility in carbon dioxide at a pressure of about 185 bar. Recently, this model was successfully applied to model the solubility data of naphthalene in supercritical carbon dioxide to within 15% RMSE (Salim, 1996).

One significant advantage of this method is that the solvent solubility in the solid phase can be accounted for. Another advantage is that equilibrium calculations in multicomponent solid phases (such as waxes) can be done using a simple, regular flash routine. This operative solid phase EOS can also be used to predict the properties of the solid phase such as the isobaric and isochoric heat capacities and vapour pressures.

2.4.13 Conclusions

In spite of the development of complex equations of state and other models for modeling the phase behavior of supercritical fluid mixtures, relatively simple methods and equations of state are still widely used because the representation of pure compounds is simple and the adaptation to mixtures and the calculation of phase equilibria are straightforward. It was demonstrated that such simple equations can be successfully applied to supercritical fluid mixtures. However this requires the adapting of new mixing rules that take into consideration the differences in properties between the solute and the solvent. Most of the works involving solubility in supercritical solvents listed in Table 2.1 use cubic equations of state along with a compressed gas model with the pure solid phase assumption to model the solid-fluid phase equilibria. Some of those are listed here in Table 2.2 along with other significant models used to describe the solid-fluid phase behavior. Part of this table and parts of the above discussion of modeling the phase behavior of supercritical fluid mixtures are taken from a recent review paper (Johnston et al, 1989b). Similar discussion can be found in another review paper (Brennecke and Eckert, 1989).

It is difficult to directly compare the abilities of different models for the prediction of solubilities in a quantitative manner, since some models use highly accurate pure fluid equations of state to calculate the density, while others calculate density with the same EOS used to calculate the fugacity coefficient. The latter method can cause inaccuracies in density for the pure fluid. There is also no consistent testing procedure on a specified data set for all the models. Moreover, it is clear from the above discussion that a single model cannot treat all cases and only a few general recommendations can be made.

If the objective is to correlate the solubility isotherms, simple empirical correlations of the logarithm of the enhancement factor versus the density are recommended. Because of the large disparity in sizes and energies of components, binary interaction parameters based on corresponding states theory are unpredictable. A limitation in all models based on the ideal gas reference state is the lack of vapor pressure data for nonpolar solids in the range 10^{-6} - 10^{-2} Pa. For dilute solutions, better equations

Table 2.2 Thermodynamic Models Applied to Solid(Liquid)-Fluid Systems

Solid(Liquid)-Fluid Systems			
model type	reference	no. of systems studied	no. of adjustable parameters
cubic	Deiters and Schneider (1976)	2	2
cubic	Mackay and Paulaitis(1979)	2	1-2
cubic	Kurnik et al. (1981)	9	1
cubic	Kurnik and Reid (1982)	8	3
cubic	Debenedetti and Kumar (1986)	3	1
cubic	Moradinia and Teja (1987)	5	1
cubic	Park et al. (1987)	2	3
cubic	Rao and Mukhopadhyay (1988)	16	0
cubic	Chen et al. (1995)	11	1
cubic	Barber et al. (1991)	1	3
cubic	Mori et al. (1992)	2	2
translated cubic	Salim and Tebble (1994)	2	2-4
regular solution	Iwai et al. (1993)	3	1
EOS/G ^E	Spiliotis et al. (1994)	5	4
EOS/A ^E	Barna et al. (1994)	11	2
EOS/A ^E	Sheng et al. (1992)	5	2
mean field	Jonah et al. (1983)	1	1
CSVDW	Johnston and Eckert (1981)	4	1
HSVDW	Wong et al. (1985)	16	0
AVDW	Johnston et al. (1982)	12	0
AVDW-DDLC	Johnston et al. (1987)	23	0-1
AVDW-DDLC	Lee et al. (1994)	3	1
PHCT	Mart et al. (1986)	6	0-1
lattice	Leblans-Vinck (1985)	1	2-4
lattice	Nielson and Levelt-Sengers (1987)	3	7
lattice	Kumar et al. (1987)	2	1
lattice	Van der Haegen et al. (1988)	1	2-4
lattice	Bamberger et al. (1988)	2	1
lattice	Balbuena et al. (1991)	4	1
decorated lattice	Gilbert and Eckert (1986)	5	2
correlation	Schmitt and Reid (1985)	12	3
empirical	Mitra and Wilson (1991)	21	3
semi-empirical	Jonah (1981)	10	2
semiempirical	Adachi (1983)	37	5
Kirkwood-Buff	Pfund et al. (1988)	19	2-3
Kirkwood-Buff	Barber et al. (1991)	1	1
integral equation	Tanaka and Nakamishi (1994)	1	1
SAFT	Huang and Radosz (1991)	3	1
SAFT	Rowley et al. (1990)	8	1

Table 2.2 (Contd...) Thermodynamic Models Applied to Solid(Liquid)-Fluid Systems

model type	reference	no. of systems studied	no. of adjustable parameters
Monte Carlo	Shing and Chung (1987)	1	0
Monte Carlo	Iwai et al. (1995)	6	2
Molecular Dynamics	Cui and Harris (1995)	1	1
Molecular Dynamics	Rowley et al. (1990)	1	1

Solid(Liquid)-Fluid Systems including Cosolvents

model type	ref	no. of systems studied	no. of adjustable parameters
cubic	Chen et al. (1995)	7	2
HSVDW	Dobbs et al. (1986)	6	0
HSVDW	Dobbs et al. (1986)	11	0
APACT	Walsh et al. (1987)	2	2
AVDW-DDLC	Kim and Johnston (1987)	5	1
integral equation	Tanaka and Nakamishi (1994)	1	1

cubic-cubic equation of state

CSVDW - Carnahan Starling van der Waals

HSVDW- hard-sphere van der Waals

AVDW-augmented van der Waals

DDLC- density-dependent local composition mixing rules

APACT - associating perturbed anisotropic chain theory

PHCT - perturbed hard-chain theory

SAFT-statistical associated fluid theory

of state are needed to calculate pure fluid densities. For concentrated solutions, better equations of state are needed for calculation of mixture densities.

The design and evaluation of SCF separation processes relies heavily on the ability to model the phase behavior. The goals of modeling efforts are both to correlate existing data and to attempt prediction of phase equilibria in regions where experimental results are not available. Correlations often contain a large number of regressed parameters, contain a varying degree of theoretical basis, and may succeed in fitting the data with some accuracy. Conversely, models developed for the purpose of prediction attempt to minimize the number of parameters and link those parameters closely to real physical phenomena while maintaining theoretical justification for the form of the equation. Both methods serve distinct and useful purposes. In reality, however, the distinction between the two approaches is often lost, as theoretically based models are forced to fit the data better by the introduction of additional adjustable parameters. The prediction of phase behavior of the supercritical fluid state has been the focus of attention for the past few years and its challenging nature has led to the development of innovative and efficient thermodynamic models. In spite of the recent developments in the thermodynamic analysis of SCF mixtures, there is no universally applicable method for predicting the solubilities of various solutes in supercritical fluids. A better fundamental understanding of the molecular behavior in supercritical fluids is needed to further develop predictive models.

3.0 Experimental Design

Solubility determination methods can be broadly classified as dynamic, static, chromatographic and spectroscopic. In the dynamic method, the solute is continuously swept with the solvent whereas in the static methods, the solute and the solvent are loaded into some type of high pressure cell. In the chromatographic methods, the retention time of the solute is related to the solubility of the solute in the solvent. The relative advantages and disadvantages of these methods are described elsewhere (McHugh and Krukoni, 1986).

As described in Chapter 1, a wide variety of phase behaviour can occur for mixtures at high pressures. It is extremely important to pinpoint the P-T location of phase border curves, such as LLV and SLV curves, before doing solubility studies, so that solubility behaviour can be interpreted and catalogued correctly. The objective of this study is to design an experimental apparatus, that would be capable of obtaining solid solubilities of heavy hydrocarbons in supercritical solvents. As mentioned in the scope of this work in Chapter 1, static and chromatographic techniques are not capable of measuring solid solubilities above the UCEP temperatures. This is because the solute would start melting above the UCEP temperature if its composition in the mixture is too small. To avoid this problem, as shown in Figure 1.3b, the composition of the solute in the mixture has to be very high. This can be achieved using the dynamic method, where a bed of solute is swept with the solvent and an excess solid condition can be maintained in the extractor at all times.

In this study, such an extractor was designed and the dynamic method was used to obtain the experimental solid solubilities. This single-pass flow system is representative of the type used by several researchers (Van Leer and Paulaitis, 1980; McHugh and Paulaitis, 1980; Krukoni and Kurnik, 1985; Adachi et al, 1983; Johnston and Eckert, 1981). In many previous works the solubility was determined gravimetrically, by weighing the amount of solute extracted. This is done by allowing the solute to be dropped out of the supercritical solvent on depressurization and using a cold trap to capture it. This technique of measuring solubility requires longer run times, because the

amount of solute extracted should be significant for an efficient weight measurement. In this work, the solubility was determined by dissolving the solute dropping out of the solution on depressurization, in toluene. The amount of the solute was then obtained by analysing the toluene+solute mixture in a gas chromatograph, by liquid injection. This method was used recently for some mass transfer studies (Lim et al, 1989). This eliminates the requirement of long run times, as the precision of the GC (Gas Chromatograph), is much higher than that of gravimetric analysis.

In addition to the above mentioned distinctive capability of being able to measure solid solubilities, the dynamic method has the following advantages(McHugh and Krukonis, 1986):

- 1) off the shelf equipment is used.
- 2) reasonably large amounts of solubility data can be obtained rapidly and reproducibly
- 3) equilibrium, stripping and fractionation data can be obtained by using the same apparatus
- 4) a straightforward sampling procedure is used.

This method does have a limitation in that undetected phase changes can occur inside the extractor. This problem can be avoided by studying the P-T and P-x phase diagrams of the system in operation and by identifying the pressure and temperature regions for a required phase separation. In this work the operating regions are limited to those between the LCEP and UCEP and also just above the UCEP.

The experimental set-up designed for this work has four main components as shown in Figure 3.1 and are described below:

- 1) Solvent pumping section
- 2) Extraction section
- 3) Depressurization section
- 4) Sampling section

These sections are arranged in order from the left to the right in the schematic of Figure 3.1. The different equipment used in these sections are described here. In addition to the above mentioned sections, the accessories which consist of the Gas Chromatograph

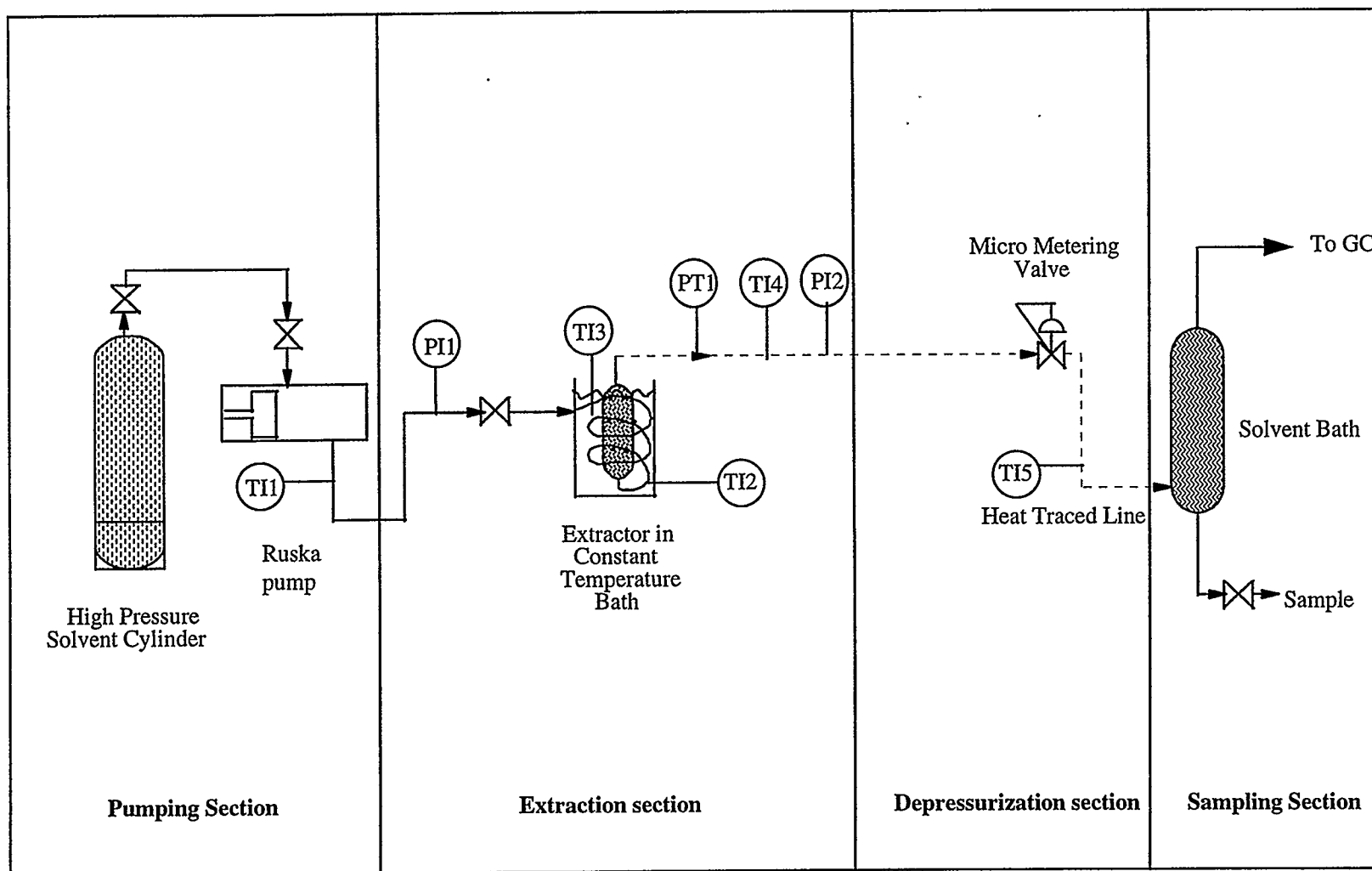


Figure 3.1 Schematic Diagram of the experimental apparatus

(GC) and Data Acquisition System (DAS) are also described. The start-up and experimental procedures are included at the end of the Chapter.

3.1 Solvent pumping section

The main equipment for this part of the set-up includes the Ruska pump, solvent supply unit and a temperature measuring device.

3.1.1 Ruska pump

A Ruska pump was used in this work for compressing ethane to the desired pressures and for delivering the solvent at fixed flow rates. It also measures the total amount of the solvent pumped through the system, thus eliminating the use of a flow totaliser. The pump used in this work (catalogue number 2248 WIII) is a proportioning pump capable of delivering the fluid up to a maximum pressure of 27 MPa. It has two cylinders and each cylinder has a volume of 500 cc. The two arms can be used separately or can be interconnected. A photograph of the pump is presented in Figure 3.2.

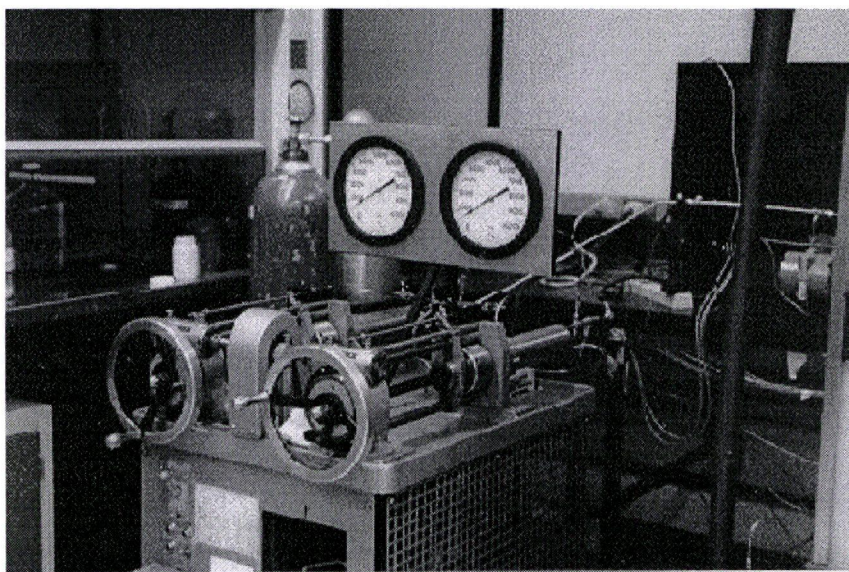


Figure 3.2 Photograph of the Ruska pump used in this work

The pressure of the fluid in the two cylinders can be read off the pressures gauges connected to the cylinders. The total flow of the solvent can be read to 0.01 cc. The pump has gears which can be adjusted to allow the fluid to be pumped at several different flow rates. The gears are arranged in such a way that a total of (4 X 7) 28 different combinations of the gears are possible, thus producing 28 different feed rates ranging from 5 to 1120 cc/hr. This flow rate can be easily set on the pump by adjusting the two levers for the gears in the following combinations:

Lever	A	B	C	D
1	5	20	80	320
2	6.25	25	100	400
3	7.5	30	120	480
4	10	40	160	640
5	12.5	50	200	800
6	15	60	240	960
7	17.5	70	280	1120

Table 3.1 Flow rates of the Ruska pump in cc/hr/cylinder

3.1.1.1 Safety devices

The pump has a pressure rating of 27 MPa. To protect the pump from exceeding this pressure, spring type pressure relief valves were mounted on both the arms of the pump. Since the maximum pressure used in this work was around 20 MPa, one of the valves had a relief pressure of 23.5 MPa and the other had a relief pressure of 27 MPa. Another possibility of failure of the pump, is the bottoming out of the piston against the cylinder. If the piston on the cylinder reaches its maximum value of 500 cc, and the pump is still in operation, the piston would buckle and break. To avoid this failure, electrical circuit breakers are provided at both ends of the cylinder at 0 and 500 cc marks. If these

limits are reached by the piston, then tripping occurs and the pump is automatically switched off. In addition, a flammable gas detector is installed in the vicinity of the pump, to detect any leakage from the pump or the high pressure lines surrounding it.

3.1.2 Solvent supply unit

The solvent(ethane) was supplied from a cylinder, in which ethane is stored at its saturation pressure. The cylinder is equipped with liquid withdrawal facility. The solvent is drawn into the Ruska pump by connecting the solvent cylinder to one of the cylinders of the pump and pulling the piston back.

3.1.3 Temperature measurement

The solvent was delivered by the pump at the desired pressure and room temperature. Since the solvent was pumped at a fixed volumetric flow rate in order to obtain the mass flow rate of the solvent through the extractor, it was necessary to measure the temperature and pressure at which the solvent was pumped. For this purpose a thermocouple was attached to the line coming out of the pump which measured the temperature of the solvent at pump conditions. This is represented as TI1 in the schematic of Figure 3.1.

All the thermocouples; TI1-TI5 used in this work were T type (copper-constantan). They are metal sheath thermocouples and are ungrounded. They can be used in the temperature range -101 °C to 371 °C. All the thermocouples are obtained from All Temp Sensors and have the catalogue No. BE-T-60-AS-SS-16-U-T-1/2". The thermocouples have a special calibration and the limits of error for the operating range used in this work are estimated to be +/- 0.1°C. The thermocouple TI4 used to measure the bath temperature has a probe diameter of 1/8" whereas the other thermocouples have a probe diameter of 1/16".

3.2 Extraction section

This is the most important and crucial component of the experimental set-up. This consists of a temperature bath, a temperature controller, a preheating coil, the extractor, thermocouples and thermometer, a pressure gauge and a pressure transducer.

3.2.1 Temperature bath

The heating medium used in this work is a mixture of glycol and water. The temperature bath is a cylindrical container with an approximate length of 38 cm and a diameter of 30 cm. The container is filled with the mixture of water and glycol up to the brim. The temperature bath is insulated all around with fibre wool. In addition some pieces of Styrofoam are floated on the top of the liquid to prevent any heat loss. The temperature in the bath is maintained by using a temperature controller.

