THE UNIVERSITY OF CALGARY

THERMAL DESORPTION OF CONTAMINATED SOILS: A STUDY OF SOIL FRACTION-CONTAMINANT INTERACTIONS

by

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled "Thermal Desorption of Contaminated Soils: A Study of Soil Fraction–Contaminant Interactions" submitted by Vineeta Maguire in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering.

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ABSTRACT

It has been well documented that the organic or humic content in soils is a major contributing factor to a soil's sorptive capacity. Humic material can be divided into three major fractions; humic acid (HA), fulvic acid (FA), and humin. Hydrophobic organic pollutants such as polynuclear aromatic hydrocarbons such as fluorene, naphthalene, and anthracene are known to have an affinity to humic substances resulting in severe environmental problems.

Thermal desorption is considered to be an economic and effective method for the removal of volatile organic pollutants when heated in an enclosed chamber at 200-500 °C. The characteristic behaviour and binding capacity of soil humic substances in influencing the removal of organic pollutants is therefore an important design parameter for this process.

In the following research, the degree of interaction between humic substances, (e.g. HA, FA and humin with attached inorganic components in soil), and polynuclear aromatic hydrocarbons was studied over a concentration range of 0.8–7.0 mass%. The soil fraction and contaminant mixture was tested by heating from 20 to 390 °C (at 10 °C/min) in a differential scanning calorimeter (DSC). The results of the DSC tests demonstrated a distinct variation between soil organic fractions when combined with the model contaminants. A thermodynamic model was utilized to provide a qualitative interpretation of the DSC results.

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ALL MY FAMILY

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NOMENCLATURE

a	component 'a'
Α	constant
b	component 'b'
В	constant
<i>C</i> .	constant
C_p	heat capacity
Cp_i^L	heat capacity of component i in liquid phase
D	constant
E	energy required to vaporize a liquid
Ē	constant
F	Total feed in moles of components 'a' and 'b'
$\Delta H_{\nu}^{\ i}$	molar enthalpy of vaporization of pure liquid i
H_T	total molar enthalpy
H_L	total molar liquid enthalpy
H_V	total molar vapour enthalpy
\overline{H}_{Li}	partial molar liquid enthalpy of component i
\overline{H}_{Vi}	partial molar vapour enthalpy of component i
i	<i>i</i> th component ('a' or 'b')
L_i	liquid moles of component i
LF	liquid mole fraction in system

т	mass
P_T	total pressure
P_i^{sat}	vapour pressure of component i
Q	heat
q	heat flow per unit mass
t	time
Т	temperature
T _b	boiling temperature
T_c	critical temperature
T_f	final temperature
T _o	initial temperature
T_r	reduced temperature
V _i	vapour moles of component <i>i</i>
VF	vapour mole fraction in system
w	fraction of initial mass remaining
Y_i, y_i	mole fraction of component i in vapour phase
X_i, x_i	mole fraction of component i in liquid phase
Z_{0i}	initial feed mole fraction of component i
θ	temperature (in °C) in mass-loss correlations

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CHAPTER 1

INTRODUCTION

1.1 General Description

Thermal desorption is a soil remediation process that is considered to be an economic alternative to the complete incineration for removing volatile organic contaminants (Razzaghi, 1993). The thermal desorption process involves heating of contaminated soil in an enclosed chamber, in either an oxidizing or non-oxidizing atmosphere, at relatively low temperatures of 200 to 500°C for the vaporization and possible recovery of volatile organic contaminants. Thus, the thermal desorption process differs from the incineration process in two aspects: (i) the maximum temperature (500°C) in the thermal desorption process is much lower than those (approximately 1200°C) reached in the incineration process and (ii) the hydrocarbon contaminants are not combusted in the thermal desorption process.

The thermal desorption process is shown schematically in Figure 1.1. The key parameters which affect the operation of the thermal desorption process and the product quality in terms of the residual pollutant concentration include contaminant properties, soil characteristics, and the operating parameters such as the treatment time and heating rate.

The organic fraction of soils has long been recognized as a controlling factor in determining the extent of sorption of the hydrophobic organic compounds in soils. The humic material is considered to be the major fraction of the organic matter in most



Figure 1.1 Schematic of the Thermal Desorption Process

soils (Schnitzer, 1982). Schnitzer (1978) estimated that 65 to 75 percent of the organic matter in mainly inorganic soils is made up of humic materials consisting of humic acid (HA), fulvic acid (FA) and humin. It was shown by Troxler *et al.* (1993) that the humic content of soil is an important soil characteristic influencing the application of thermal desorption. The organic matter in surface soils can range from less that 0.1% in desert soils to 100% in organic soils (Schnitzer, 1982). In inorganic soils, the organic and inorganic components are closely linked; hence, they need to be separated in order to examine their role in chemical adsorption. The HA is the acid component of humic substances which are soluble in bases but precipitate in acids, whereas the FA is the acid component that is soluble in both bases and acids. The humin is the portion remaining once the HA and FA components have been removed, and it is the organic fraction that binds itself to the inorganic portion of the soil.