3.2.2 Temperature controller

The temperature of the liquid inside the bath is maintained by using a Haake E-52 temperature controller. This controller can be used for a temperature range of 30-80 °C. The temperature reading of this controller is calibrated against a high precision thermometer and the set-point is determined using this calibration and the readings of the thermocouples and thermometer.

3.2.3 Pre-heating coil

A preheating coil made of 1/4" stainless steel piping is placed inside the temperature bath. This is used to preheat the solvent (ethane) to the bath temperature. The preheating coil has a diameter of 20 cm and has a total length of approximately 10 m.

3.2.4 Extractor

The extractor is the most important element of the experimental set-up. The solute to be extracted is packed into the extractor and the solvent is swept through it. The extractor is placed inside the temperature bath. The volume of the extractor is an

important design consideration because the contact time between the solvent and the solute depends on it. For a given extractor, the flow rate should be low enough for equilibrium to be reached inside the extractor and vice versa. For this reason three extractors were designed to provide some flexibility with the flow rates of the solvent. All the extractors were made of stainless steel and were pressure tested to 20 MPa. The dimensions of these extractors are given below in Table 3.2.

Extractor No.	Length cm	Diameter cm
1	26	1.1
2	29	2.1
3	28.5	2.65

Table 3.2 Dimensions of the extractors

After conducting some preliminary experiments and calculations it was found that extractor No.1 was too small and required very low flow rates to achieve equilibrium and extractor No. 3 was too big and required large amounts of solute. Due to these reasons extractor No. 2 was used in this work. The extractor is packed with a layer of glass beads at the bottom, where the solvent enters. The glass beads are packed to a length of approximately 5-6 cms. Then the extractor is filled with the powdered solute. Finally a layer of glass wool packing is added to the top of the extractor to prevent the entrainment of the solute. The length of packing of the solute varied from 15-20 cms. A detailed diagram of the assembly of the extractor, the preheating coil and the temperature bath is provided in the schematic of Figure 3.3.

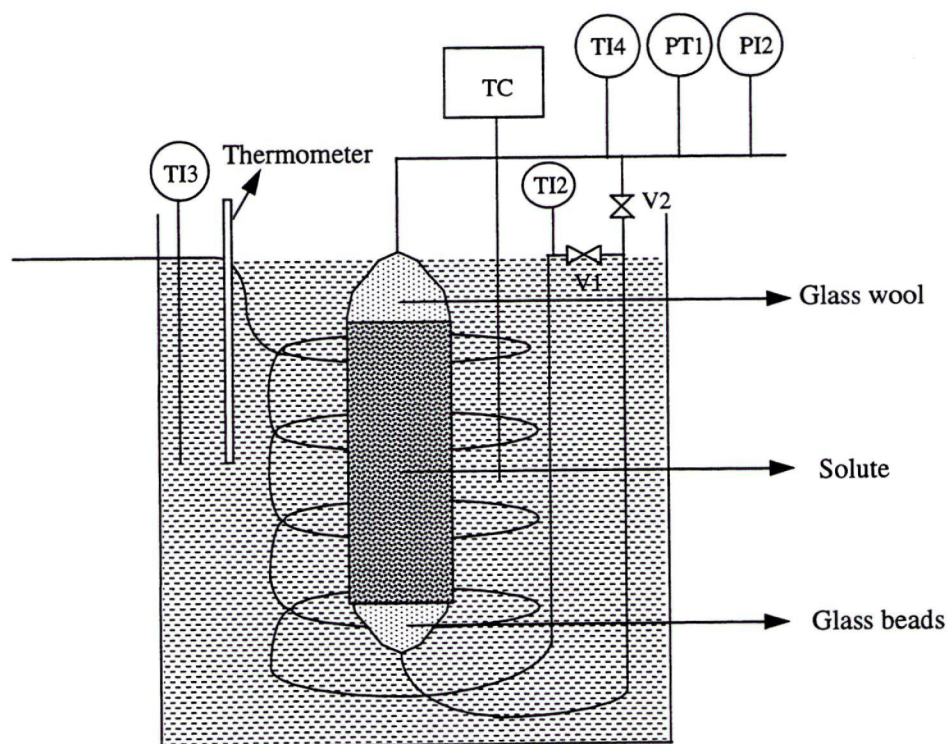


Figure 3.3 Enlarged view of the extraction section

3.2.5 Temperature measurement

The solvent enters the extractor after preheating in the coil. The temperature of the solvent is measured using two thermocouples, one at the entrance of the extractor indicated by TI2 in Figure 3.3 and the other at the exit of the extractor indicated by TI4 in Figure 3.3. Another thermocouple is placed inside the temperature bath indicated by TI3 in Figure 3.3, to monitor the temperature of the heating medium. Preliminary measurements showed that all the three thermocouples indicated the same temperature within their limits of error. There was a problem however with the thermocouple at the exit of the extractor. As the extraction proceeded the thermocouple got plugged in certain instances. Due to this reason and due to the fact that all three thermocouples indicated the same temperature, it was decided to use the bath temperature indicated by TI3 as the temperature of extraction.

In addition to the thermocouples, a high precision thermometer capable of reading to 0.1 °C is placed inside the temperature bath to monitor the temperature. The thermometer is obtained from Fischer and is capable of measuring temperatures in the range 0-100 °C. The temperature indicated by the thermocouple TI3 and the thermometer were also exactly the same and the difference is within the error limits of the thermocouple. Throughout the extraction the temperatures indicated by the thermometer were checked with those of the thermocouple. The fluctuations in the temperature reading of the thermocouple TI3 and in the temperature of the bath are tabulated in Chapter 4.

3.2.6 Pressure measurement

The pressure of extraction or the pressure at the exit of the extractor is another important measurement that governs the solubility. For this purpose the pressure of the solvent before it enters the extractor was measured by a pressure gauge indicated by PI1 in Figure 3.1. The pressure gauge is manufactured by Wika. It is capable of measuring pressures up to 35 MPa but has only divisions of 500 KPa making it too imprecise to record. At the exit of the extractor, two pressure measurements are made. One is a digital pressure gauge, that is accurate to 0.25% (BFSL) and indicates pressure to a precision of 1 psi. This pressure gauge is used to indicate the operator of any plugging or leakage problems in the experiment. This pressure gauge is the model PG 4000 and is supplied by PSI-Tronix and is capable of measuring the pressure up to 27 MPa. This is indicated by PI2 in Figure 3.1. The most important pressure measurement is made by using a pressure transducer at the exit of the extractor. This is indicated by PT1 in Figure 3.1. This transducer is capable of measuring pressure up to 27 MPa. This model 2088 transducer was obtained from Rosemount measurement. This transducer has a piezoresistive silicon sensor for measuring pressure. This transducer is calibrated for the range 3.35-33.5 Mpa. and is accurate to 0.25% including effects of linearity, hysteresis and repeatability. The distinctive feature of this transducer is that it measures absolute pressure instead of gauge pressure, thus avoiding the recording of barometric pressure.

3.3 Depressurization section

The supercritical solvent saturated with the solute exiting the extractor has to be depressurized to atmospheric pressure before it is analysed. This causes a serious experimental problem because isothermal expansion of the saturated supercritical solvent causes precipitation of the solute. Due to this reason careful design of this section is extremely important. This section consists of a micrometering valve and heat traced lines. In addition a toluene pump is used to flush the precipitated solute.

3.3.1 Micrometering valve

In this work a micrometering valve is used to expand the saturated supercritical solvent and also to control the pressure during the extraction. This micrometering valve has a C_v of 0.007 and goes down to as low as 0.0005. This makes this flow control valve ideal for low flow rates utilized in this work. This valve is obtained from Whitey (Catalogue No. SS22RS4) and has a pressure rating of 3000 psi. It can be used in the temperature range of -21 to 230 °C.

To avoid the problem of solute precipitation, the micrometering valve has to be heated to a temperature for which the equilibrium solubility minimum is greater than the measured solubility in the equilibrium cell. But this heating of the valve may cause an additional problem. During the isobaric temperature increase between the extractor and the expansion valve, solute redeposition may occur, if the temperature increase is not monotonic, due to under and over saturation of the solvent which can lead to erroneous experimental results. To avoid this problem the entire line is heat traced using a heat tape, starting from the exit of the extractor to the beginning of the sampling section. The temperature of the heat traced line is controlled using a transformer and the temperature of the solvent is monitored using a thermocouple; indicated by TI5 in Figure 3.1.

3.3.2 Toluene pump

In spite of the above mentioned precautions being taken, it was suspected that there might be some precipitation of the solute (Moradinia and Teja, 1986). To recover

this deposited solute in the lines a toluene pump was used. This pump was attached just before the micrometering valve and at the end of each run toluene was pumped through the micrometering valve and the lines were flushed. A D.B.Robinson Jefri pump was used for this purpose. This toluene was later analysed for the deposited solute. Fortunately, no precipitation was detected to occur in any of the runs.

3.4 Sampling section

This section forms the analytical part of the experimental apparatus where the equilibrium solubility is obtained. This section consists of a toluene bath used to dissolve the deposited solute. A Gas Chromatograph (GC) is later used to analyse the toluene .

3.4.1 Toluene Bath

A stainless steel tube with an approximate diameter of 2.54 cm and an approximate length of 30 cm is used as a toluene bath. This is filled with measured amounts of toluene. The heat traced line from the micrometering valve ends at the entrance of the toluene bath, which is maintained at room temperature. The solvent (ethane) is then bubbled through the toluene. The temperature drop causes the solute to be dropped out of the solution and the toluene dissolves the solute that is dropped out. The amount of toluene used varied for each run based on the amount of solute extracted and the solubility of the solute in toluene. A sampling port is provided for the removal of the toluene with the dissolved solute and these samples were later analysed using a GC.

3.5 Accessories

There are two main accessories used in this work. One is the Gas Chromatograph used to analyse the samples and the other is the Data Acquisition System used to record the different temperatures and pressures.

3.5.1 Gas Chromatograph (GC)

This is the most important accessory to the experimental apparatus used in this work. The solubility of the solute (hydrocarbons) in the solvent (ethane) is determined by this equipment. The solute dissolved in toluene is injected into the GC and the amount of solute extracted is determined. In addition, the solvent exiting the toluene bath was also analysed in the GC to determine whether all the solute is deposited in the toluene. In all the runs no solute was detected in this stream. For this purpose a Shimadzu GC-9A is used. This GC has a capability of using either a Thermal Conductivity Detector (TCD) or a Flame Ionisation Detector (FID). In this work the TCD is used to analyse the samples. The details of the column, the TCD and accessories needed for liquid injection are described below.

3.5.1.1 Column

Hydrocarbons are to be detected in the analysis of the sample in this work. To achieve this a megabore capillary column had to be used. The column used in this work has a diameter of 530 μm . The column used here is obtained from Chromatographic Specialities (Model No. DB5/87555A). The column is connected to the injection port using split liners and graphite ferrules. The details of the programming of the column and the detector are presented in Chapter 4.

3.5.1.2 Detector (TCD)

The TCD used in this work, which is a part of the GC-9A, has a Tungsten (Rhenium) filament with a constant current control method of power source. The TCD has a maximum temperature rating of 399 $^{\circ}\text{C}$. The details of the amount of current and temperature are presented in Chapter 4. The current can be changed from 0 to 200 mA depending on the flow rate of carrier gas. Helium is used as carrier gas in this work. The TCD has a sensitivity of about 7000mV.ml/mg which differs depending on the sample and is proportional to the current supplied.

3.5.1.3 Injector

The injection ports located on the top of the GC are used for liquid injection. For the gas injection a Valco 10 port sampling valve attached to the side of the GC is used. For liquid injection special microliter syringes had to be used. These syringes with a maximum volume of 1.0 microliters are obtained from Hamilton. Special split liners are also obtained that accommodate these 22 and 26 gauge needles and also connect to the megabore capillary column. Details of injection temperature are presented in Chapter 4.

3.5.2 Data Acquisition System (DAS)

A DAS is used in this work to monitor and record the temperatures obtained from the thermocouples TI1-TI5 and the pressure obtained from the pressure transmitter PT1. The DAS used in this work is the QMON data acquisition and control package developed by Sciometric Instruments Inc. This is a multi-level menu driven program which allows for real time data processing based on user defined algebraic equations. Custom screen displays are created and the data is displayed and monitored using graphic schematics and real time plots. A typical QMON display screen used in this work is presented here in Figure 3.4.

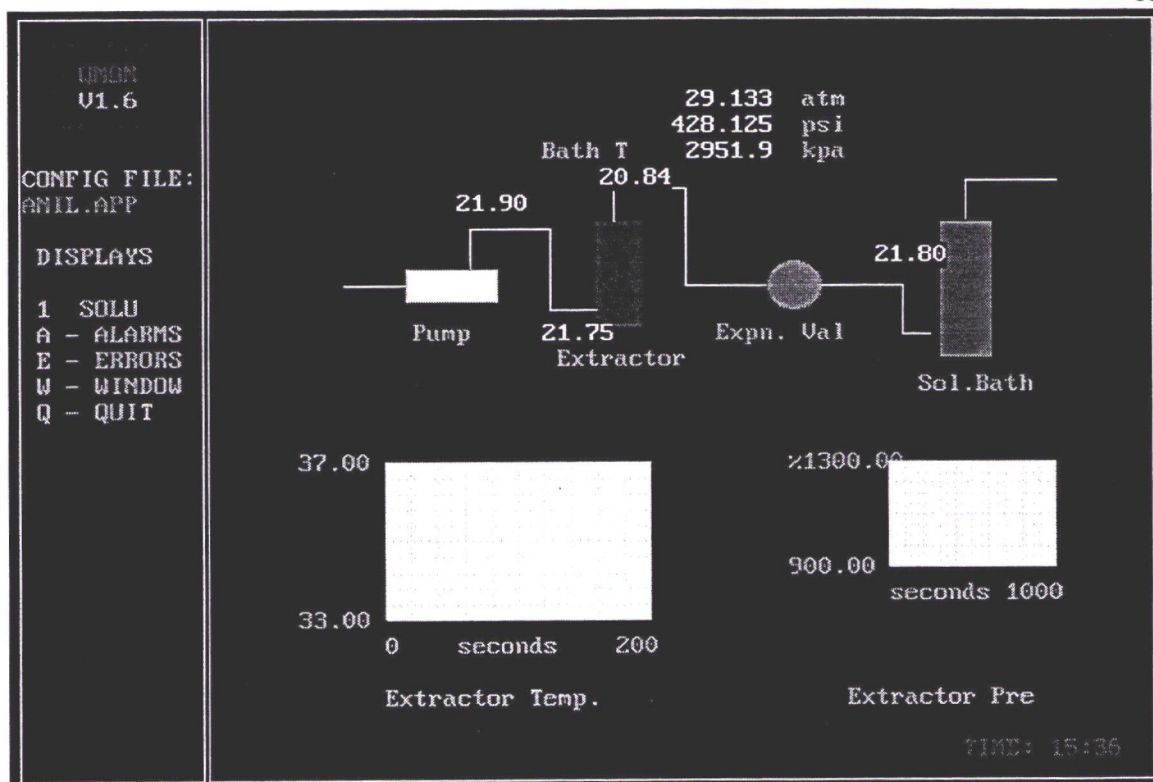


Figure 3.4 Typical QMON data acquisition screen display

The data are recorded once every 10 seconds and the average value of each measurement during this time is recorded. The software uses least squares curve fitted equations based on standard thermocouple tables. The equation used for the T type thermocouples is a third order polynomial with an average error of 0.012 °C. Since the reference temperature used in this package is not 0 °C, both the forward and inverse equations are required. The inverse equation allows the new reference junction to be computed based on the known reference temperature. The equations for the forward and inverse equation are given below:

$$\text{Forward Equation : } T(C) = -0.0099 + 25.883 V - 0.6964 V^2 + 0.02613 V^3 \quad (V \text{ in mv})$$

$$\text{Inverse Equation : } V(mv) = -0.00119 + 0.03862 T + 4.365 E - 5 T^2 - 2.067 E - 8 T^3 \quad (T \text{ in } ^\circ\text{C})$$

The calibration for the pressure transmitter is user defined. The calibration was done at pressures of 500 and 300 psi. The relation between the current and pressure in KPa is given by the following equation:

Pressure Calibration: $P \text{ (kPa)} = -861.9 + 4309.4 V \text{ (V in volts)}$

All the wires connecting the measuring devices are made of Teflon with shield and copper drain wire. This prevents the possibility of noise in the signal from electrostatic and electromagnetic induction and also protect the wire from moisture and abrasion.

3.6 Materials

All the solutes (C24, C28, C32C) used in this work were obtained from Aldrich Chemical Co. and they are used without further purification. The solutes were crushed to a fine powder before they were loaded in the extractor. The manufacturer's specifications are given below:

Solute	Melting Point (°C)	Molecular Weight(gms)	Purity
n-C24	49-52	338.66	>99%
n-C28	61-63	394.77	>99%
n-C32	68-70	450.88	>97%

Table 3.3 Manufacturer's specifications of solutes

The solvent Ethane used in this work is obtained from Linde Air Products and is of C.P. grade with 99% purity.

3.7 Experimental Procedure

A photograph of the actual experimental set-up is shown here in Figure 3.5 to give an idea of the relative position of different equipment.

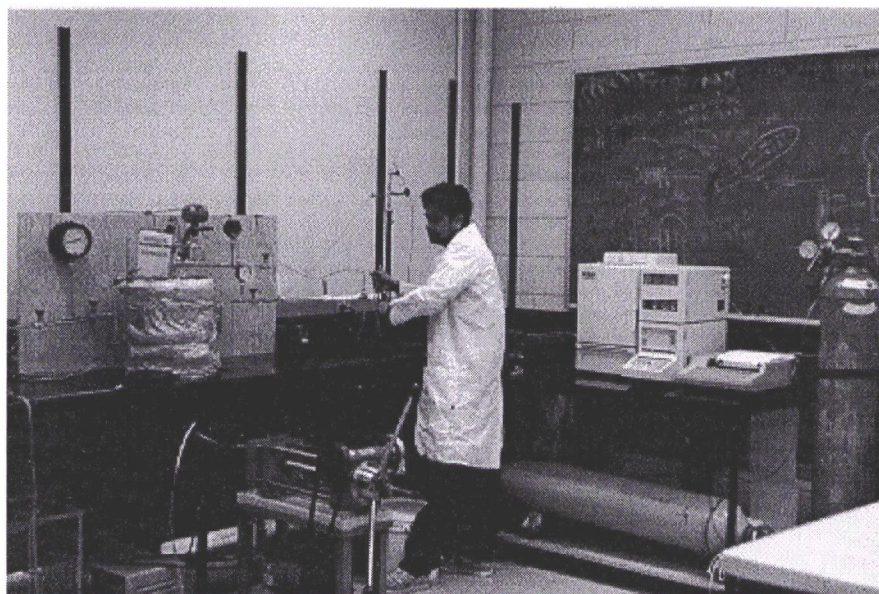


Figure 3.5 Photograph of the experimental set-up

Before the experiment is started, the extractor is packed with the desired solute as explained in section 3.2.4. The temperature of the bath is set at the desired temperature and is maintained constant at that temperature. The toluene bath is also filled with the known amount of toluene. The heat traced lines are also maintained at the desired temperature (approximately 100 °C) by switching on the transformers controlling the heat tape.

The solvent (ethane) is drawn into one of the cylinders of the Ruska pump. Then the solvent in the cylinder is compressed to a pressure higher than the desired pressure to account for the pressure loss that occurs when the solvent is expanded to the rest of the lines. The valve controlling the outlet from the pump is then opened and the rest of the lines to the micrometering valve are filled with the solvent.

As shown in the schematic of Figure 3.3 there is a by-pass line that prevents the solvent from passing through the extractor. This by-pass line is controlled by two valves V1 and V2 as indicated in Figure 3.3. Before starting the flow in the pump, the valve V1 is opened and the extractor is also filled with the solvent, to prevent a big pressure drop from occurring when the solvent is pumped through it. Then the valve V1 is closed to

prevent the flow to the extractor. The by-pass line is used initially to control the pressure at the desired value. At this point if the pressure in the set-up is less than the desired value, it can be compressed using the pump by closing the micrometer valve.