A knowledge of the interactions between soil fractions and contaminants, and their effect on contaminant desorption rate, is considered useful for predicting the performance of the thermal desorption process. Hence, an understanding of the effect of humic materials on the process of thermal desorption, the interactions of chemical contaminants with HA, FA, and humin with attached inorganic components, were the focus of this research. An investigation of the three soil fractions, with and without the added contaminants, using a differential scanning calorimeter (DSC) was carried out. The model contaminants selected for this study were three polyaromatic hydrocarbons (PAHs), namely anthracene, naphthalene, and fluorene.

1.2 Scope of the Study

The technique of differential scanning calorimetry (DSC) is used to study the interaction of the three soil humic fractions and three polyaromatic hydrocarbons as a means of further understanding and modelling the thermal desorption remediation process. The four main objectives of this investigation are as follows:

- (1) To understand the solid-liquid and liquid-vapour transition behaviour of three polyaromatic hydrocarbons (PAHs) when combined with soil organic fractions at varying concentrations.
- (2) To comprehend the phase behaviour of a binary mixture of soil and contaminant using the differential scanning calorimetry technique.
- (3) To simulate the actual DSC experimental tests with a thermodynamic model of ideal miscible and immiscible equilibrium systems.
- (4) To extend the experimental and simulation results to the thermal desorption process.

Chapter 2 of this thesis provides a literature review on the thermal desorption process, humic substances, polyaromatic hydrocarbons, and the existing theories of interaction between these two substances. It also discusses the applicable background of thermal analysis in the analyses of soils.

Chapter 3 outlines the experimental program completed as part of this study and provides a brief description and background on the differential scanning calorimetry technique. This chapter discusses the materials used, their analysis, sample preparation techniques, and the instrumentation and calibration methods for the DSC for obtaining data. It also introduces the experimental tests completed on pure components and soil+contaminant mixtures.

Chapter 4 gives a detailed description of the thermodynamic model utilized to simulate the DSC data related to binary miscible and immiscible systems. The results and discussion are divided into sections dealing with each contaminant and soil fraction in order to compare the model predictions with respect to the actual experimental results.

Chapter 5 provides a summary of experimental results and a discussion of each soil humic fraction with the contaminants tested. The experimental results are evaluated based on the predictions presented in Chapter 4 with the variations in interactions being validated.

Finally, Chapter 6 summarizes the major conclusions of this research and provides recommendations for further study.

CHAPTER 2

LITERATURE REVIEW AND BACKGROUND

2.1 Pilot Studies and Results of Thermal Desorption Units

Thermal desorption units have been successfully utilized for soil remediation on an international scale including countries such as Canada, the United States and the Netherlands (Razzaghi, 1993; Troxler *et al.*, 1993). Companies such as TriWaste Reduction Services Inc., Calgary (Alberta) in Canada and Waste-Tech Services Inc., Golden (Colorado) in U.S.A. have successfully designed and operated full sized models to treat hydrocarbon-contaminated soils and sludges. Both laboratory and full scale studies have confirmed that thermal desorption is an effective soil remediation method for the removal of hydrocarbon contaminants.

Troxler *et al.* (1993) have reviewed the results from six full-scale and nine laboratory, bench, and pilot scale thermal desorption studies dealing with the removal of organochlorine pesticides in soil and have identified the key parameters affecting the thermal desorption process. The key soil characteristics include the initial soil moisture content, soil particle size distribution, and the fraction of humic material. Evaporating moisture from soil can result in the largest energy requirement for the process, while soil particle size characteristics affect the mass transfer rates and the adsorption of pesticides to the soil. The concept of adsorption of pesticides to soil has to be reviewed further since the actual mechanism may be more dependent on other soil characteristics such as the humic content. The humic material was found to affect the efficiency of pesticide removal by what was thought to be due to the adsorption of pesticides to humic material. DeLeer *et al.* (1986) found that there was an interaction with humic material such that the minimum required soil treatment temperature was directly proportional to the humic content in the soil.

The particle size effects have been studied in greater depth by Lighty *et al.* (1988, 1989, 1990). In these studies, it was determined, that although parameters such as bed thickness, thermal conductivity, and effective diffusivity are important in the desorption of contaminants from the soil bed, experimental results and model predictions indicated that the temperature was the most important variable. It was shown that heat and mass transfer resistances in the soil matrix were also important. However, the rate of desorption could always be increased with a higher temperature when the bed depth was also increased.

Wu *et al.* (1992) demonstrated that organic molecules favour transfer to the gas phase at higher temperatures. This re-confirms the need to study the phase transitions and temperatures for the thermal desorption process. This requires further knowledge on the interactions of organic molecules (e.g. PAHs) with soil constituents, particularly humic substances. Hence, the energy requirements for heating along with the minimum temperatures required, should still be considered as the dominant variables in the thermal desorption process.

Although the term "adsorption" has been used to describe the interaction of chemicals with organic material, the actual mechanism has also been considered to be closely related to partitioning of the contaminant in the organic phase and will therefore be termed more loosely as 'sorption' and will be described further in Section 2.4. The mechanism of interaction for humic materials and the need to further determine the variations of these interactions between humic materials will begin to provide the path towards optimizing the energy and temperature requirements for contaminant removal.

2.2 Chemical Properties and Structure of Humic Materials

Although the humic content in soil has been determined to be a key parameter for the design and operation of a thermal desorption unit, the definition of humic material still remains vague. Of all the parameters of soil that could affect a soil remediation method along with the many variations in operating parameters, the humic content in soil is the least understood parameter and therefore the least controlled or modelled.