At this point, the micrometer valve should be turned on and the flow rate of the pump is set at the desired rate and the pump is switched on. The pressure starts to rise as the flow is started in the pump. This increase in pressure should be balanced by a suitable number of turns on the micrometer valve. At this point the experimental set-up is dynamic and the flow is maintained at constant pressure. This can be checked by using the digital gauge PI2. The temperature can also be checked by using the thermometer inserted in the bath.

At this point, the reading from the pump that indicates the amount of solvent pumped is taken and the valve to the extractor V1 is opened and V2 closed all at the same time. The solvent is then flowing through the extractor at the desired temperature and pressure. If there are any fluctuations in the pressure, the pressure can be maintained at the set value by monitoring the digital gauge and manually controlling the opening in the micrometering valve.

Once the required amount of solvent is pumped through the extractor, the flow from the pump is switched off and the valve V1 is closed simultaneously. At the same time the reading on the scale of the pump is noted to obtain the total amount of solvent pumped through. The samples from the toluene bath consisting of toluene and the extracted solute are collected in a sample bottle and later injected into the GC to obtain the composition.

4.0 Experimental results and data analysis

The experimental set-up described in Chapter 3 was successfully installed and operated in this work. Solubility experiments were carried out for three different systems with ethane as the solvent. The three different solutes used in this work are tetracosane (C24), octacosane (C28) and dotriacontane (C32). All the experiments were carried out at a temperature of 35 °C, but the set-up can be used at any temperature above room temperature. The solubilities were determined at pressures from 50 bar to 200 bar.

This Chapter deals with the data gathered during these experiments and the analysis of this data to arrive at the required solubility. It also describes the calibration details of the Gas Chromatograph (GC) and the preliminary experiments carried out to establish the equilibrium flowrate of the solvent. The computation of this solubility data is necessary before it is modelled. The details of the thermodynamic modelling are presented in Chapter 5. A discussion on the comparison of these results with other works and the performance of the model is presented in Chapter 6.

The experiments conducted in this work can be classified as preparative experiments and the solubility experiments. These are described below in sections 4.1 and 4.2 respectively.

4.1 Preparative experiments

The preparative experiments deal with the calibration of the different temperature and pressure measuring devices and the calibration of the GC. This section also includes the experiments conducted to establish the flowrate required to ensure that equilibrium is reached in the extractor. The calibration details of the measuring devices were presented earlier in Chapter 3 and the rest are described here.

4.1.1 Experiments with the Gas Chromatograph (GC)

The GC used in this work is equipped with a Thermal Conductivity Detector (TCD) for analysing the injected sample. The details are given earlier in Chapter 3. Liquid samples are used in this work for the analysis of the mixtures. The operating

temperatures of the GC have to be high enough to vaporise the injected liquid sample. In addition, the different operating conditions of the GC such as the injector, column and detector temperatures and the detector current have to be optimised based on the detection of the peaks and separation and resolution of the peaks. These conditions depend on the type of mixture being injected. In this work, the following conditions given in Table 4.1 were chosen.

Parameter	Toluene + Tetracosane	Toluene + Octacosane	Toluene + Dotriacontane
Injector temp (°C)	300	300	350
Column temp (°C)	235	235	275
TCD temp (°C)	250	250	300
TCD Current (mA)	100	100	50
Carrier gas flow (ml/min)	30	30	20

Table 4.1 Optimum operating conditions of the GC

In addition, to these parameters programmed into the GC, the integrator used for recording the results of the analysis is also programmed for proper separation and resolution of the peaks. The parameters programmed into the integrator are the same for all three systems and are given below in Table 4.2.

Attenuation	2
Threshold	2
Area Rejection	50
Chart speed	1
Peak width	0.05

Table 4.2 Optimum parameters for the integrator

4.1.1.1 Calibration of the GC

The most important preliminary step in the determination of solubilities is the calibration of the GC. In this work, the calibration was done by preparing the standard samples gravimetrically. The samples are prepared by adding known amounts of the solid solute to known amounts of toluene and preparing mixtures of known composition. The samples are prepared with varying compositions starting from pure toluene to the solubility limit of the solutes in toluene. The solutes and the toluene were weighed using a balance accurate to 1 mg and mixture samples of 5 g were prepared. More than one sample was prepared for each composition.

All the samples used in this work are binary mixtures. The area % obtained from the chromatographic peaks is calibrated against the weight % of the standard sample. At least four runs were taken for each sample and the repeatability was within 3%. The calibration curves were linear as expected. The calibration curves of weight % versus area % for tetracosane, octacosane and dotriacontane in toluene are shown in Figures 4.1, 4.2 and 4.3 respectively.

Figure 4.1 Calibration Curve For Toluene+Tetracosane Mixture

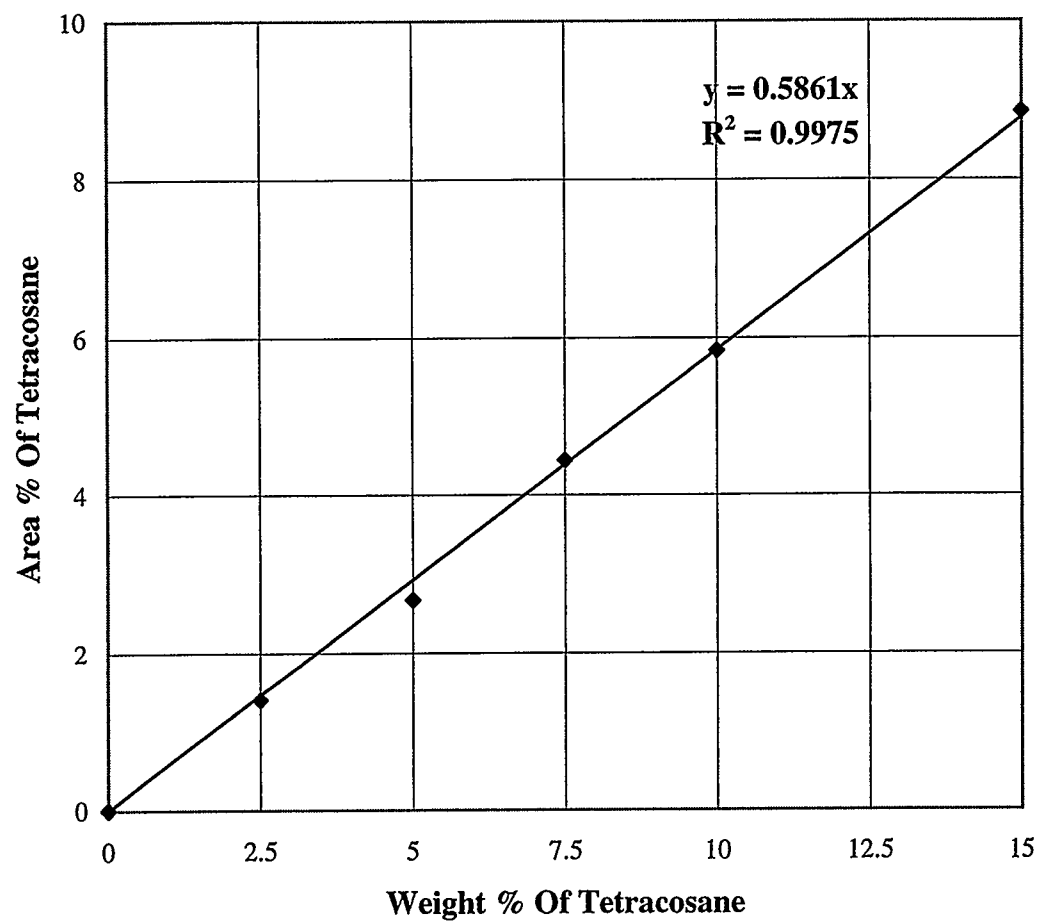


Figure 4.2 Calibration Curve for Toluene+Octacosane Mixture

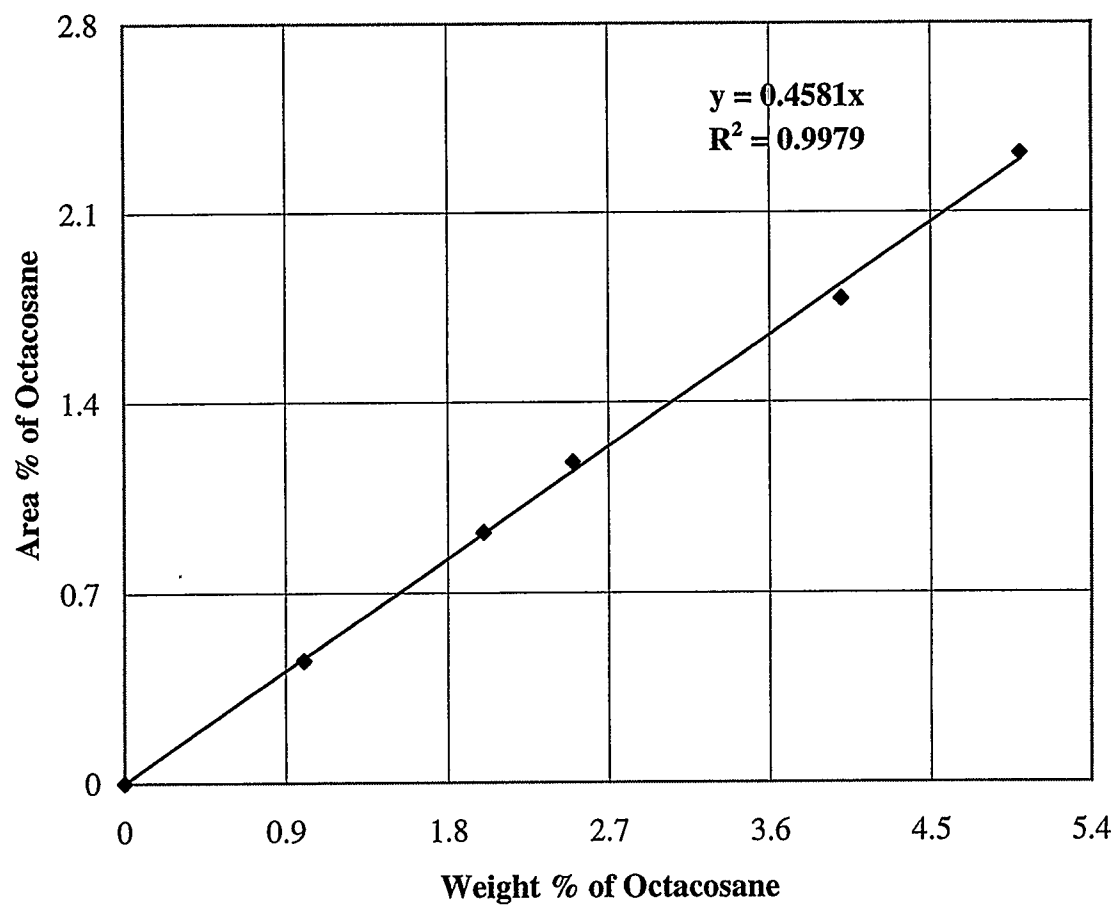
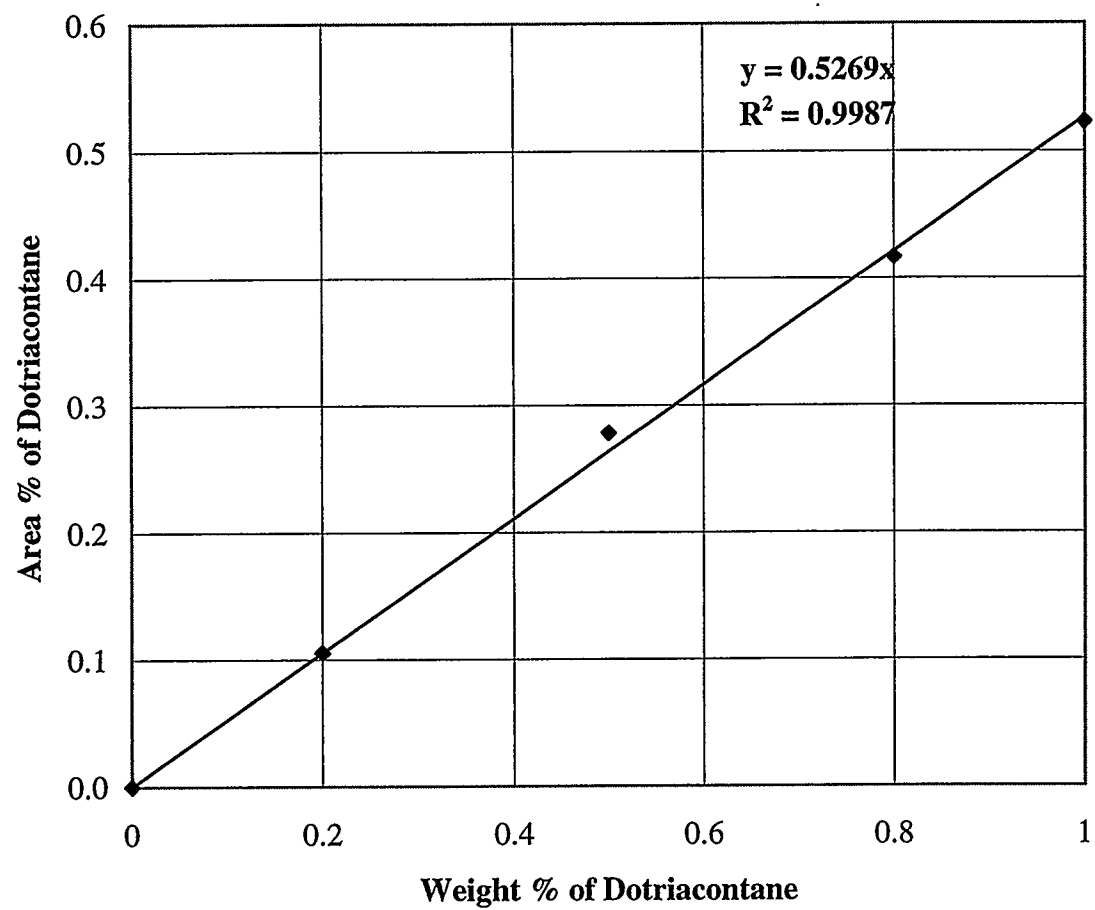


Figure 4.3 Calibration Curve for Toluene+Dotriacontane Mixture



4.1.2 Experiments to determine the equilibrium flowrate

In a dynamic method to determine the solubility, the flowrate of the solvent through the extractor is a very important factor. The solvent exiting the reactor should reach equilibrium or should be saturated with the solute. There is a maximum flowrate at which the equipment can be run to obtain solubility information. This would mean that the contact time between the solvent and the solute in the extractor should be sufficiently long in order to reach equilibrium.

Preliminary experiments showed that the extractor 1 described in section 3.2.4 is very small and the flowrate required to ensure equilibrium in this extractor is very low and long run times are required. Extractor 3 was very big and large amounts of solute are required for this extractor. In this work extractor 2 was consequently used to determine the solubility. Experiments were conducted for the systems of ethane + tetracosane and ethane + octacosane at low and high pressures to determine the equilibrium flowrate of the solvent.

Experiments were conducted at different flowrates starting from as high as 500 cc/hr to as low as 50 cc/hr. The results are presented in the form of graphs in Figures 4.4 and 4.5. These experiments are conducted for the ethane + octacosane system at low and high pressures and at low pressure for the ethane + tetracosane system.

The composition data is shown in Figure 4.4 as a plot of flowrate versus mole fraction. This plot includes the variation of composition of octacosane with ethane flowrate at a lower pressure of 65 bar and a higher pressure of 200 bar. As can be seen from this plot as the flowrate drops to about 150-160 cc/hr the solubility reaches a maximum value of around 0.0025. After this point the mole fraction does not increase even at very low flowrates indicating that equilibrium was reached at a flowrate of around 160 cc/hr. Similar results are obtained for both the pressures though the maximum flowrate for both pressures might be different. Figure 4.5 shows the variation of composition of the solute with flowrate of the solvent for the ethane + tetracosane system at 60 bar. The equilibrium is reached at a flowrate of around 120 cc/hr.

Figure 4.4 Variation of composition of octacosane with ethane flowrate

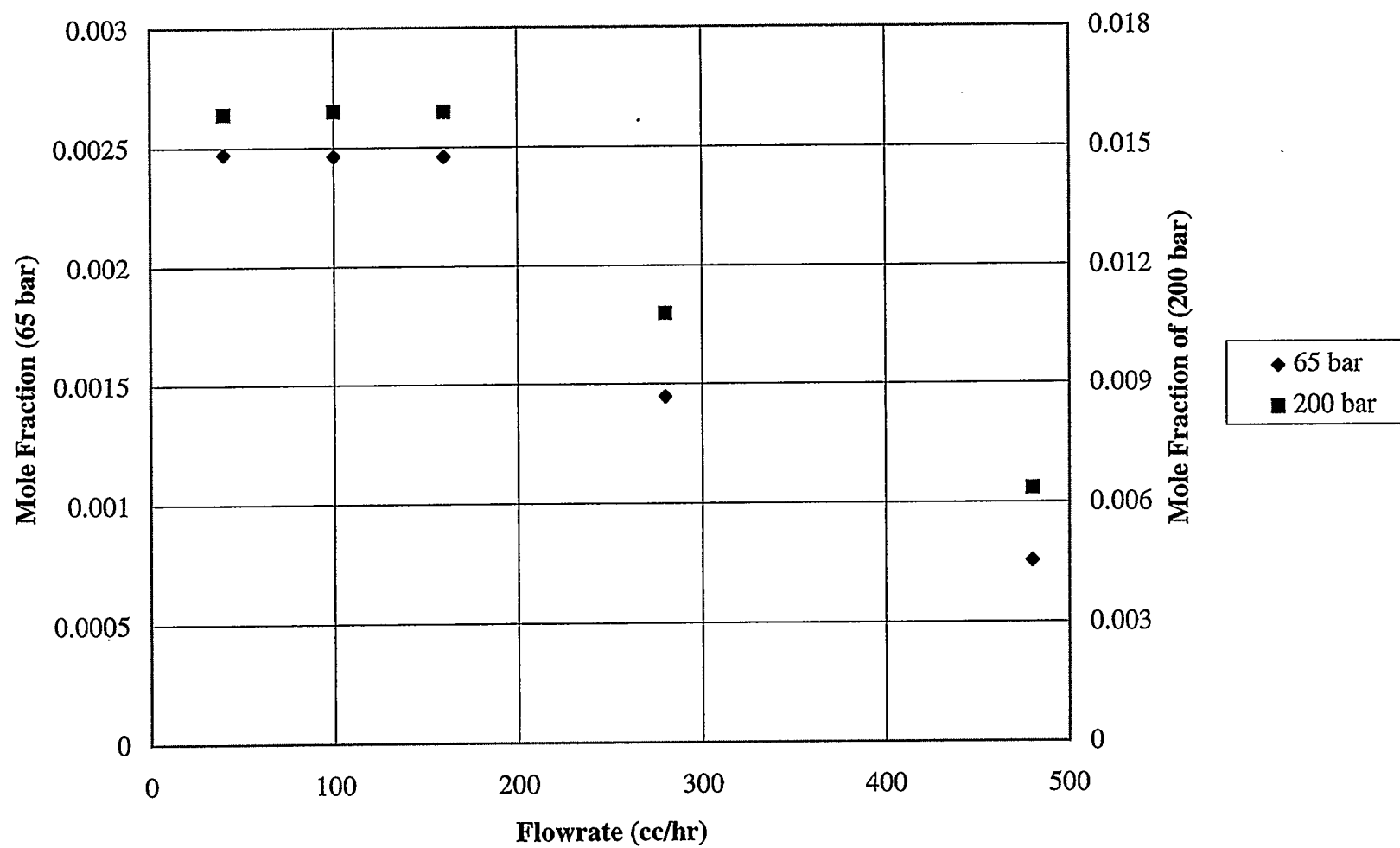
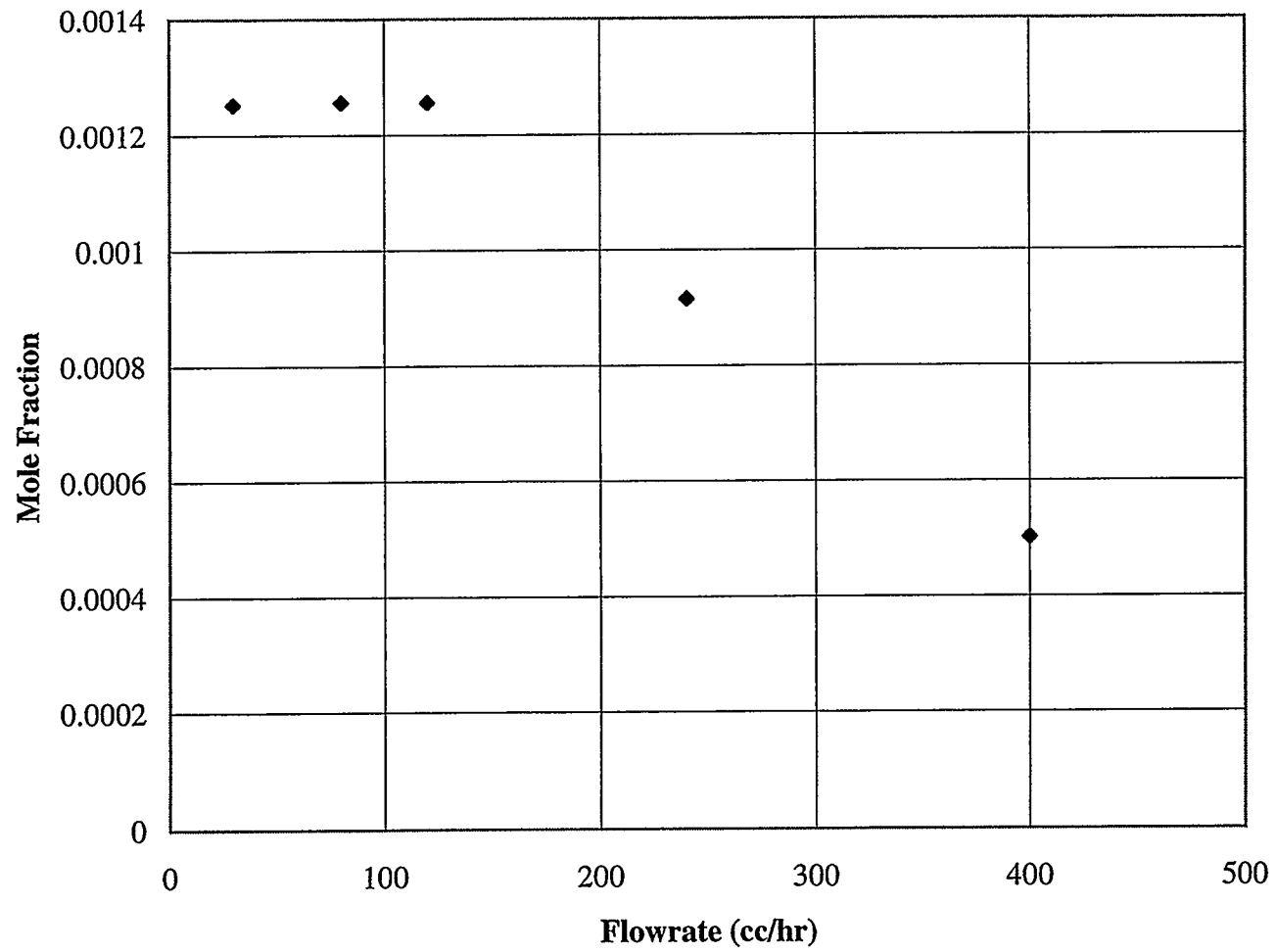