Humus, or organic matter, has long been recognized for properties such as buffering capacity, sorption of hydrophobic organic compounds, stability of aggregates of soil particles and water holding capacity (Wershaw, 1993). The sorption or interaction of hydrophobic (i.e. water repelling) compounds with soil organic matter is an especially important property since soil remediation processes such as thermal desorption can only be optimized or even modelled once this behaviour is understood. Although the information on humic substances is still being researched, a basic description of the composition and proposed structure of the soil humic fractions is

provided here.

2.2.1 Formation of Humic Substances and Their Composition

The humification process is one of the basic steps of the carbon cycle and is the process where dead plant and animal remains are converted into humus. Once the organisms containing organic compounds die, they are converted back to carbon dioxide and water by various degradation reactions. However, not all of the biomass is initially converted and the material that is only partially oxidized produces a residue that is the source of the organic compounds that combine to form humus (Wershaw, 1993). Kononova (1968) explained that the transformation of soil organic matter consists of three major stages:

- a) The accumulation of organic residues
- b) Their humification
- c) The breakdown of humic substances.

Humic substances are considered to be formed during the humification process for which lignin is considered the initial substance. The formation of these substances are generally composed of the following steps that can occur either successively or simultaneously (Helgeland, 1975):

- a) The formation of structural units
- b) Their condensation
- c) Polymerization of the condensation products.

These steps result in a multi-component mixture of humic substances in soils that show similar patterns but can vary in the structural details, the specific chemical nature, and can contain molecules of different sizes between fractions of humic substances such as humic acids and fulvic acids. Humin is considered to be the third major fraction of humic materials but is also more difficult to analyze due to its interaction with the inorganic fraction in soil. Kononova (1968) described fulvic acids as the humic substances that contain a less condensed aromatic nucleus, and a more highly developed peripheral component. Fulvic acids can also be considered as the precursors or products of destruction of humic acid components, (Helgeland, 1975).

It is important to note that the differences between the humic acid and fulvic acid fractions. Schnitzer and Wright (1960) and Schnitzer and Desjardins (1964) described humic acid as containing aliphatic and aromatic groups while fulvic acid material to be mainly aromatic in composition. This compositional difference explains the more pronounced stability of fulvic acid than humic acid determined experimentally by Schnitzer and Hoffman (1961).

Fulvic acids are yellow or orange acids that can contain low and high molecular weight organic compounds. They are, however, the lower molecular weight substance in humus compared to humic acids and are therefore often related to the extent of humification which is dictated by the soil environment (Helgeland, 1975). The dark coloured compounds are humic (and hymatomelanic) acids, while the organic fraction of soil that cannot be extracted by alkaline solution and that can bind themselves strongly to the inorganic fraction of soil is humin. In this study, only fulvic acid, humic acid, and humin (with attached inorganic) will be studied. The formation of complex humic acids are favoured by factors such as a moderate amount of moisture and a neutral pH along with intense microbiological activity. Kononova (1966) for instance, determined that excess moisture, acidic pH, and weak microbiological activity cease the formation of humus substances at the stage of fulvic acids and fulvic acid like substances.

The composition of humic and fulvic acids are often characterized by an elemental analysis involving the percentage of carbon (C), hydrogen (H), oxygen (O), and nitrogen (N), and sometimes sulphur (S). A typical C/H/N analysis was completed by Schnitzer (1965) for fulvic acid and humic acid with the results shown in Table 2.1. The percentage of each element, along with the physical properties of humic and fulvic acid fractions, have been found to be dependent upon the climatic conditions, the plant species and the inorganic constituents of the soils from the area where they were obtained (Helgeland, 1975). The question therefore arises as to whether or not general correlations between humic substances and the extent of sorption or desorption of organic compounds can be made at all. In response to this, Lowe (1969) studied nine soils representing the major groups in the principal soil zones of Alberta and found that there was little variation between the de-ashed humic fractions of the soils in terms of elemental composition, functional groups or infrared spectra.

Since the soil tested for this particular research was obtained near Devon (Alberta), the studies by Lowe (1969) and Helgeland (1975) on the characterization of humic acids derived from several selected soils from various areas in Alberta, are of particular importance. The results obtained by Helgeland (1975), however, did indicate some variability between regions of varying climatic conditions and vegetation in terms of amino acid analyses between humic acid fractions and the susceptibility to enzyme

Elementary Composition (mass%)		
Element	Humic Acid	Fulvic Acid
Carbon	56.72	50.92
Hydrogen	5.21	3.34
Nitrogen	2.37	0.74
Sulfur	0.35	0.26
Oxygen (by difference)	35.35	44.74
(meq] Total acidity	5.7	12.4
Carboxyl	1.5	9.1
Total hydroxyl	6.9	6.9
Phenolic hydroxyl	4.2	3.3
Alcoholic hydroxyl	2.7	3.6
Carbonyl	0.9	3.1
Molar mass [*]	1,684	669
* average molar mass dete	ermined by Schnitzer and D	esjardins (1962)

Table 2.1 Analytical Characteristics of Humic and Fulvic Acid (Schnitzer, 1965)