Figure 4.5 Variation of composition of tetracosane with ethane flowrate



The equilibrium flowrate varies with each system and also depends on the length and type of packing. This is also a function of the pressure and temperature of extraction. For these reasons a safety factor of over 100% is chosen for the difference in this equilibrium flowrate and all the experiments in this work are conducted at a flowrate of 50 cc/hr. This flowrate was later checked for some runs during the course of the solubility experiments.

4.2 Solubility experiments

This section deals with the experiments carried out to determine the solubilities of tetracosane, octacosane and dotriacontane at a temperature of 308.15 K and at pressures ranging from 50 to 200 bar. This section also includes the experiments conducted to test the dynamic response of the toluene bath.

4.2.1 Data analysis and solubility calculations

The experimental data obtained from these experiments has to be processed to determine the solubility of the solutes in ethane. These computations are presented here in Tables 4.3, 4.4 and 4.5 for tetracosane, octacosane and dotriacontane respectively. The pressure reported here is obtained from the data acquisition system. This is the pressure indicated by the pressure transducer (PT1) at the exit of the extractor. The value reported here is the average value for the course of each run. The temperature reported here is the value indicated by the thermocouple in the temperature bath, and is also averaged over the time period of each run. The fluctuations in the pressure and temperature reported here are indicated by the % standard deviation (SD) over the time period of each run. The temperature at the pump is indicated by the thermocouple at the pump and is also averaged value obtained from the DAS. The amount of ethane pumped is determined by computing the difference between the initial and final readings of the Ruska pump. The density used to calculate the moles pumped is taken from the NIST EOS for ethane and was computed at the pump temperature and extractor pressure. The amount of toluene in the bath is measured at the atart of the experiment. The loss of weight in the extractor is

Table 4.3 Data Analysis and Solubility Calculations for the system ethane + tetracosane

Run No.	Pressure	% SD	Temperature	% SD	Temperature at the pump	Amount of Ethane pumped
	bar	%	C	%	C	moles
1	59.71	0.35	35.02	0.06	27.01	3.43724
2	74.83	0.52	35.03	0.08	27.04	0.90216
3	100.01	0.37	35.03	0.07	27.04	0.69588
4	129.99	0.38	34.96	0.05	27.00	0.98799
5	163.92	0.24	35.01	0.01	26.84	0.81747
6	199.32	0.21	35.01	0.02	26.83	0.90999

Run No.	Amount of Toluene in the bath	Loss of Weight in Extractor	Weight % of solute in toluene	Amount of Solute Extracted (From GC)	Solubility from weight loss	Solubility of solute in ethane from GC analysis
	g	g		moles	Mole fraction	Mole fraction
1	15	0.5	2.17834	0.00096	0.00043	0.00028
2	35	1.4	3.20497	0.00331	0.00458	0.00367
3	40	2.7	4.52890	0.00535	0.01146	0.00769
4	45	4.8	8.26174	0.01098	0.01435	0.01111
5	45	5.3	9.41144	0.01251	0.01914	0.01530
6	50	7.3	12.66389	0.01870	0.02369	0.02055

Table 4.4 Data Analysis and Solubility Calculations for the system ethane + octacosane

Run No.	Pressure	% SD	Temperature	% SD	Temperature at the pump	Amount of Ethane pumped
	bar	%	C	%	C	moles
1	55.84	0.32	35.03	0.08	26.78	1.12892
2	65.27	0.58	35.03	0.08	27.04	1.16956
3	78.13	0.31	35.01	0.12	27.00	0.91086
4	99.30	0.38	34.96	0.09	27.00	0.75912
5	140.33	0.27	35.02	0	26.79	0.33333
6	171.68	0.3	35.01	0.07	26.79	0.27435
7	200.64	0.35	35.00	0.06	26.80	0.28028

Run No.	Amount of Toluene in the bath	Loss of Weight in Extractor	Weight % of solute in toluene from GC analysis	Amount of Solute Extracted (From GC)	Solubility from weight loss	Solubility of solute in ethane from GC analysis
	g	g		moles	Mole fraction	Mole fraction
1	25.0	0.3	0.95491	0.00060	0.00067	0.00054
2	30.0	0.6	3.82841	0.00291	0.00130	0.00249
3	30.0	0.8	3.61370	0.00275	0.00222	0.00301
4	30.0	0.9	4.28259	0.00325	0.00300	0.00429
5	35.0	1.1	3.19814	0.00284	0.00836	0.00851
6	35.0	1.2	3.82092	0.00339	0.01108	0.01235
7	40.0	1.7	4.39042	0.00445	0.01536	0.01587

Table 4.5 Data Analysis and Solubility Calculations for the system ethane + dotriacontane

Run No.	Pressure	% SD	Temperature	% SD	Temperature at the pump	Amount of Ethane pumped
	bar	%	C	%	C	moles
1	120.07	0.52	35.04	0.09	26.83	1.04239
2	136.73	0.68	35.02	0.08	27.03	0.72979
3	166.67	0.41	35.01	0.11	27.00	0.75119
4	200.68	0.58	34.98	0.07	27.01	0.42013

Run No.	Amount of Toluene in the bath	Loss of Weight in Extractor	Weight % of solute in toluene from GC analysis	Amount of Solute Extracted (From GC)	Solubility from weight loss	Solubility of solute in ethane from GC analysis
	g	g		moles	Mole fraction	Mole fraction
1	50.0	0.5	0.73230	0.000812	0.00106	0.00078
2	50.0	0.4	0.58690	0.000651	0.00122	0.00089
3	50.0	0.5	0.83393	0.000925	0.00148	0.00123
4	50.0	0.4	0.58153	0.000645	0.00211	0.00153

the difference between the initial and final weight of the extractor. The weight % of solute in the toluene bath is computed by using the area % obtained from injection of toluene samples and the calibration curves given by Figures 4.1, 4.2 and 4.3. The amount of solute extracted is determined from the weight % of the solute and the amount of toluene in the bath. The solubilities are calculated as a mole fraction from the amount of ethane pumped and the amount of solute extracted. These are calculated both from the weight loss and by the GC analysis.

4.2.2 Fluctuations in the pressure and temperature of the extractor

The solubilities measured in this work are at a fixed pressure and fixed temperature. The extractor has to be maintained at an isobaric and isothermal condition during the course of each run. For this reason it is very important that there are minimum fluctuations in the pressure and temperature of the extractor. The pressure and temperature are monitored every 10 seconds and are plotted as a function of time for the system of octacosane + ethane at 55 bar. These plots are shown in Figures 4.6 and 4.7 for temperature and pressure respectively. The minimum, maximum and average values of these parameters are also shown on the Figures along with the standard deviation. Similar behaviour is observed even at higher pressures and for all the systems. These values of standard deviation are reported for each run in the data analysis sheets of 4.7, 4.8 and 4.9 for tetracosane, octacosane and dotriacontane. These values of % SD are very low indicating that the pressure and temperature of the extractor are reasonably constant and that the fluctuations are minimal.

Some experiments were conducted with the same set-points of pressure and temperature for a few runs. The solubilities obtained from these experiments were very close and followed the physical trend of the solubilities with pressure and temperature. In addition, the constant pressure runs carried out to determine the equilibrium flow rate and the dynamic response of the toluene bath (described in section 4.2.3) support the conclusion that the performance and the data obtained from the apparatus are repeatable.

Figure 4.6 Temperature Fluctuations in the Bath @308.15 K

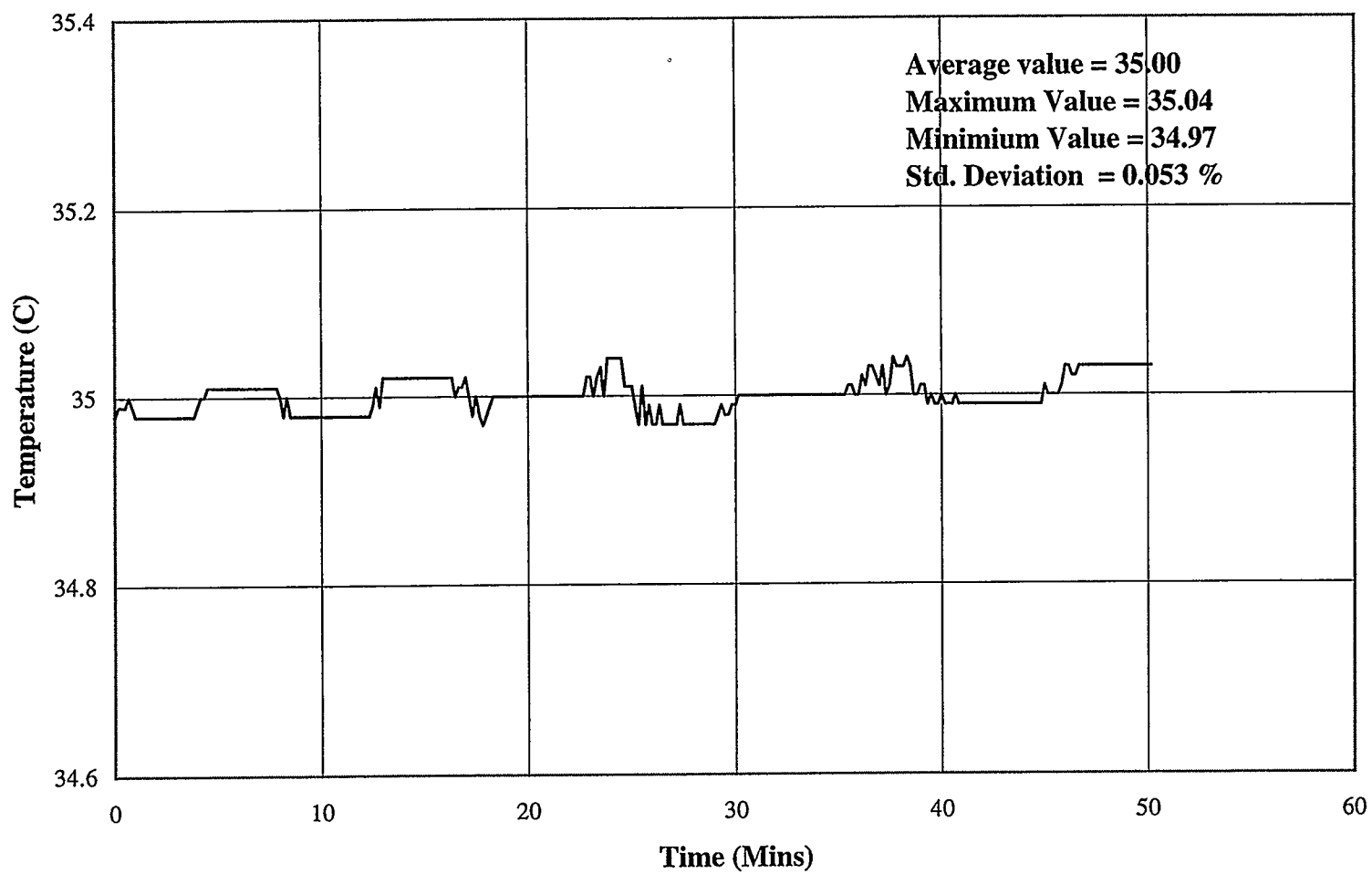
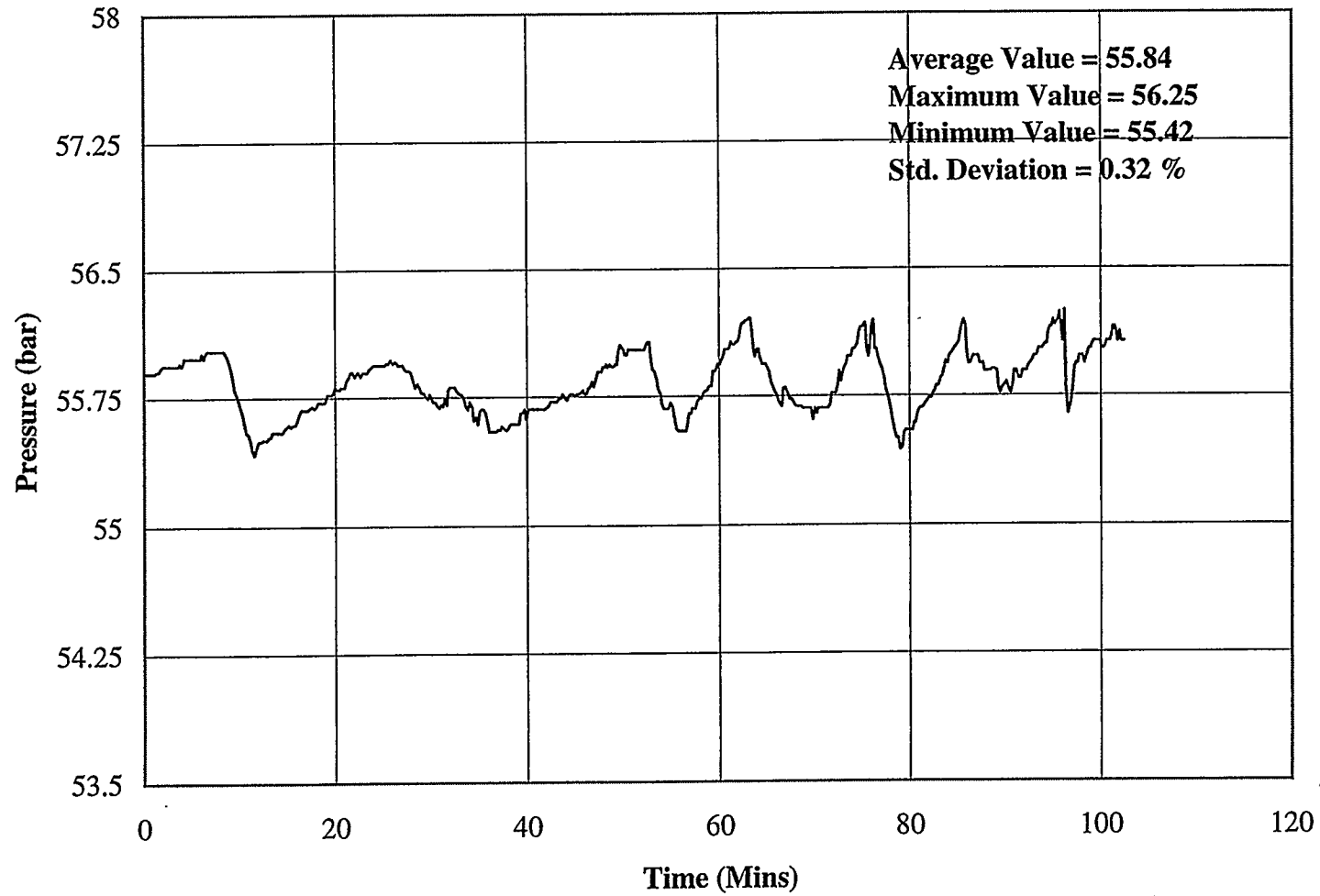


Figure 4.7 Pressure Fluctuations in the Extractor



4.2.3 Dynamic response of the toluene bath

As mentioned earlier in Chapter 3, in the dynamic method of measuring solubilities the solvent is continuously swept through the solute. In this work the solvent exiting the extractor is saturated with the solvent and the solute is later dissolved in toluene in the toluene bath. The samples from the toluene bath are collected at the end of each run and are analysed in the GC. The amount of solute extracted in each run is an important operating factor for this kind of experimental design. As the amount of toluene in the bath is fixed, it is very important to ensure that the toluene in the bath is not saturated with the solute. If the amount of toluene in the bath corresponding to the amount of solute extracted is too low the measurement error increases and if it is too high the solution approaches saturation which could lead to erroneous solubility information.

As the solvent exiting the extractor is saturated with the solute, it is expected that the deposition of the solute in the toluene should be linear with time or with the total amount of solvent pumped. This behaviour of the toluene bath is studied in this work by collecting several samples from the toluene bath during the course of some runs. These samples were analysed in the GC and the dynamic response of the toluene bath is studied. This was done for the systems of ethane + tetracosane and ethane + octacosane. This dynamic response is plotted as a curve between the weight % of solute in the toluene bath and the amount of ethane pumped through. These plots are shown in Figures 4.8 and 4.9 for tetracosane and octacosane respectively. The curves obtained between the weight % of solute in toluene and ethane pumped for both the systems are linear as expected. This linear dynamic response of the toluene bath indicates that there is no plugging of the solute in the system and that there is sufficient amount of toluene in the bath to dissolve the extracted solute.