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hydrolysis. When the humic acid was extracted using 0.5N NaOH, there were small differences in ash (mineral) content between different sites within the same soil region, but this ash content varied much more between soils of different regions (e.g. different climates and vegetation). It was also noted that the ash content seemed to vary with the method of extraction used. Overall, however, on an elemental basis, Helgeland (1975) concluded that when the same primary extraction procedure was used to obtain humic acids, there was little variation between carbon contents for soils from different regions in Alberta. Although the total nitrogen content varied, three of the four soils studied were very similar in percent nitrogen with the fourth soil varying only by a maximum of 2%. The elemental composition, in particular the organic carbon content, is considered to be one of the dominating properties dictating the extent of interaction of organic compounds with humic substances. For the purposes of this study, it can therefore be assumed that for soils from similar climatic regions the properties relating to the extent of sorption and ultimately desorption of hydrophobic compounds would be similar. It should be noted that the elemental carbon content in soil includes both the inorganic and organic carbon values.

It has been determined by Flaig *et al.* (1975) that the carbon content decreases as the humification process is extended. Therefore, since fulvic acids can be considered the degradation products of humic acids, it is expected and confirmed by Schnitzer (1965) that the carbon content along with the hydrogen and nitrogen content is lower in fulvic acids than in humic acids. The oxygen content, however, is higher in fulvic acids. Data obtained by Schnitzer (1965) also showed that with increasing average molecular weight, the number of carboxyl groups decreased and the number of hydroxyl groups increased as shown in Table 2.1.

The acidic property of fulvic and humic acids are related mainly to the carboxyl content and, to a lesser extent, the phenolic group. Fulvic acids are known to contain a higher content of carboxyl groups (resulting in the higher oxygen content), since decarboxylation did not occur before polymerization or condensation to higher molecular weight humic acids. It could also be due to oxidative degradation of humic acids. It is important to note, however, that some of the organic compounds are only partially oxidized to carbon dioxide and water. As previously mentioned, the residue of this partial oxidation of dead biomass is considered as being the organic matter that humus is composed of. The main source of biomass on land is from vascular plants, i.e. those with water and food conducting tissues. These plants are composed of cellulose, hemicellulose, and lignin polymers. Although all humic substances are composed of similar structures, the varying amounts prove significant in terms of the degree of interaction with contaminants such as polyaromatic hydrocarbons.

2.2.2 Chemical Structure

The major difficulty in determining the chemical composition, and ultimately the chemical structure of humic substances, stems from the existence of the high molecular compounds from which they are composed of. Even though humic and fulvic acids are considered to be complex macromolecules, they can also be described as polymers consisting of several basic molecular building blocks. It is the form in which these basic molecular structures are linked that defines a particular humic polymer (Chin *et al.*, 1989). Due to their high molecular weight, humic substances are difficult to separate by hydrolysis or oxidative degradation for the purpose of obtaining and analysing definite intermediate compounds such as proteins and polysaccharides.

Results from nuclear magnetic resonance and chemical degradation studies on humic and fulvic acids extracted by basic solutions from soils have shown that both of these acids are similar to lignin in terms of consisting of the same functional groups and plant polymers; however, these acids contain more carboxylic acid functional groups (Wershaw, 1993). A study by Rice *et al.* (1989) determined that the humin is composed of humic acids, fulvic acids and lipids. In other words, humin is considered to be similar to humic acid, but the characteristics of humin are intermediate between humic acid and fulvic acid. Rice *et al.* (1989) also described humin as a substance with a mineral fraction of finely grained material that contains relatively little organic matter dispersed in a more abundant inorganic matrix. They concluded that due to the existence of some humic acids or clay sized material associated with the humin, this organic fraction is also considered to have an affinity for hydrophobic hydrocarbons. The extent of this interaction, however, was not discussed.

An extended model for the chemical and physical structure of humus has been suggested by Wershaw (1993). Humus is described as being ordered aggregates of amphiphiles (a molecule that consists of a separate hydrophobic nonpolar part and a hydrophillic polar part) of plant polymer segments attached to carboxylic acid groups. The hydrophobic parts are found in the interiors and the hydrophillic part compose the exterior surface of the molecules. A globular aggregate of amphiphile molecules is called a micelle. The humus on a whole then is considered to be best modelled as a membrane-micelle model where the formation of membrane-like coatings of amphiphiles on the soil mineral grains are a result of plant degradation products and lignin-carbohydrate complexes interacting with the soil mineral grains. These amphiphilic molecules are stabilized in soils and sediments by being incorporated into the membrane structure that coat the mineral grains. These coatings are considered to be the humus in soils. Although humus is often a small percentage of the total mass of soils and sediments, ionic species have been found to interact with the hydrophillic surfaces of these humic membranes and micelles. The hydrophobic species, such as those tested in this study, are known to partition into the hydrophobic interiors of the humic membranes and micelles (Wershaw, 1993). Flaig et al. (1975) related the importance of the affinity of compounds such as PCB, DDT (pesticide) and PAHs to humic substances. The question, however, still remains whether hydrophobic compounds partition, and subsequently desorb from different humic polymers, in varying degrees.