The linear plots shown in Figures 4.8 and 4.9 for dynamic sampling do not pass through the origin as might be expected. There is a negative intercept indicating that there is a time lag between the start of the flow of ethane and the detection of the solute in the toluene bath. It can be seen from the graph that at least 2-3 cc of ethane has to be pumped before the solute can be detected. This could result from the fact that at low flow rates used in this work, there is a time delay between the start of the flow at the pump and the

Figure 4.8 Dynamic sampling of toluene for ethane+tetracosane system

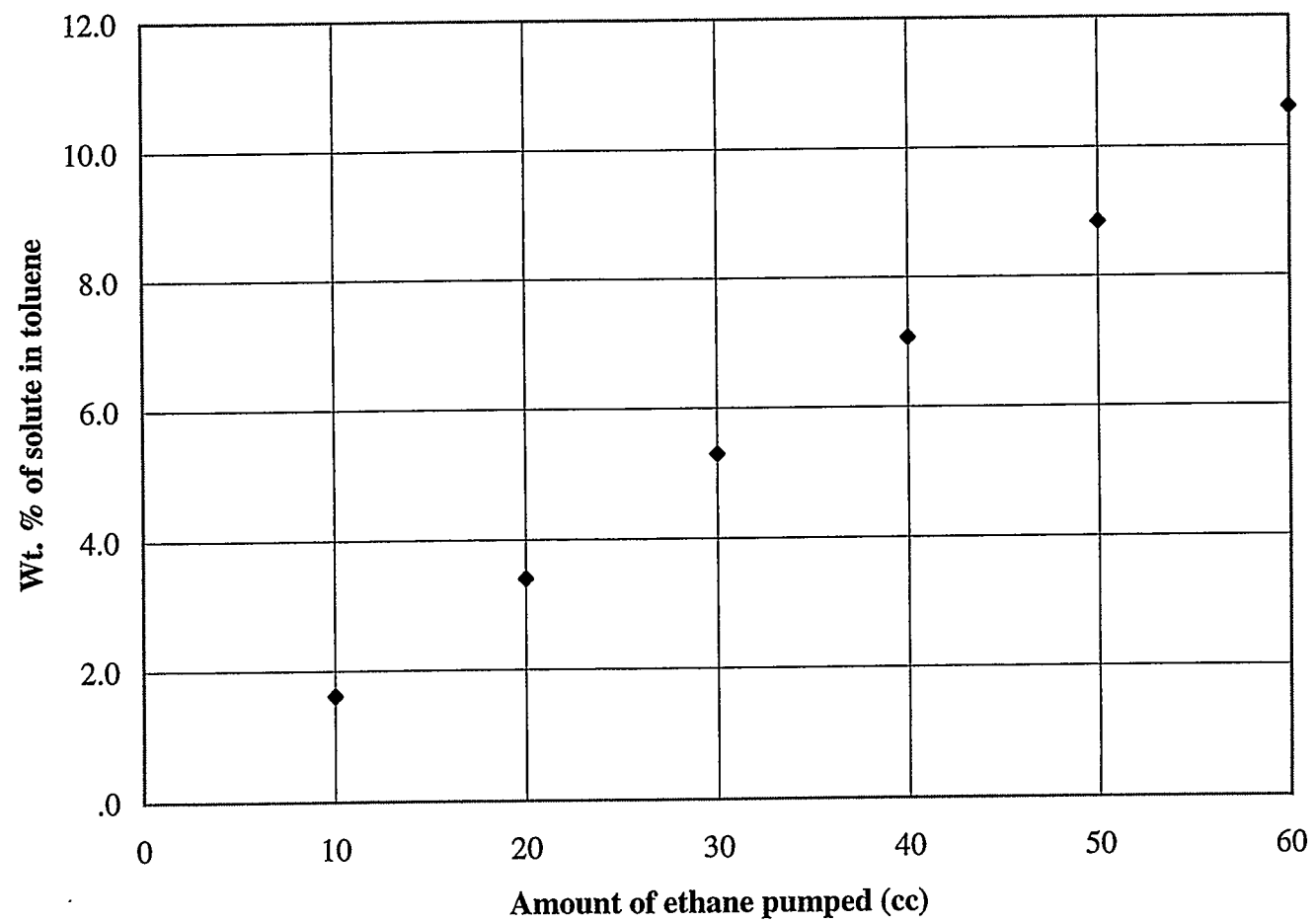
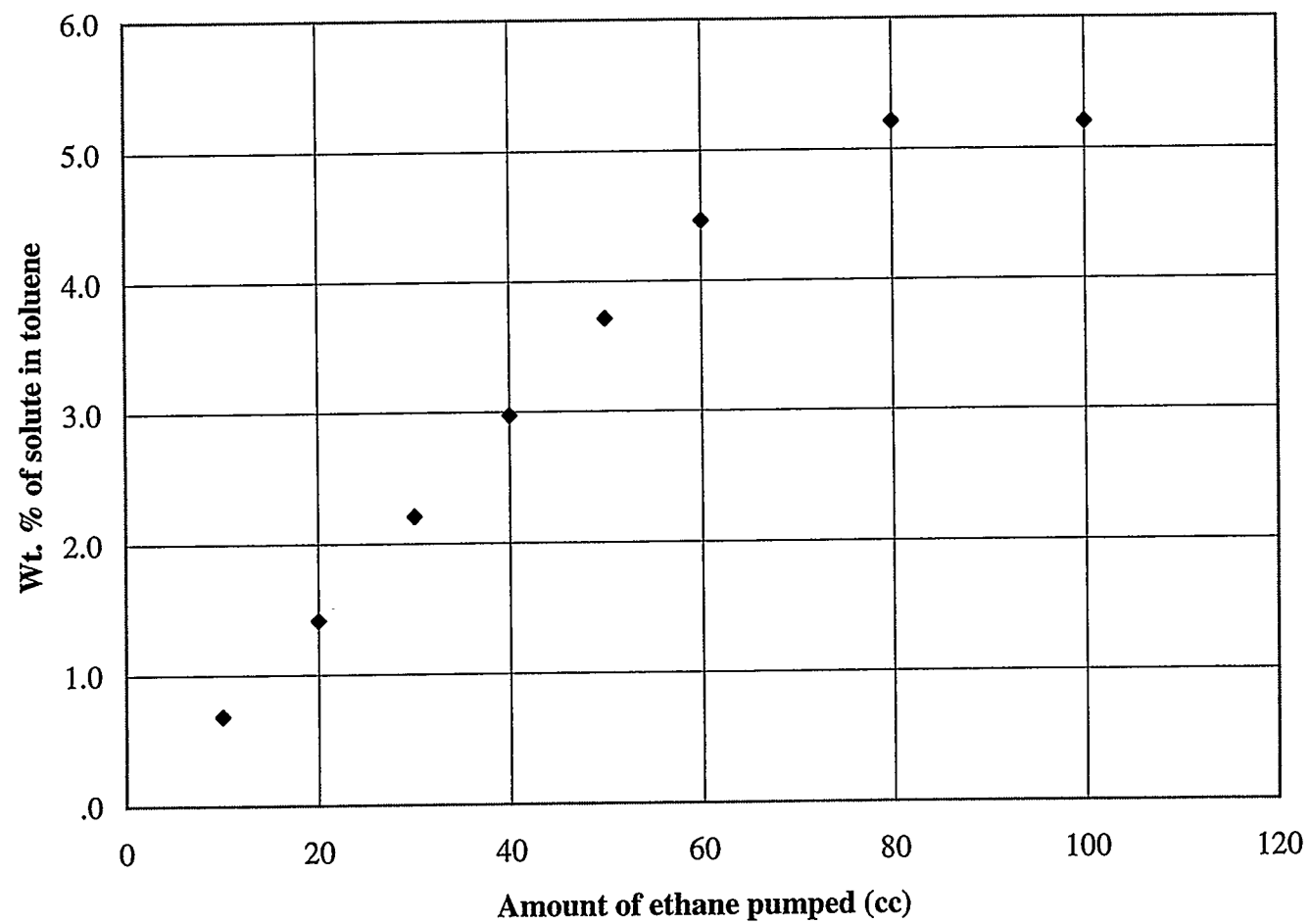


Figure 4.9 Dynamic sampling of toluene for ethane+octacosane system

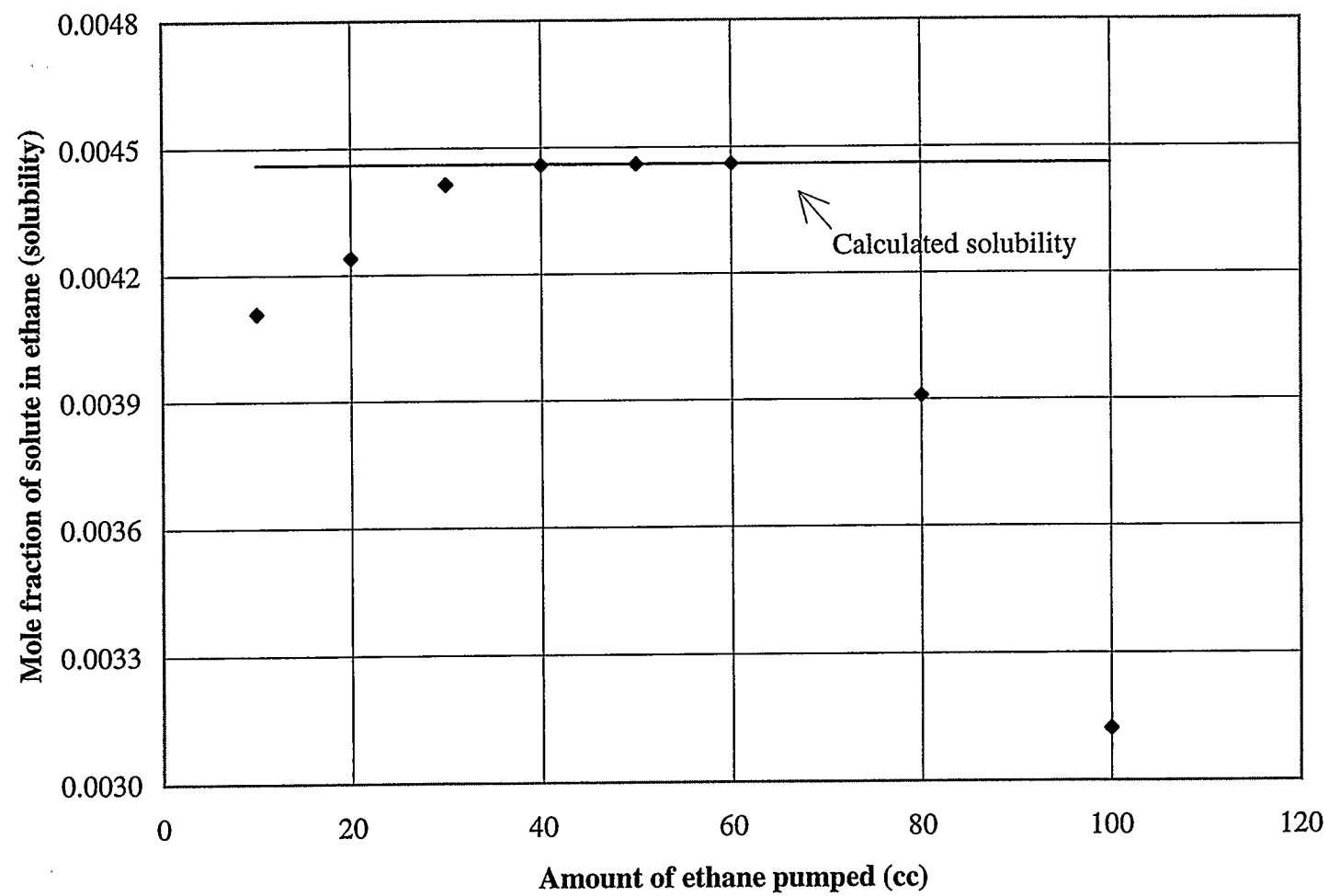


solvent reaching the toluene bath. This residence time in the apparatus could cause the time lag between the start of flow and the detection of the solute. In this work, the extractor was saturated with the solvent before the flow of the solvent is started. This was done to minimize this initial time lag effect by reducing the time delay which is caused only by the lines between the extractor and the toluene bath. This initial time lag would not cause any significant errors in the solubility measurement because the residual volume at the end of the run would still pass through the toluene bath balancing the initial delay.

The dynamic response of the toluene bath can also be used to study the effect of too short and too long run times for the experiments. The effect of too long a run time was studied for the system of ethane + octacosane. The actual design value of ethane to be pumped for this system was less than 60 cc, but 100 cc of ethane was pumped through to study the effect of excess run time. The curve obtained between the weight % of solute in the toluene bath and ethane pumped for excess solvent pumping is shown in Figure 4.9.

As the amount of ethane pumped exceeded 60 cc the toluene in the toluene bath was saturated with the solute and the weight % remains constant at the saturation value.

Figure 4.10 Experimental solubilities from dynamic sampling for ethane+octacosane system



The effect of short and long run times can also be clearly seen in Figure 4.10 which is the plot of the mole fraction of the solute in ethane, which represents solubility and amount of ethane pumped. If the amount of ethane pumped is less than 20 cc the solubility obtained is lower than the actual solubility value. This is because there are some initial effects in the apparatus causing a time lag and unstable flow at the start-up. In addition, the amount of solute extracted is very low and the analysis of these samples for the toluene bath is not sufficiently accurate. If the amount of ethane pumped is higher than 60 cc the solubility obtained is also very erroneous. This is because the toluene in the bath is saturated with the solute. For all intermediate values of ethane pumped (40-60cc) the obtained value of solubility is very accurate. All the experiments carried out in this work are carefully designed to avoid this problem of too little and too much extracted solute.

5.0 Modelling the SCF-solid solubility data

SCF technology has been shifting towards significantly more complex molecules, undergoing broader types of physical and chemical transformations. The molecular complexity of the phase behaviour of these systems is increasing. They are especially challenging because of high compressibility and the asymmetry of the systems encountered. This has led to a wide variety of models representing the phase behaviour in the SCF state. Any application of SFE technology is highly dependent on the ability to understand and predict the phase equilibria in these complex systems. As mentioned in Chapter 2, these models range from simple cubic equations of state (EOS) to complex lattice gas models.

One such simpler method is the translation of a cubic EOS to model solid phases in thermodynamic calculations (Salim and Trebble, 1994) described in section 1.3.2. In this Chapter the principle of translation will be described and applied to the TBS EOS. The solvent (ethane) and the solutes (tetracosane; C24, octacosane; C28, and dotriacontane; C32) used in this work will be translated at their triple points using the TBS EOS. The translated equations will then be used to model the solubility data obtained in this work, for the SCF ethane-hydrocarbon systems.

5.1 TBS EOS for the vapour-Liquid domain

The development of the TBS EOS for the vapour-liquid (v-l) domain has been described elsewhere (Salim and Trebble, 1991 a,b) and is given as:

$$P = \frac{RT}{v - b} - \frac{a_c \alpha}{v^2 + (b + c)v - (bc + d^2)} \quad (5.1)$$

where b is the smallest positive root of the following equation:

$$b^3 + (2 - 3\xi_c) \frac{RT_c}{P_c} b^2 + 3 \left(\frac{RT_c \xi_c}{P_c} \right)^2 b - \left(\frac{RT_c d^2}{P_c} + \left[\frac{RT_c \xi_c}{P_c} \right]^3 \right) = 0 \quad (5.2)$$

and:

$$c = \frac{RT_c}{P_c} (1 - 3\xi_c) \quad (5.3)$$

$$a_c = P_c \left(2bc + b^2 + d^2 + (b + c) \left[\frac{RT_c}{P_c} \right] + 3 \left[\frac{RT_c \xi_c}{P_c} \right]^2 \right) \quad (5.4)$$

$$\alpha = 1 + m(1 - \sqrt{T_r}) + p(\sqrt{0.7} - \sqrt{T_r})(1 - \sqrt{T_r}) \quad (5.5)$$

The TBS EOS has four parameters a , b , c and d and four adjustable parameters m , p , ζ_c and d . These parameters are generally obtained from the regression analysis using VLE or vapour pressure data.

5.1.1 TBS EOS parameters for the v-l domain

In this work, the four adjustable parameters m , p , ζ_c and d are regressed from vapour pressure data for tetracosane, octacosane, and dotriacontane. The vapour pressure data are obtained from the DIPPR property package and the equations are as follows:

Tetracosane:

$$P = \exp \left(136.02 - \frac{17955}{T} - 15.024 \times \ln(T) + 2.1305 \times 10^{-18} \times T^6 \right) \quad (5.6)$$

Octacosane:

$$P = \exp \left(288.10 - \frac{28137}{T} - 36.880 \times \ln(T) + 1.0468 \times 10^{-5} \times T^2 \right) \quad (5.7)$$

Dotriacontane:

$$P = \exp \left(607.28 - \frac{50819}{T} - 81.769 \times \ln(T) + 2.3984 \times 10^{-5} \times T^2 \right) \quad (5.8)$$

where P is in Pa and T is in K.

The regression analysis was performed using Gauss-Newton minimisation with the following objective function:

$$E = \sum_{i=1}^N dP_{\text{sat}}^2 \quad (5.9)$$

where

$$dP_{\text{sat}} = 100 \left[\frac{P_{\text{sat}}^{\text{EOS}} - P_{\text{sat}}^{\text{exp}}}{P_{\text{sat}}^{\text{exp}}} \right] \quad (5.10)$$

The regression was carried out over the entire PT range from the triple point to the critical point. The initial estimates for these parameters are obtained from the generalised TBS EOS for the v-l region (Salim, 1990).

In addition to the regression using the vapour pressure data, the parameters are readjusted to match the experimental liquid volume at 25 °C at saturation pressure. The liquid volumes used for this purpose are also obtained from the DIPPR property package and are given below:

Molar liquid volumes at 25 °C and saturation pressure :

Tetracosane: 434.698 cc/mol

Octacosane: 505.676 cc/mol

Dotriacontane: 576.792 cc/mol

All the other properties of these compounds used in this work are given in Table 5.1.

.Property	Tetracosane	Octacosane	Dotriacontane
Molecular weight (g/mol)	338.661	394.769	450.876
Critical temperature (K)	810.0	843.0	871.0
Critical pressure (atm)	10.0667	8.7639	7.7671
Critical volume (cc/mol)	1360	1580	1799.99
Critical compressibility	0.206	0.200	0.195999
Melting point (K)	323.75	334.35	342.35
Triple point temperature(K)	323.75	334.35	342.35
Triple point pressure (atm)	1.8469e-8	9.6047e-10	1.7477e-12
Normal boiling point (K)	664.45	704.75	740.15
Acentric factor	1.03035	1.14461	1.22318

Table 5.1 Properties of the solutes used in this work

The results of the regression analysis are presented in the following Table 5.2.

Regressed Parameter	Tetracosane	Octacosane	Dotriacontane
m	2.3299	2.3558	2.3734
p	4.6853	-3.0098	-1.8209
ζ_c	0.2185	0.2201	0.2183
d (cc/mol)	454.8377	489.2750	553.0727

Table 5.2 Regressed TBS EOS v-l parameters for the solutes used in this work

The TBS EOS parameters for ethane are taken from the regression analysis done previously (Salim, 1990) and are reported here in Table 5.3. and the critical properties of ethane used for regression are reported in Table 5.4.

Regressed parameter	Ethane
m	0.9918
p	0.4546
ζ_c	0.3093
d (cc/mol)	34.86

Table 5.3 TBS EOS v-l parameters for ethane

Property	Ethane
Critical temperature (K)	305.3
Critical pressure (atm)	48.08
Critical volume (cc/mol)	147.1
Acentric factor	0.0980

Table 5.4 Critical properties of ethane used in this work

5.1.2 Property predictions using the v-l TBS EOS:

With the above obtained values of m , p , ζ_c and d , the values of a , b , c and d can be calculated using equations (5.2) to (5.5). The TBS EOS given by equation (5.1) can then be used to predict the thermodynamic properties of these compounds in the v-l region.

In this section comparisons are made between the experimental and regressed properties of vapour pressure. Shown in Figures 5.1, 5.2, 5.3 and 5.4 are the comparisons between DIPPR values and regressed values of vapour pressures for tetracosane, octacosane, dotriacontane and ethane respectively. The absolute average deviations for tetracosane, octacosane, dotriacontane and ethane are 2.69%, 3.29%, 7.48% and 0.68% respectively.

In addition to these properties, other thermophysical properties like internal energy, enthalpy, entropy, isobaric and isochoric heat capacities, speed of sound, Joule-Thomson coefficient, virial coefficients can also be predicted using the TBS EOS. The equations required for the prediction of these properties can be found elsewhere (Salim and Trebble, 1991 b).

Figure 5.1 Regression of Vapor Pressures using TBS EOS for tetracosane

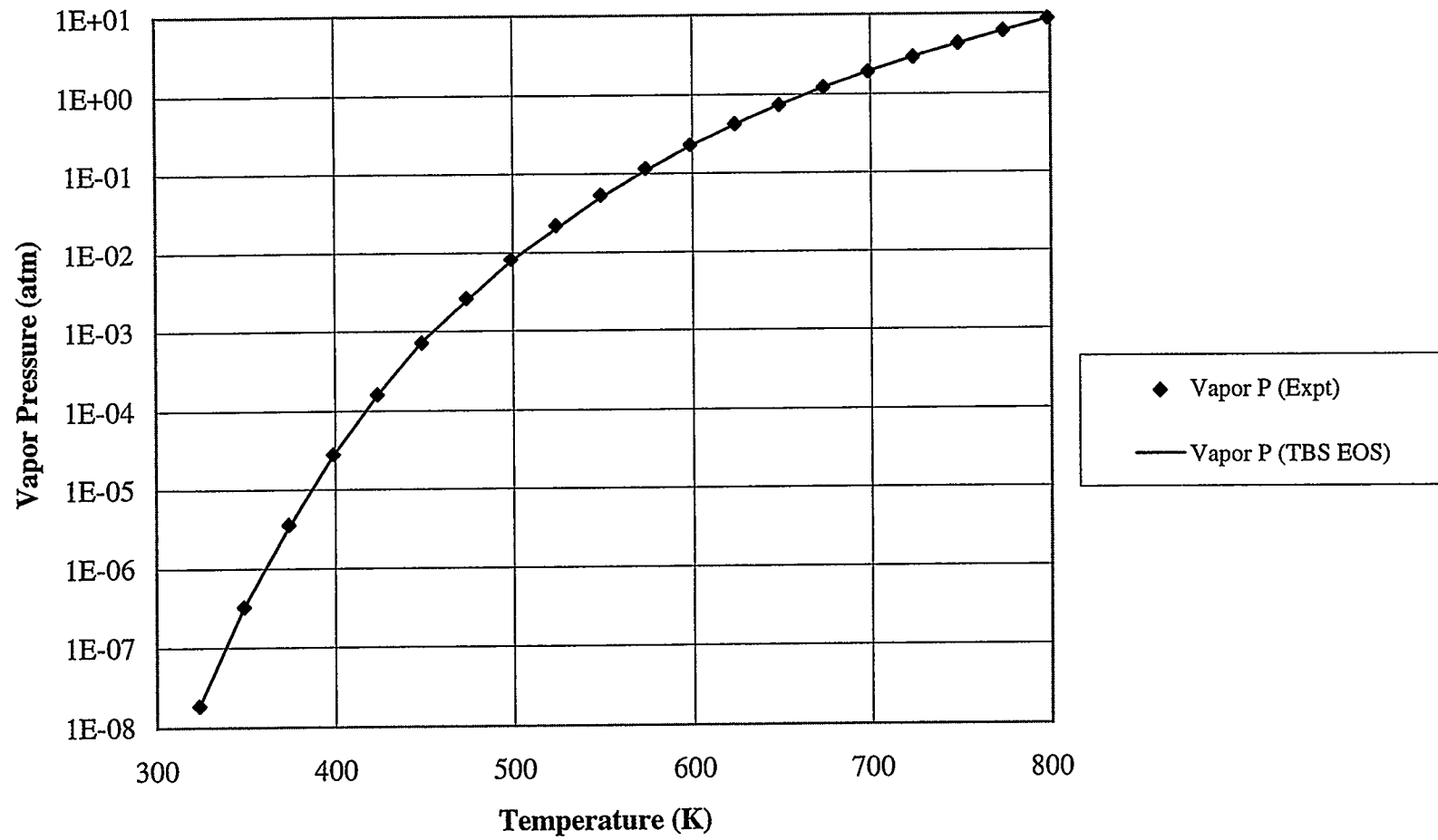


Figure 5.2 Regression of Vapor Pressures using TBS EOS for octacosane

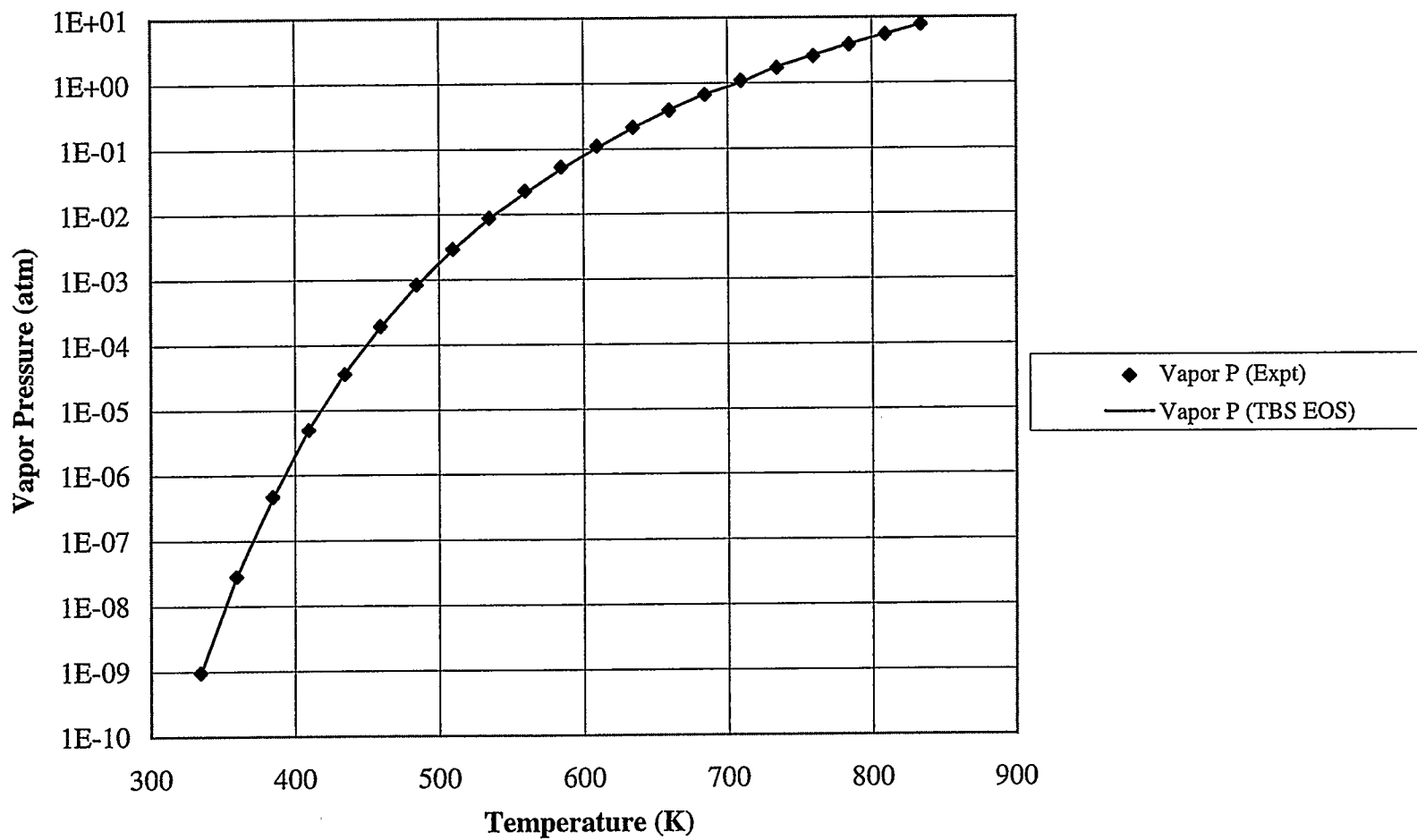


Figure 5.3 Regression of Vapour Pressures using TBS EOS for dotriacontane

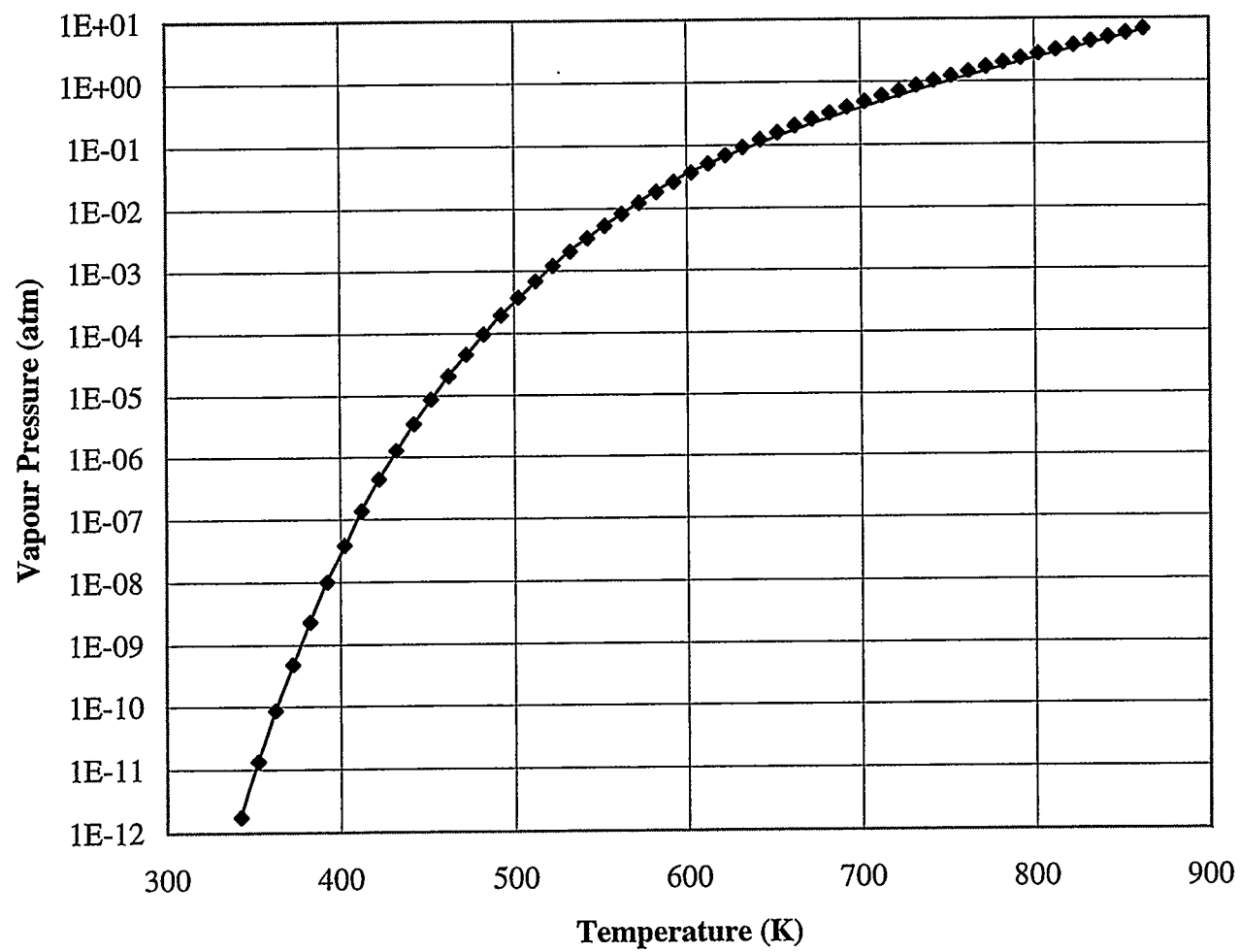
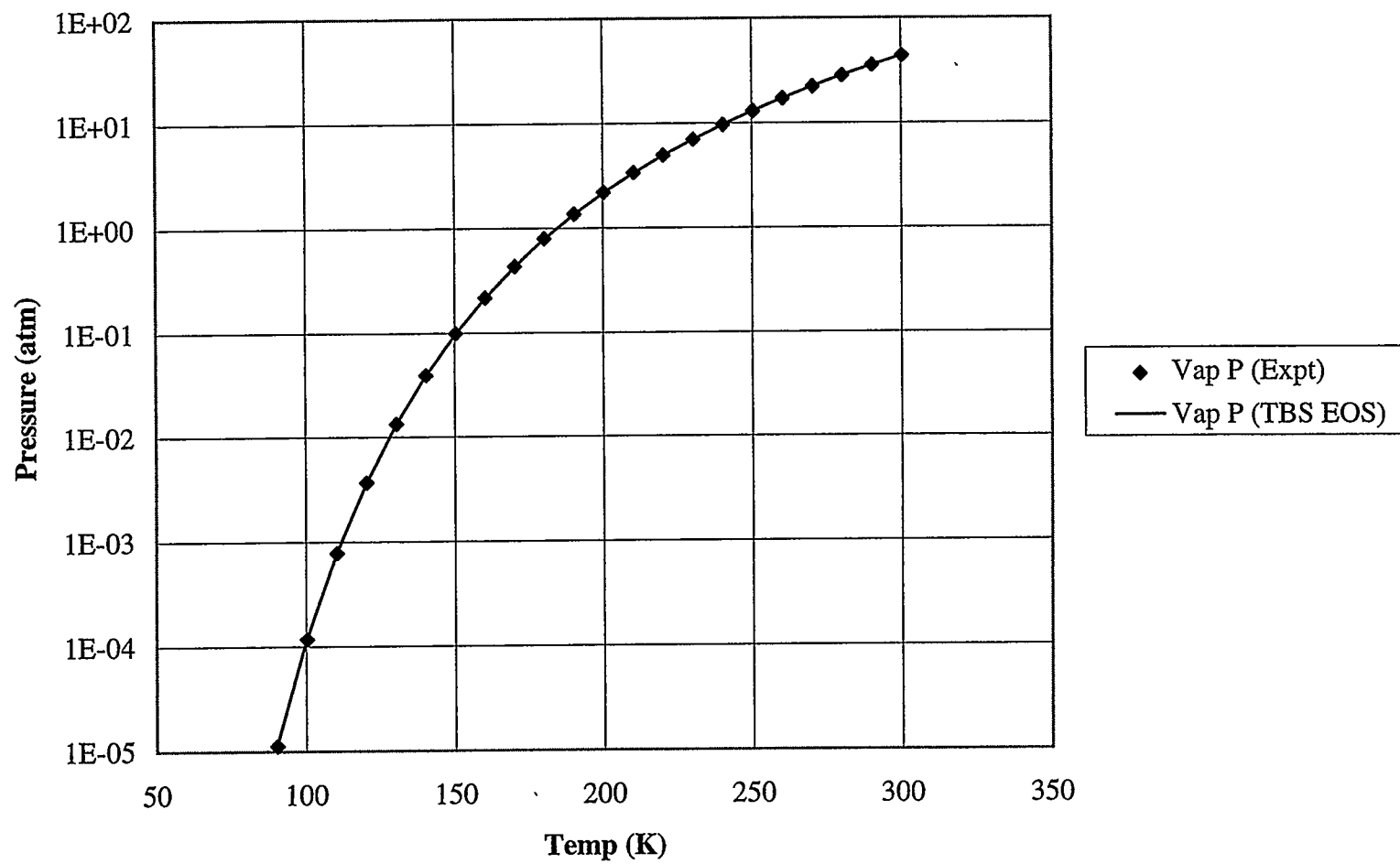


Figure 5.4 Regression Of Vapor Pressure using TBS EOS for ethane



5.2 Translation of the TBS EOS at the triple point

The translation of the TBS EOS at the triple point, denoted by ‘ $\bar{\cdot}$ ’, results in the following form:

$$P = \frac{RT}{v - \bar{b}} - \frac{\bar{a}\hat{\alpha}}{v^2 + (\bar{b} + \bar{c})v - (\bar{b}\bar{c} + \bar{d}^2)} \quad (5.11)$$

where

$$\hat{\alpha} = 1 + \hat{m}(\bar{T}_r - T_r) + \hat{p}(\bar{T}_r \ln \bar{T}_r - T_r \ln T_r) \quad (5.12)$$

$$\bar{T}_r = \frac{\bar{T}}{T_c} \quad (5.13)$$

5.2.1 Principle of translation

In order to determine the constants $\bar{a}$, $\bar{b}$, $\bar{c}$ and $\bar{d}$ in the translated equation, it is necessary to impose four conditions. The first constraint is that the translated equation must match the experimental value of solid density at the triple point temperature. The second is that the saturation pressure calculated from the original EOS must be matched by the translated equation. Thirdly, the solid phase fugacity from the translated equation (TEOS) must match the vapour phase fugacity from the TEOS at the triple point to ensure an equilibrium condition. Finally, the vapour phase fugacities calculated from both the EOS and TEOS must match at the triple point. These constraints are shown in Figure 5.5.

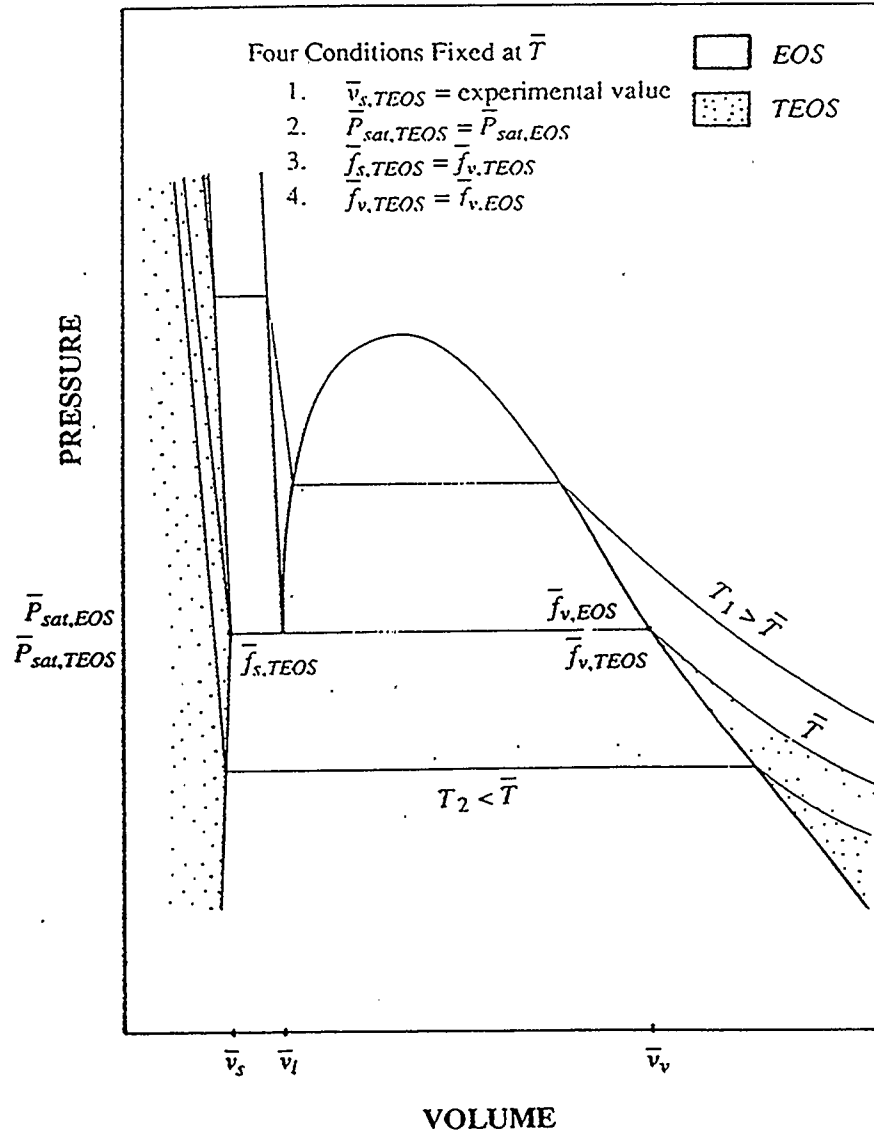


Figure 5.5 Criterion for the translation of EOS at the triple point
(Salim and Trebble, 1994)

5.2.2 Solution algorithm

The above restraints are met by the simultaneous solution of the following equations using experimental values of for $\bar{T}$ and $\bar{v}_s$:

$$\bar{P}_{sat} = \frac{R\bar{T}}{\bar{v}_s - \bar{b}} - \frac{\bar{a}}{\bar{v}_s^2 + (\bar{b} + \bar{c})\bar{v}_s - (\bar{b}\bar{c} + \bar{d}^2)} \quad (5.14)$$

$$\bar{P}_{sat} = \frac{R\bar{T}}{\bar{v}_v - \bar{b}} - \frac{\bar{a}}{\bar{v}_v^2 + (\bar{b} + \bar{c})\bar{v}_v - (\bar{b}\bar{c} + \bar{d}^2)} \quad (5.15)$$

$$\bar{f}_{s,TEOS} = \bar{f}_{v,TEOS} \quad (5.16)$$

$$\bar{f}_{v,TEOS} = \bar{f}_{v,EOS} \quad (5.17)$$

A solution algorithm for calculation of $\bar{a}$, $\bar{b}$, $\bar{c}$ and $\bar{d}$ is summarized elsewhere (Salim and Trebble, 1994) and is as follows:

(1) Obtain experimental values or estimates of $\bar{T}$ and $\bar{v}_s$, and calculate the values of $\bar{P}_{sat}$, $\bar{f}_{v,EOS}$, $\bar{v}_l$ and $\bar{v}_v$ from the liquid-vapour EOS.