2.3 Polynuclear Aromatic Hydrocarbons

2.3.1 Properties and Structure

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Polyaromatic hydrocarbons (PAHs) are known to be formed naturally from sources such as natural fires and also from reactions of organic material in sediments. The PAHs in uncontaminated soils are also generated from natural pyrolytic processes. Basically, these compounds are formed when the organic material containing carbon and hydrogen is subjected to temperatures over 700°C. Therefore, the environmental importance of PAH in soil at low levels is often complicated with the existence of these compounds formed naturally. Regardless of the cause of their formation, limiting the total concentration of these compounds in the environment is essential. PAHs can be hazardous at low concentrations and some of these compounds degrade slowly (Tabak et al., 1981). Garbarini et al. (1986) found that hydrophobic chemicals (whose octanol-water partition coefficient is greater than 100) such as trichloroethylene (TCE) accumulate in the soil organic phase, whereas the water molecules are repelled. Therefore, other nonpolar, high molecular weight, hydrophobic chemicals such as fluorene, naphthalene and anthracene, have also been considered to be a major environmental threat. This concern is also due to the potential of contaminants being transported to the groundwater. The soil, and ultimately groundwater contamination, is a major concern. Environmental fate of polyaromatic hydrocarbons formed as a result of petroleum drilling activities, oil spills or chronic leakage has gained exposure especially in Alberta due to the obvious focus of the oil industry in this province.

Very few of these PAHs are industrially produced in a pure form. PAHs are most often used as an initial ingredient in the synthesis of dyestuffs, herbicides, pesticides and pharmaceuticals. In the manufacture of metallurgical coke, the byproduct coal tar is considered to be a main source for the industrial production of chemicals such as anthracene, fluorene, and naphthalene.

2.4 Interaction of Polyaromatic Hydrocarbons and Organic Matter

Due to the heterogeneous nature of a soil matrix, the physical and chemical properties affecting the adsorption of PAHs on soil are difficult to determine specifically. Many researchers (Means, 1980; Karickhoff, 1979; Voice, et al. 1983; Weber, 1983) have concluded that the organic fraction in soil experiences the majority of the sorption. It must be noted, however, that other soil properties may also be strongly related to the extent of sorption (Zamani et al., 1984). The cation exchange capacity (CEC) and the pH were also suggested as playing a dominant role in sorption capacity. Felsot and Dahm (1979) reported that the higher the CEC, the higher the adsorption capacity. Walker (1984), however, found the relationship of the organic matter content of the CEC fraction of the soil as being the major contribution to the sorption capacity of the soil. Means et al. (1980) also stated that organic matter and clay mineral content are the main sources of cation exchange capacity which along with the hydrous oxides are considered to be the most active sorptive fractions in soils. Cation exchange capacity is most often reported as milliequivalents (meq) per 100 grams of soil and is a measurement of the readily exchangeable cations neutralizing the negative charge in soil. Walker (1984) reported that the organic content can contribute from 25 to 90% of the CEC, and that although a pH change can alter the number of CEC sites, no direct correlation between pH and adsorption of nonpolar chemicals exists. Kaufman (1981) and Rogers et al. (1980) also reported the importance of higher organic carbon associated with higher CEC instead of correlating CEC with sorption directly. Walker (1984) agreed with Hamaker and Thompson (1972) that although the effects of pH, CEC and organic matter are so interrelated, the dominating effect of organic matter (or humic substances which is the largest fraction of organic matter) and the extent of sorption and desorption of chemicals is still the dominating soil characteristic. Schwarzenbach and Westall (1981) also observed a high correlation between the organic content of the medium and the extent of adsorption, whereas Karickhoff (1979) specifically demonstrated that hydrophobic chemicals (e.g. PAHs) readily adsorb to organic carbon. Although the average particle size or surface area has been related to adsorption capacity, Zytner *et al.* (1989) found no correlation between smaller particle sizes (i.e. higher surface area) and the extent of adsorption in comparison to the effect of the organic carbon content. MacNamara and Toth (1970) found that 70 times more of the pesticides linuron and malathion were adsorbed by humic acid than the K⁺-montmorillonite clay type. They also demonstrated a noticeable sorption difference between humic substances and clay type particle size.

Pierce *et al.* (1974) suggested that the binding of the pesticide DDT to humic acids was due to hydrophobic bonding with nonpolar fractions of the humic molecules. This is consistent with the model proposed by Wershaw (1993). Many authors (Karickhoff, 1979; Means, 1980; Voice and Weber, 1983) focused on the organic carbon content of a sorbent as being the principal factor dictating the extent of sorptive partitioning. Garbarini *et al.* (1986) also found that the sorbents' oxygen content affects the affinity for compounds such as toluene and TCE. Since the results demonstrated an increase in hydrophobic bonding or sorption in general as the carbon to oxygen ratio increased. Garbarini *et al.* (1986) also observed that it was essential to consider the specific nature of organic materials that may be present in soil in order to fully comprehend the extent or mechanism of interaction. It was also found that organic compounds partitioned to a much larger degree in humic acids than fulvic acids. Garbarini *et al.* (1986) stated that fulvic acid would result in a lower degree of sorption of organic compounds due to it being more polar in nature, with more carboxylic acid groups and a lower carbon to oxygen ratio than humic acids. Although the humin component of humic substances is often considered to be made up of humic and fulvic acid components, it is also found to have a lower organic carbon content than the acid fractions therefore suggesting that the relative sorption characteristics would be lower.