(1) Initiate $\bar{b}$ and $\bar{d}$ from

$$\bar{b} = b - (\bar{v}_l - \bar{v}_s) \quad (5.18)$$

$$\bar{d} = d - (\bar{v}_l - \bar{v}_s) / 3 \quad (5.19)$$

(3) Calculate $\bar{a}$, and $\bar{c}$ from simultaneous solution of equations (5.14) and (5.15).

(4) Adjust $\bar{b}$ and $\bar{d}$ to satisfy equations (5.16) and (5.17) by minimising the following objective function:

$$F = F_1^2 + F_2^2 \quad (5.20)$$

$$F_1 = \frac{\bar{f}_{v,TEOS} - \bar{f}_{v,EOS}}{\bar{f}_{v,EOS}} \quad (5.21)$$

$$F_2 = \frac{\bar{f}_{s,TEOS} - \bar{f}_{v,TEOS}}{\bar{f}_{v,TEOS}} \quad (5.22)$$

(5) Return to step 3 unless the adjustment to $\bar{b}$ and $\bar{d}$ is within a suitable tolerance (10^{-13} %) or until $\sqrt{F}$ is less than 10^{-3} .

5.2.3 Development of temperature dependence in the solid-vapour (s-v) region

The parameters that describe the temperature dependence in the translated TBS (TTBS) EOS are $\hat{m}$ and $\hat{p}$. Optimum values of these parameters are obtained by regression of PVT data in the s-v region and are generally fit to solid vapour pressure data. In the case of non-availability of vapour pressure data, a predictive method was also proposed (Salim and Trebble, 1994) to determine these parameters. This predictive method is based on the derivation of heat of sublimation $\Delta\bar{H}_{subl}$ and solid isobaric heat capacity $\bar{C}_{p,s}$ at the triple point. The development of these expressions can be found elsewhere (Salim and Trebble, 1994).

In order to ensure that the temperature dependence in the TTBS EOS does not violate thermodynamic consistency, $\bar{\alpha}$ was developed based on

$$\Delta H_{subl} = \text{finite} \quad (5.23)$$

and its constants were constrained by using the inequality

$$C_{v,s} \geq 0 \quad (5.24)$$

This condition was imposed only for translation of ethane which violated the thermodynamic consistency.

5.2.4 Properties required for the translation of the EOS

In addition to the triple point temperature $\bar{T}$, the translation requires the experimental value of solid density at triple point $\bar{v}_s$, heat of sublimation $\Delta\bar{H}_{subl}$ and solid isobaric heat capacity $\bar{C}_{p,s}$ at the triple point. These triple point properties used in this work are obtained from the DIPPR property package. Since the experimental values of solid isobaric heat capacity were not available at the triple point, they have been extrapolated from available experimental data below the triple point from the DIPPR property package.

All the properties used in this work are listed here in Table 5.5.

Property	Tetracosane	Octacosane	Dotriacontane	Ethane
$\bar{T}$ (K)	323.75	334.35	342.25	90.3499
$\bar{v}_s$ (cc/mol)	369.727	432.919	492.635	41.197
$\Delta\bar{H}_{subl}$ (J/mol)	1.6165 e 5	1.8566 e 5	2.0617 e 5	2.0712 e 4
$\bar{C}_{p,s}$ (J/mol K)	730.505	1067.985	1079.075	81.873

Table 5.5 Triple point properties used for translation of TBS EOS

5.2.5 Translated parameters for the TBS EOS in the s-v region

Using the solution algorithm mentioned in section 5.2.2 to determine $\bar{a}$, $\bar{b}$, $\bar{c}$ and $\bar{d}$ and section 5.2.3 to determine $\hat{m}$ and $\hat{p}$ and the following parameters are obtained for the translated equation for tetracosane, octacosane, dotriacontane and ethane.

TTBS EOS parameter	Tetracosane	Octacosane	Dotriacontane	Ethane
$\bar{a} \times 10^{-8}$ (cm ⁶ mol ⁻² atm)	5.8556	7.9105	9.6679	0.09728
$\bar{b}$ (cm ³ mol ⁻¹)	361.282	426.219	492.338	43.353
$\bar{c}$ (cm ³ mol ⁻¹)	4201.460	5277.626	5947.827	109.390
$\bar{d}$ (cm ³ mol ⁻¹)	345.879	462.759	502.867	77.953
$\hat{m}$	4.334	4.484	3.509	2.548
$\hat{p}$	2.071	-0.916	-1.325	0.777

Table 5.6 Translated parameters of the TTBS EOS

5.2.6 Property predictions using the TTBS EOS

With the calculation of the temperature dependence parameters the TEOS can be utilised at temperatures above and below the triple point by extrapolation, with the result that the entire P-T space for a pure component can be accurately reproduced. With an operative EOS based solid phase model like the TTBS EOS, thermophysical properties like the density, vapour pressures, enthalpy and isobaric and isochoric heat capacities can be predicted for the solid phase.

Among all these properties the solid isobaric heat capacity is the most important one. The equations required for predicting the solid isobaric heat capacities can be found elsewhere (Salim and Trebble, 1994).

5.3 Solid-Supercritical fluid (SCF) equilibria

Having developed satisfactory thermodynamic models for the l-v and s-v regions, all kinds of phase transitions including s-l, s-v and s-l-v transitions can be effectively predicted with the combination of these two models. The use of the translated equation for multiphase equilibrium calculations was demonstrated for binary s-l equilibrium in the CO₂-CH₄ binary and for binary s-v equilibrium in the systems CO₂-benzoic acid and ethylene-benzoic acid (Salim and Trebble, 1994). The match to the experimental data was very good. The translated equation can be used by itself to model the s-v transitions by calculating the solid phase fugacity using the smallest volume root greater than $\bar{b}$ and the vapour phase fugacity using the greatest volume root, both from the TEOS. The s-l transitions can be modelled by calculating the solid phase fugacity from the TEOS and the liquid phase fugacity from the original EOS. The s-v transitions can also be modelled similar to the s-l transitions by using the TEOS to calculate the solid phase fugacity and using the original EOS to calculate the vapour fugacity.

The last approach is used in this work to model the solid-SCF equilibria of tetracosane-ethane, octacosane-ethane and dotriacontane-ethane systems. This approach is used because it makes the algorithm and the program generalised to model any type of transition including the s-v, s-l, and v-l transitions with minor modifications.

5.3.1 Mixing rules

Based on the conclusions drawn from earlier studies (Salim, 1990; Salim and Trebble, 1994; Salim, 1996), it was decided to use the conventional mixing rules with k_a and k_d as the only binary interaction parameters. $\hat{k}_a$ is also set to unity as low solvent solubility is suspected. The following mixing rules are used in this work to model the solubility of solid in the SCF solvent in the systems of tetracosane-ethane, octacosane-ethane and dotriacontane-ethane.

For the v-l region:

$$a = \sum \sum x_i x_j (a_i a_j)^{0.5} (1 - k_a) \text{ where } a = a_c \alpha \quad (5.25)$$

$$b = \sum \sum x_i x_j \left(\frac{b_i + b_j}{2} \right) \quad (5.26)$$

$$c = \sum \sum x_i x_j \left(\frac{c_i + c_j}{2} \right) \quad (5.27)$$

$$d = \sum \sum x_i x_j \left(\frac{d_i + d_j}{2} \right) (1 - k_d) \quad (5.28)$$

For the solid region:

$$\bar{a}\hat{\alpha} = \sum \sum x_i x_j |\bar{a}_i \bar{a}_j \hat{\alpha}_i \hat{\alpha}_j|^{0.5} (1 - \hat{k}_a) \quad (5.29)$$

$$\bar{b} = \sum \sum x_i x_j \left(\frac{\bar{b}_i + \bar{b}_j}{2} \right) \quad (5.30)$$

$$\bar{c} = \sum \sum x_i x_j \left(\frac{\bar{c}_i + \bar{c}_j}{2} \right) \quad (5.31)$$

$$\bar{d} = \sum \sum x_i x_j \left(\frac{\bar{d}_i + \bar{d}_j}{2} \right) \quad (5.32)$$

5.3.2 Solution algorithm

The solution algorithm involves the regression of the binary interaction parameters and prediction of solubilities over the entire P-T range. Optimum binary interaction parameters were obtained from regression analysis of the experimental binary data. This is achieved by solving a minimisation problem, utilising a common isobaric-isothermal (P-T) flash algorithm. The details of the algorithm can be found elsewhere (Salim, 1990). As k_a and k_d are used as the only binary interaction parameters, the minimisation is done with respect to these two variables. The objective function used for minimisation in this work is given as follows:

$$W = W(k_a, k_d) = \sum_{m=1}^N \left[\left(\frac{x_{m,1,v}^{EOS} - x_{m,1,v}^{exp}}{x_{m,1,v}^{exp}} \right) \times 100 \right]^2 \quad (5.33)$$

where N is the number of data points and 1 refers to the less volatile component.

5.3.3 Performance of the model

Having established the model parameters given in section 5.3.1 and the solution algorithm given in section 5.3.3, to determine the parameters the required program was developed and executed successfully. The solubility data obtained in this work for the systems of tetracosane-ethane, octacosane-ethane, and dotriacontane-ethane has been used to regress the interaction parameters. The data used for regression is given in Tables 4.3 to 4.5. The goodness of the fit of solid solubilities in the supercritical solvent is represented as %AAD. In addition, the standard deviation (SD) of the regressed binary interaction parameters is also computed which indicates the variation in these parameters. The results of the regression analysis are presented here in Table 5.7.

System	k_a	k_d	% AAD	% SD of k_a	% SD of k_d
Tetracosane-ethane	-0.0147	-0.3128	4.25	1.76	6.53
Octacosane-ethane	-0.2009	-0.6544	10.65	1.97	5.66
Dotriacontane-ethane	-0.1185	-0.9131	2.00	2.42	4.48

Table 5.7 Results of regression of interaction parameters

A discussion on the behaviour of the solubility data and also the performance of the model in representing the experimental data are presented in Chapter 6.

6.0 Discussion of results

The solubilities determined in this work for the systems of ethane + tetracosane, ethane + octacosane and ethane + dotriacontane are computed in Tables 4.3, 4.4 and 4.5 respectively. These experimental solubilities are summarized here in Table 6.1. This table also contains the results of the error analysis performed on the experimental solubility data. These results are expressed as a +/- precision for each solubility value. These errors were calculated by considering the cumulative effect of all the errors in the measured variables. The errors in the measurement of pressure and temperature at the pump were taken into account to recalculate the density of ethane and hence the amount of ethane pumped. The errors caused by the analysis of the toluene for the amount of solute by the GC were also taken into account. This was done by determining the difference between the calibrated value and the actual value of the weight % of solute obtained during the calibration procedure. This also includes the errors caused by imprecision of the GC. A sample calculation for the determination of the precision of solubility data is shown in Appendix A. The difference between these new values and the original values are reported here as +/- precision. The comparison of these solubilities to other works and the performance of the model described in Chapter 5, are discussed in this Chapter.

6.1 Experimental

The solubilities listed in Table 6.1, are plotted in Figures 6.1, 6.2 and 6.3 respectively. These plots also contain the solubility data obtained by other works. These figures also show the performance of the model used in this work, which was described in Chapter 5. The solubility data of the ethane + tetracosane system are compared to the data of Suleiman and Eckert (1995). The data of ethane + octacosane and ethane + dotriacontane are compared to both the works of Suleiman and Eckert (1995) and Moradinia and Teja (1986). As the solubilities obtained from the chromatographic analysis are more accurate than those obtained from the weight loss method, all the comparisons are made with respect to the former method. The solubilities obtained from the weight loss method are not shown in these figures. The inaccuracy in the weight loss

Table 6.1 Experimental solubility data obtained in this work**System : Ethane + Tetracosane @ 308.15 K**

Pressure bar	Mole fraction of Tetracosane
59.71	0.00028 +/- 0.000004
74.83	0.00367 +/- 0.000042
100.01	0.00769 +/- 0.00013
129.99	0.01111 +/- 0.00016
163.92	0.01530 +/- 0.00034
199.32	0.02055 +/- 0.00046

System : Ethane + Octacosane @ 308.15 K

Pressure bar	Mole fraction of Octacosane
55.84	0.00054 +/- 0.000006
65.27	0.00249 +/- 0.000033
78.13	0.00301 +/- 0.000046
99.30	0.00429 +/- 0.000062
140.33	0.00851 +/- 0.00016
171.68	0.01235 +/- 0.00027
200.64	0.01587 +/- 0.00035

System : Ethane + Dotriacontane @ 308.15 K

Pressure bar	Mole fraction of Dotriacontane
120.07	0.00078 +/- 0.000007
136.73	0.00089 +/- 0.000013
166.67	0.00123 +/- 0.000015
200.68	0.00153 +/- 0.000019

method arises from the fact that the accuracy of the weight measurement is only 0.1 g and also the weight loss is very small compared to the total weight being measured. Figure 6.1 shows that the solubility data obtained in this work for the system of ethane + tetracosane, does not match very well with that of Suleiman and Eckert (1995) and are consistently low. The data obtained in this work deviates from the other work by an average of 46 %. In this work the solubilities are determined at low pressures of 60 and 75 bar whereas the minimum pressure used in the other work is 80 bar.

The solubility data obtained in this work for the system of ethane + octacosane shown in Figure 6.2 matches the solubility obtained by both Suleiman and Eckert (1995) and Moradinia and Teja (1986) extremely well. Small deviations from other works are shown at low and high pressures, but the match is excellent for intermediate pressures. The data obtained in this work shows an AAD of 0.2 % with that of Moradinia and Teja and 5.1 % with that of Suleiman and Eckert. For this system the solubilities were determined for two data points close to the critical point of ethane (48 bar), which was not done in earlier works.

The solubilities of the system ethane + dotriacontane are shown in Figure 6.3. The solubilities are measured in this work only at high pressures ranging from 120 to 200 bar. This system was chosen to validate the experimental method used in this work, as the data obtained for the system of ethane + tetracosane did not agree with the other published data of Suleiman and Eckert (1995). There is considerable discrepancy in the solubility of dotriacontane in ethane reported in the earlier two works. The data obtained by Suleiman and Eckert is overpredicted from that of Moradinia and Teja by over 200 %. Since the deviations are higher at higher pressures between the two works, these high pressures are chosen to test the performance of this work. As can be seen from Figure 6.3 there is very close agreement between the data obtained from this work and that of Moradinia and Teja. The data obtained in this work agrees to that of Moradinia and Teja to within 7.3 %, but shows a deviation of about 72 % from that of Suleiman and Eckert. Similar to the trend observed in the system ethane + tetracosane, the solubilities obtained in this work are consistently lower than those of Suleiman and Eckert.

Figure 6.1 Comparison of solubility data for ethane + tetracosane system @ 308.15 K

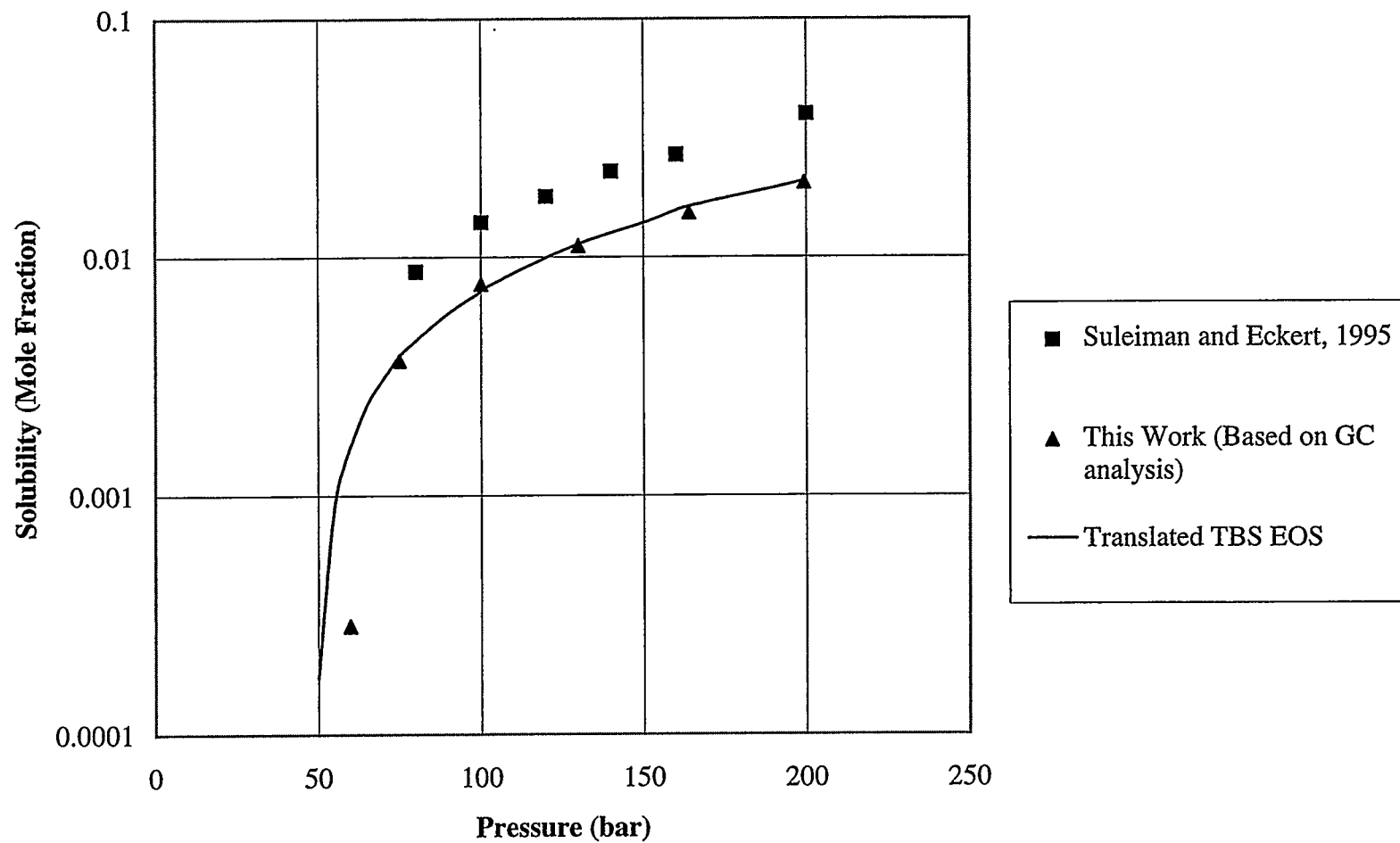


Figure 6.2 Comparison of solubility data for ethane +octacosane syatem @ 308.15 K