Nonpolar molecules such as PAHs have been found to have an affinity for hydrophobic surfaces in soil organic matter such as waxes, fats, resins, aliphatic side chains on humic and fulvic acids, and lignin-derived materials of high carbon content (Weed and Weber, 1974; Bohn *et al.*, 1979). Hydrophobic bonding is considered to be the mechanism that allows for the accumulation of these molecules on the organic phase. According to Weed and Weber (1974) and Kile and Chiou (1989), hydrophobic bonding is best described as being similar to partitioning between a solvent and a nonspecific surface instead of active adsorption. Weed and Weber (1974), however, also noted that hydrophobic bonding can produce linear isotherms similar to that of an active adsorption. For the present study, adsorption isotherms such as the Freundlich isotherm are not very useful because the temperatures where the isotherms are applicable are too low (e.g. 25°C) for the analyses of the process of thermal desorption which can reach temperatures over 500°C.

Zytner *et al.* (1989) found that a hydrophobic chemical such as perchloroethylene has a tendency to accumulate in the soil organic phase with the water molecules being repelled. McCall *et al.* (1981) stated that the more hydrophobic a molecule, the greater is its tendency to partition from the aqueous to the organic phase.

As mentioned in Section 2.2.2, the hydrophobic interiors of the membranes and micelles serve as hydrophobic phases where nonpolar chemicals such as PAHs partition. It is interesting to note, however, that the micelle hydrophobic phase and the membrane hydrophobic phase move independent of each other (Wershaw *et al.*, 1993).

After reviewing the information available regarding the adsorption of polycyclic aromatic hydrocarbons in water/soil systems, Dzombak and Luthy (1984) concluded that although a correlation between the adsorption of these compounds and the organic matter in soil exists, the fundamental mechanisms of interaction of these hydrophobic organics (PAH) with soil organic matter (humic substances) requires further research. These authors conceded, however, that although it may not be possible to predict PAH adsorption or interaction by knowing all the structural details of complex humic materials such as humic acid, fulvic acid and humin, more fundamental correlations and general relationships regarding organic matter and contaminants are required. Dekkers (1978) also found that organic matter was an important factor in desorption
studies since the extent of desorption decreases with an increase in organic matter. Dekkers (1978) stated the importance of knowing the composition of organic matter for predicting the adsorption for chemicals such as PAHs and repeated the concern with respect to the lack of information in this area.

2.5 Thermal Analysis

2.5.1 Introduction

Thermal analysis is a general term that describes the methods which determine a physical parameter such as energy, mass, dimension and evolved volatiles as a function of temperature. These measured parameters vary with temperature. The three major types of thermal analysis techniques that are most often applied to soil research are differential thermal analysis (DTA), differential scanning calorimetry (DSC), and thermogravimetry analysis (TGA).

There are soil components that undergo thermal reactions such as the removal of adsorbed water at lower temperatures and oxidation of organic compounds at intermediate temperatures. Some other reactions such as the removal of crystal-lattice OH^- ions as water and the conversion of CO_3^{2-} into CO_2 occur at high temperatures. The reactions may be endothermic or exothermic and can be measured with any of the above three methods and often by combinations of these methods in order to obtain valuable information when identifying substances. Endothermic reactions involve processes such as dehydration, dehydroxylation, fusion, evaporation and sublimation,

whereas exothermic reactions involve oxidation, crystalline structure formation and some decomposition reactions.

2.5.2 Soil Thermal Analysis

Differential thermal analysis (DTA) was originated by Le Chatelier in 1887 and has been utilized in areas such as geology, in ceramic glass, polymer cement and plaster industries. As of 1922, the first soil research was completed by Matejka using DTA for the determination of a specific clay type - kaolinite. Since then, DTA has become an important tool in the analysis of clays and clay minerals in soils.

The methods of DTA and differential scanning calorimetry (DSC) are similar in principle. The DSC is very useful in the determination of the amount of energy required for a particular endothermic or exothermic reaction to take place. The DSC measures the amount of energy required to establish a zero temperature difference between a sample and a reference material as they are heated side by side at a controlled heating rate (Tan *et al.*, 1986). Conversely, with DTA, although it heats a sample and reference side be side at controlled rate, the temperature difference between the two is measured, but not the energy difference. Therefore if a sample undergoes a transformation, the heat effect results in a temperature difference between the sample and the reference. In DSC, the sample and the reference are heated side by side and the differential heat flow between the two is recorded as a dynamic, linear function of temperature. As previously mentioned, both endothermic and exothermic reactions can occur as the soil sample is heated. Since a DSC establishes a zero temperature difference between the sample and reference, when an endothermic reaction occurs, thermal energy is added to the sample and subtracted when an exothermic change occurs. This balancing energy or energy input is equal to the energy absorbed or evolved during a particular reaction. The thermal energy required to balance the temperature differences is recorded and can yield valuable calorimetric measurements of the transition energy and ultimately lead to information regarding the thermal properties and constituents of the soil sample.