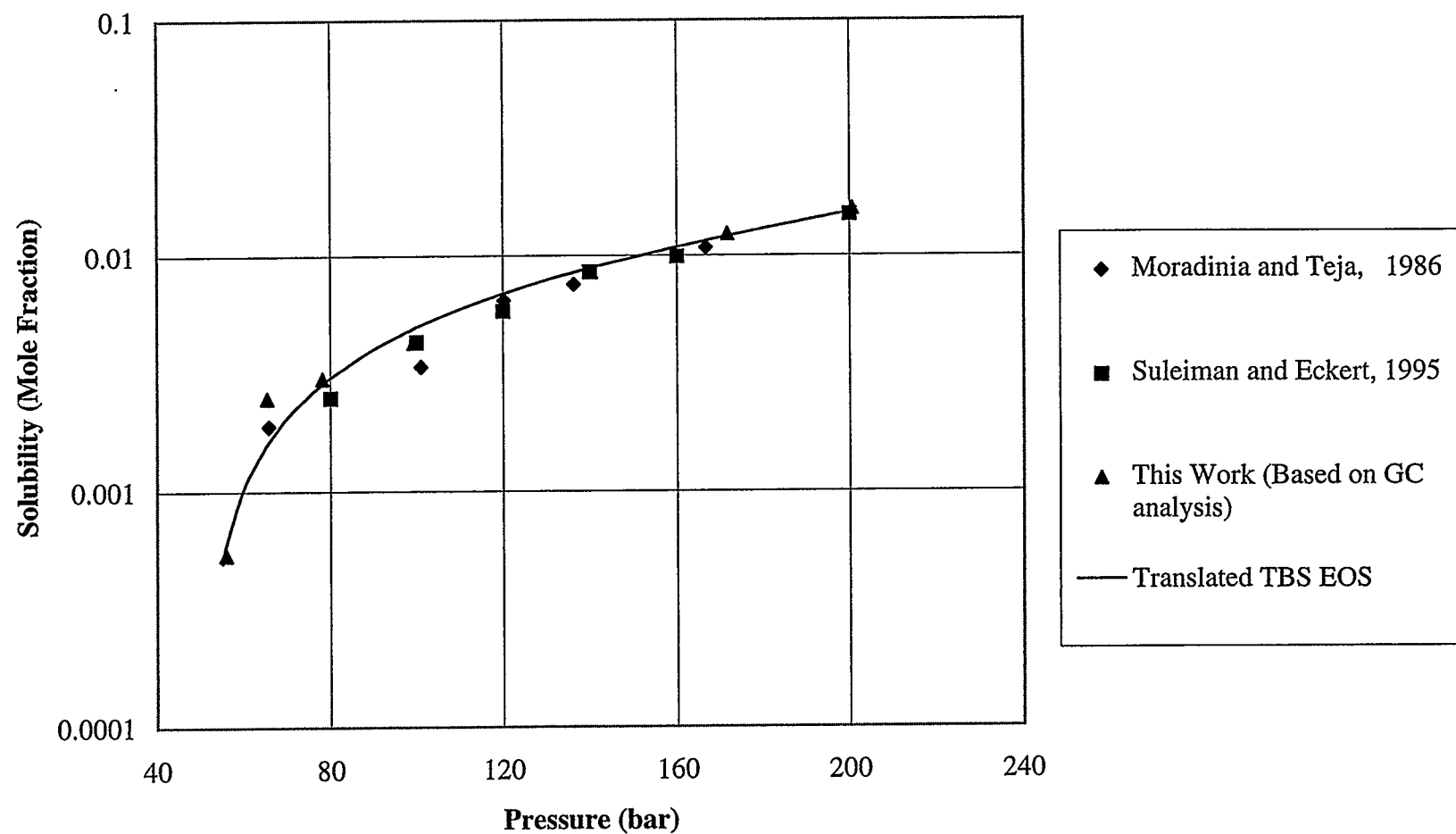
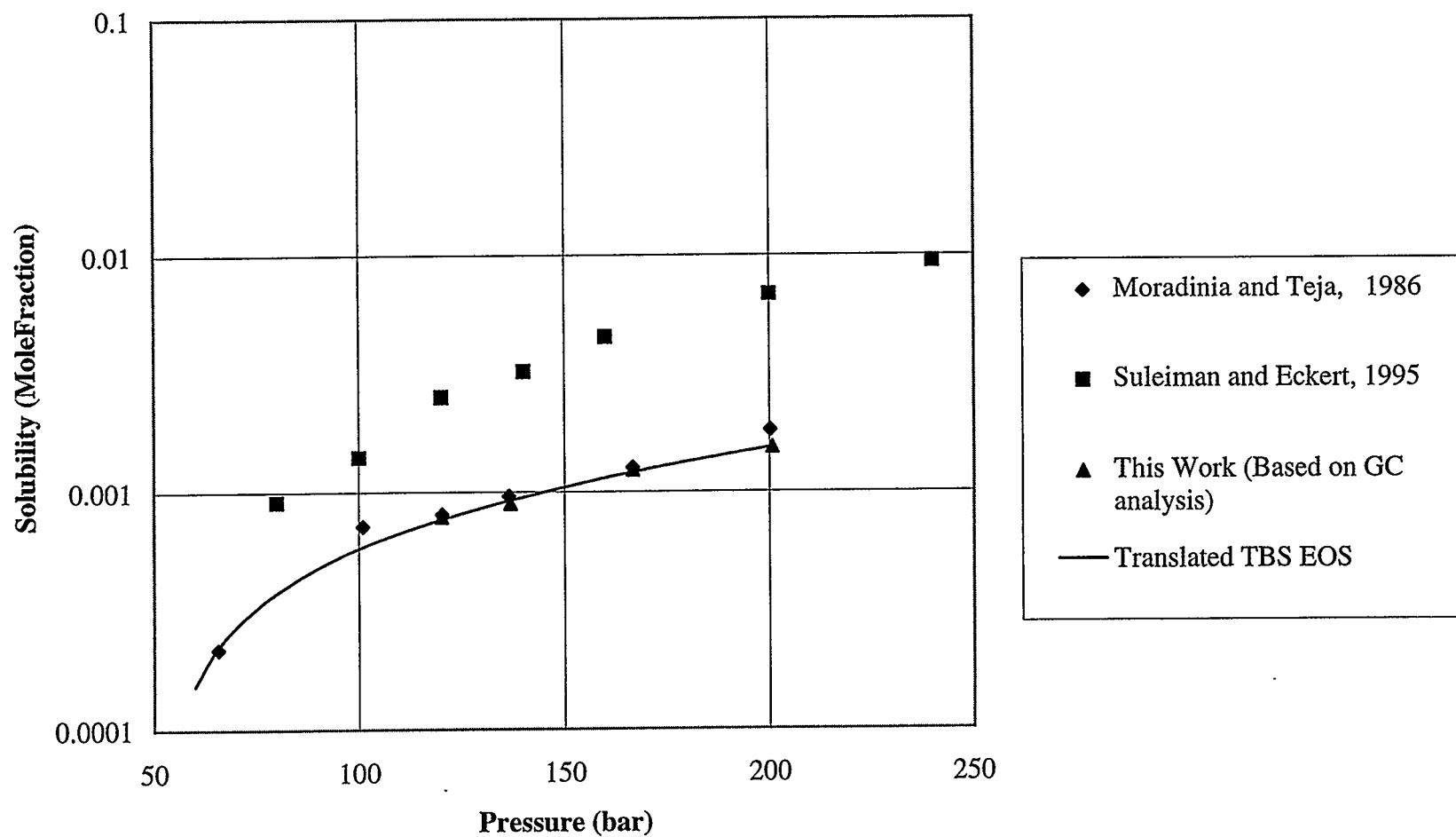


Figure 6.3 Comparison of solubility data for ethane+dotriacontane system @ 308.15 K



For the system ethane + tetracosane the solubilities obtained by the weight loss method are by 23 % higher than those determined by GC analysis. The solubilities obtained by the weight loss method for the ethane + octacosane system are underpredicted by 13 %. The solubilities of dotriacontane in ethane are also overpredicted by 32 %. In spite of these errors the weight loss method gives a qualitative description of the solubility behavior.

The experimental methods used by Moradinia and Teja (1986) and Suleiman and Eckert (1995) are described in detail in Chapter 2. The method used by Moradinia and Teja is similar to the one used in this work. They have a single pass flow system in which the solvent is continuously swept through an equilibrium cell packed with the solute. The major difference between their method and the method used in this work is that they have obtained the solubilities by weighing the solute that was collected in the separation vessel. Their measurements were accurate to 0.1 mg and hence the solubilities would be accurate as long as the amount of solute extracted is high enough. Another difference between the two works is that although they had heat traced all the lines outside the constant temperature bath, they found that some of the solutes still precipitated in the lines upon depressurization. This precipitated solute was flushed with hexane and later weighed. In this work, similar heat tracing was used for all the lines from the exit of the extractor to the separation vessel (toluene bath), but no appreciable precipitation of the solute was found in any of the lines. All the solute was deposited in the toluene bath. The method of deposition of the solute in a suitable solvent (toluene) provides more flexibility than that of weighing the solute. Even small amounts of solute extracted can be detected in the chromatographic analysis by using correspondingly smaller amount of toluene.

The experimental method used by Suleiman and Eckert (1995) is considerably different from that of Moradinia and Teja and this work. Their method is chromatographic in nature, where the solubility of a solute in the solvent is related to the retention time of the solute. The degree of retention is characterized by a capacity factor which is experimentally determined. Currently, this method is limited by the need of one additional parameter $C_i(T)$ to determine the capacity factor. This parameter $C_i(T)$ is a

function of temperature and the solute for a given chromatographic column. To determine $C_i(T)$, it is necessary either to measure at least one solubility value at that temperature with an independent method or to predict it. In addition there are several theoretical simplifications required to arrive at solubility information from capacity factors. The solubility parameters required to calculate the infinite dilution activity coefficients between the solute and the stationary phase were estimated from Fedor's group contribution method. The vapor pressure and the sublimation pressure of the solute were also predicted. The densities of the mixtures required in the calculations were assumed to be the same as pure fluid densities. Any errors in the prediction of the temperature dependence of $C_i(T)$ might lead to erroneous solubility information. Suleiman and Eckert have calculated the error in estimation of $C_i(T)$ to be 10 % and this leads to an estimated error in solubilities of about 15 %. The experimental method involves injection of preheated supercritical solvent along with the solute dissolved in some suitable solvent into a chromatographic column and observing the peaks obtained. With this method there is no differentiation between the solid and liquid solubilities, as the injection into the chromatographic system is independent of the physical state of the solute. Hence, the solubilities reported could be either solid or liquid solubilities, depending on the temperature and the depression in the normal melting point of the solute. This possibility of melting of the solute is avoided in this work as explained in Chapter 1 by maintaining an excess solid condition in the extractor. It can be concluded from the above discussion that there is a possibility of obtaining erroneous solubility information with the chromatographic method, if all the parameters required are not accurately estimated. Though there is no definite trend between the solubility data obtained from the chromatographic method and the two dynamic methods, it can be concluded that the data from the chromatographic method of Suleiman and Eckert (1995) does not match well with other data obtained from dynamic methods for the systems of ethane + tetracosane and ethane + dotriacontane. The data obtained from both the dynamic methods of Moradinia and Teja (1986) and this work agrees very well for the systems of ethane + octacosane and ethane + tetracosane.

The method of dissolving the extracted solute in a suitable solvent such as toluene offers a unique advantage compared to other methods of determining solubilities. Samples can be obtained from the toluene bath as the extraction proceeds from the start to the end of each run. This dynamic sampling of toluene bath was described earlier in section 4.2.4. The analysis of these samples was used to evaluate the performance of the toluene bath. There is another more significant advantage of this dynamic sampling, which is the fact that it can provide very reliable and accurate solubility information.

The solubility obtained for most of the experiments in this work was computed from a single data point. Only one sample of toluene was drawn from the bath, which was at the end of each run. This way of obtaining solubility is typical of any other dynamic method reported in literature. The advantage offered by dynamic sampling can be clearly seen from Figure 4.10. As more and more solute is extracted and dissolved in toluene the solubility calculated from this information attains a steady value. The solubility obtained from the initial few samples is not very accurate because of the entrance effects and also due to the fact that too little solute is extracted. As the extraction proceeds and the system attains steady operation the solubility obtained from these dynamic samples reaches a constant value. This constant value is a more reliable representation of solubility than that obtained from a single point. All the experiments conducted in this work are designed in such a way that the solubility obtained is from the region where the toluene sample attains this constant equilibrium value. The solubility computed from the attainment of this constant value from dynamic sampling is more justifiable than any value obtained from a single point. This unique feature of obtaining more reliable solubility information makes the method of dissolution of solute in a solvent more attractive than the method of weighing the amount of solute collected.

The method of dynamic sampling of the toluene bath offers more insight into the operation of the apparatus. It quantifies the initial entrance effects by showing the deviations that initial few samples have from the steady state value. This implies that even the steady state value of solubility attained is not perfectly accurate as it is a cumulative measurement of the solute dissolved. This cumulative measurement will be

slightly underpredicting solubility because of averaging of the amount of solute extracted, which is lower due to the initial effects. If the toluene bath was designed so as to attain complete steady state which could be checked with more data points for dynamic sampling, then the error caused in solubility measurement due to the initial effects could be eliminated. The actual solubility values reported in this work from dynamic sampling are the steady state values observed for 2-3 consecutive dynamic sampling measurements. The magnitude of the deviation of the first sample compared to this steady state value is less than 10% and this deviation decreases exponentially.

6.2 Modeling

The solubility data obtained from the chromatographic analysis of toluene samples is used for modeling purposes because it is more accurate than that of the weight loss method. All the three systems studied experimentally, ethane + tetracosane, ethane+octacosane and ethane + dotriacontane were modeled in this work. The complete description of the model and the solution algorithm were presented earlier in Chapter 5. The quantitative results of the regression of interaction parameters are also presented in Table 5.8. The comparison between the solubilities predicted by the model and those obtained experimentally in this work was shown earlier in Figures 6.1, 6.2 and 6.3 for the systems ethane + tetracosane, ethane + octacosane, and ethane+dotriacontane respectively.

Figure 6.1 shows that the agreement between the model predictions and experimental data is very good for the system ethane + tetracosane. The data is correlated by the translated TBS EOS to within an AAD of 4.25%. For the regression of the interaction parameters for this system, the low pressure data point at 60 bar is omitted. The experimental value of solubility at this pressure could be erroneous and the inclusion of this point in the regression cause large errors in model predictions. As shown in Table 5.8 the standard deviations of both the interaction parameters K_a and K_d are also very low indicating the consistency of model predictions at all pressures. Both the interaction parameters obtained are negative, indicating the large corrections necessary to the

conventional mixing rules because of the vast difference in the properties and size of the solvent and the solute.

The behavior shown in Figure 6.2 for the system ethane + octacosane is similar to that of the system ethane + tetracosane. The solubility data is correlated by the model to within 10.65% AAD. The model accurately predicts the solubilities at both the low pressure and high pressure regions. The standard deviation of the interaction parameters is also very low indicating the consistency of model predictions in the entire pressure range. The correction introduced by the interaction parameters to the conventional mixing rules in this case is higher than that of tetracosane. This is because as the carbon number increases the dissimilarities between the solute and the solvent increase.

The solubility data obtained for the ethane+dotriacontane system was shown in Figure 6.3. For this system the solubilities were measured only at four different pressures. These four data points were used in the regression of the interaction parameters and there was an excellent fit for this data. The data was correlated to within an error of 2.00%. The predictions even at lower pressures from the model correspond to other published data.

As described earlier in Chapter 5, the model was highly successful in describing the thermophysical and thermodynamic properties of both the pure solvent and the pure solute. The success of the model used in this work proves the assumption that the conventional mixing rules with K_a and K_d as the interaction parameters are sufficient to describe the solubilities. Though the model is used here only at one temperature it can be used with any temperature with temperature dependent binary interaction parameters to provide similar results. From the performance of this model it can be concluded that the translated TBS EOS with conventional mixing rules is highly satisfactory for modeling the solubilities of heavy hydrocarbons in supercritical ethane.

6.3 Conclusions

Based on the above mentioned results and discussion the following conclusions were drawn from this work:

- Solubility data were obtained for tetracosane, octacosane and dotriacontane in ethane at a temperature of 308.15 K and at pressures ranging from 50 to 200 bar.
- The data obtained in this work agreed very well with the data of Moradinia and Teja (1986).
- The data obtained in this work showed large deviations from the data of Suleiman and Eckert (1995) for the systems of ethane-tetracosane and ethane-dotriacontane.
- Chromatographic method of analyzing solubilities is more accurate compared to the method based on weight loss of the solute.
- Dynamic sampling provides more reliable and accurate solubility data compared to conventional methods based on loss of weight of the solute.
- Translated Trebble-Bishnoi-Salim (TBS) EOS correlated the solubility data obtained in this work reasonably to within 10 % AAD.
- Conventional mixing rules are sufficient for the TBS EOS to correlate the solubility of hydrocarbons in supercritical ethane.

6.4 Recommendations

The basic dynamic flow apparatus for determining high pressure solubility data was designed and successfully operated. Conducting experiments at high pressures is a complicated task and consequently much has to be learned. Based on the difficulties encountered in this work, the following recommendations are being made to improve the performance of the experimental apparatus.

- It is highly recommended that dynamic sampling be used for future work involving either equilibrium or non-equilibrium studies.

- The use of a pressure control valve in conjunction with the micrometering valve would eliminate the need to manually maintain the pressure.
- It is recommended that a pressure transducer be installed at the pump exit which would provide a more accurate pressure measurement and thereby a more accurate mass flow rate of the solvent.
- The accuracy of the weight loss method could be improved by using a more accurate weight measuring device and minimizing the total weight being measured.
- The use of a visual cell in parallel with the extractor would make it possible to visually observe the phase transformations inside the extractor.

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APPENDIX A

Sample calculation for error analysis of solubility data

The calculation of error in the obtained solubility value is shown here for the data point corresponding to Run No. 1 for the system ethane + tetracosane given in table 4.3.

The original data is shown here along with the errors in the measured variables

Pressure = 59.71 ± 6.25 bar

Temperature = 35.02 ± 0.1 °C

Temperature at the pump = 27.01 ± 0.1 °C

At these conditions the precision in the measurement of pressure and temperature is lower than the accuracy and hence the accuracies are used for error analysis.

	Pressure bar	Temp. at the pump K	Ethane density g/cc	Ethane pumped moles
Original conditions	59.71	27.01	0.34452	3.4372
Max. Positive deviation	65.96	27.11	0.35295	3.5213
Max. Negative deviation	53.46	26.91	0.33356	3.3279

The maximum deviations in ethane pumped also consider the error in reading the amount of ethane pumped from the Ruska pump.

The errors involved in the chromatographic analysis of the toluene samples are presented below:

	Area % obtained	Weight % obtained	Amount of solute extracted (moles)
Original conditions	1.2767	2.17834	0.00096
Max. Positive deviation	1.2973	2.26378	0.000981
Max. Negative deviation	1.2664	2.09349	0.000947

The above errors lead to the following deviations in the solubility.

Original solubility	0.0002807
Max. Positive deviation	0.0002847
Max. Negative deviation	0.0002785

The maximum value of the above deviations is reported as precision on solubility which is 0.000004 mole fraction.