Another important thermal method utilized to study soils is thermogravimetric analysis (TGA) or differential thermogravimetry (DTG). In this method, the sample is heated or cooled at a controlled rate and is continuously weighed. This weight change as a function of temperature is recorded and can produce information about the thermal stability and composition of the substance being studied. The weight changes can be due to the breaking or formation of physical or chemical bonds at high temperatures, resulting in the release of volatile substances. Some examples of weight loss reactions include dehydration (loss of H_2O molecules), dehydroxylation (loss of OH^- ions), or decomposition in soils.

Differential thermogravimetry was utilized by Schnitzer and Hoffman (1961) and Schnitzer and Skinner (1965) to study the thermal decomposition of fulvic extracts from podzol (a soil type). The decomposition curve of fulvic acid demonstrated a main decomposition maximum peak at 430°C and a weak maximum between 250 and 270°C along with a low peak at 100°C due to the release of water. Farmayan *et al.* (1989) utilized a thermogravimetric analyzer for studying the thermal desorption process by providing weight loss as a function of time as a contaminated soil sample was heated and stripped of organic compounds.

Tognotti *et al.* (1991) also studied the sorption-desorption of contaminants on single soil particles using the electrodynamic thermogravimetric analyzer. They discovered significant differences among different pairs of solid-organic compounds and correlated these to solid pore structure and the chemical affinity between the organic compound and the solid. Thermal degradation properties of lignin demonstrate thermogravimetric peaks over a wide range of temperatures from 250 to 400°C.

Flaig *et al.* (1975) published a comparison of experiments showing the degasification of different substances present in peat. Some of the main degasification/ decomposition reactions determined were as follows:

150-225°C	water soluble moieties, sugars
290-315°C	cellulose
315-350°C	lignins (humic acids)
350-390°C	humic acids (bitumens).

Humic acid and lignin may contain similar structures; however, humic acids were found to be more resistant in thermogravimetrical investigations. DTG curve analyses have shown main decomposition reactions at 340–370°C and 400–420°C. At temperatures above 450°C, the decomposition reactions are due mainly to the aromatic condensation products with lower contents of oxygen but proportionally higher contents of carbon and hydrogen.

2.5.3 Identifying Humic Substances

Methods of thermal analysis such as the DSC have clearly become very popular methods for characterizing soils. As convention states, the DSC thermograms show negative peaks for endothermic reactions and positive peaks for exothermic reactions.

Tan (1978) showed DSC results demonstrating the distinct difference between fulvic acid and humic acid in the range of 20 to 390°C. The main difference seen between these two substances in this temperature range is an endothermic peak near 150°C for fulvic acid that is non-existent for humic acid.

Due to the heterogeneous nature of soils, the reproducibility of the DSC curves initially seemed impossible. Therefore, in addition to assisting in the further understanding of sorption and humic substances, the extraction of humic acid, fulvic acid and humin (with attached inorganic) were essential for obtaining reproducible curves in which to analyze results using a DSC.

2.6 Summary

An improved understanding of humic substances (organic matter), hydrophobic pollutants such as polyaromatic hydrocarbons, and the interaction mechanisms between the two is clearly important for the commercial success of the thermal desorption process. The use of a differential scanning calorimeter, along with a quantitative estimation of mass-loss of soil fraction with temperature, was the tool used to provide further insight into the thermal behaviour of individual humic substances (HA, FA and humin/inorganic) combined with selected PAHs.

CHAPTER 3

EXPERIMENTAL

3.1 Materials

3.1.1 Chemicals - Polyaromatic Hydrocarbons

The three chemicals used to contaminate the soil fractions in the laboratory were fluorene (98%), naphthalene (99%) and anthracene (99%). The chemicals were obtained from Aldrich Chemical Co. (Milwaukee, WI, U.S.A.).

Overall, polycyclic aromatic hydrocarbons (PAHs) are composed of various configurations of two or more benzene rings that form these neutral, nonpolar organic molecules. Basic properties for the three PAHs tested in this study, i.e. fluorene $(C_{13}H_{10})$, naphthalene $(C_{10}H_8)$ and anthracene $(C_{14}H_{10})$, are listed in Table 3.1. These chemicals are also important environmentally since all three are members of the class of compounds that demonstrate toxic or hazardous properties and are included in the list of pollutants by the U.S. EPA to be monitored in industrial effluents (Keith and Telliard, 1979).

3.1.2 Whole Soil Analysis

The whole soil was obtained from the Chemical Laboratories of the Energy Resources Conservation Board (ERCB) in Calgary (Alberta). The topsoil (4 inches) was obtained from a plot of land near Devon (Alberta). This soil was analyzed by

Polynuclear Aromatic Hydrocarbons			
	Fluorene	Naphthalene	Anthracene
Molar mass (kg/kmol)	166.22	128.17	178.23
Boiling Point (°C)	297.29	217.7	342.0
Melting Point (°C)	114.0	80.0	216.5
Chemical Formula	C ₁₃ H ₁₀	$C_{10}H_8$	$C_{14}H_{10}$
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Table 3.1 Properties of Selected Polyaromatic Hydrocarbons

Norwest Laboratories, Calgary (Alberta), and the results are shown in Table 3.2. The average particle size was determined to be 0.012 mm, with a porosity of 0.42. The total pore volume of 0.1806 cm³/g was measured at a maximum mercury pressure of 60,000 psi with a mercury porosimeter, as outlined by Karan (1994).

In the experiments completed in this particular study, the free moisture was removed by heating the soil at 105°C for 24 hours. Although there was no substantial aqueous phase in this soil sample, according to Wershaw *et al.* (1993), the humus is considered as being in four different pseudo-phases listed below and partitioning of hydrophobic chemicals still occurs:

- The liquid-like hydrophobic interior regions of the humus membranes coating mineral grains.
- 2) The charged surface regions of the membrane coatings
- 3) The liquid-like interiors of the humus micelles
- 4) The charged surfaces of the micelles.

3.1.3 Soil Organic Fractions

As mentioned previously, the organic matter content in surface soils is known to range from 0.1% in desert soils to 100% in organic soils. In organic soils, since the organic and inorganic components are closely linked, they need to be separated in order to examine their effect on chemical adsorption (Schnitzer, 1982). The humic content in soil is considered to be the major fraction of organic matter. As described in Section 3.2, the whole soil was divided into the following three fractions:

Table 3.2 Whole Soil Analyses

pH	7.3
CEC, meq/100 g	23
Organic carbon, mass%	1.24
Sulphur, mass%	0.061
Texture:	
Sand, mass%	36
Silt, mass%	34
Clay, mass%	30

Table 3.3 Surface Areas of Whole Soil and Tested Soil Fractions

BET Surface Area Analyses		
	Surface Area (m ²)	
Whole Soil	9.80	
Humic Acid	3.07	
Fulvic Acid	4.47 .	
Humin/Inorganic	8.11	

- 1) Humic Acid fraction
- 2) Fulvic Acid fraction
- 3) Humin (with attached inorganic constituents).

Surface area measurements on all soil fractions were completed by Mr. Jian Liu using a high speed surface area analyzer, with the results listed in Table 3.3. Briefly, the high speed surface area analyzer used nitrogen gas at the temperature of liquid nitrogen to determine the amount of gas necessary to form a monomolecular layer of gas molecules on the soil sample. The temperature for liquid nitrogen was the testing condition because it is at this point that the gas molecules are adsorbed on the solid surface. Under these conditions, the space occupied by each adsorbed molecule is known within a narrow limit.

As seen in Table 3.3, the surface areas of the three fractions were estimated to be less than that of the whole soil. This "loss" of surface area is most probably due to the effect of the chemicals used in the extraction procedure resulting in some breakdown of soil components. Chen and Schnitzer (1976) reported that the BET surface area by nitrogen adsorption on humic and fulvic acid to be approximately 2.5 m^2/g , which seems to be consistent with the values obtained in this study.

3.2 Method of Soil Organic Extraction

The basic isolation and separation procedures of humic substances were first developed by Springalin in 1826, with further developments made by Berzelius in 1833 followed by Oden in 1912–1922. Although the proposals and nomenclature is very old, an alternative method has yet not been proposed.

Humic acid is soluble in dilute alkali but is precipitated by acidification of the alkaline extract. Fulvic acid however, is soluble in both dilute alkali and dilute acid while humin (and attached inorganic components) cannot be extracted by a base or acid. As previously mentioned, the basic procedure for organic extraction outlined by Schnitzer (1982) was adapted for the purposes of this research and is shown in Figure 3.1.

3.2.1 Materials and Procedure

Dilute 0.1N NaOH was the base used to separate the humin/inorganic fraction from the humic and fulvic acid fractions. Dilute 0.1N NaOH was used in this study since it was found by Levesque and Schnitzer (1966) that it can extract more organic matter and ash than with higher concentrations. 2N hydrochloric acid was used to separate the fulvic and humic acid fractions.

The whole soil was initially removed of any moisture by heating the soil at 105°C for 24 hours. For every 10 g of oven dried soil, 100 mL of 0.1N NaOH was added into a glass flask with the air displaced by nitrogen. This mixture was then capped and shaken for 24 h at room temperature. A nitrogen atmosphere at room temperature was utilized in order to minimize the damage and modification of the chemical structure and characteristics of soil organic matter (Schnitzer and Skinner, 1965). The dark coloured supernatant solution was then separated from the residual



Figure 3.1 Method of Humic Substance Extraction (Schnitzer, 1982)

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soil by centrifugation. The process was repeated by adding distilled water to suspend the soil residue and to separate the phases until the supernatant solution was virtually clear. The washings were added to the supernatant. The soil residue was the humin/ inorganic fraction of the soil, while the supernatant included both the humic and fulvic acid fractions.

In order to separate the humic and fulvic acid fractions of the soil, the alkaline extract and washings were acidified to a pH of 2 with 2N HCl. This mixture was then allowed to stand at room temperature for 24 hours. The soluble material (FA) was then separated from the coagulate (HA) by centrifugation and washed with distilled water used once again until a virtually colourless solution was obtained. The humic acid and humin/inorganic soil fractions were initially air dried for 24 hours and then oven dried at 40°C to a constant weight. The fulvic acid, however, was only air dried to a constant weight in order to minimize loss of sample from the large amount of solution. The resulting humic acid was a solid with a very dark brown colour in comparison to the humin/inorganic fraction. The fulvic acid was yellow-orange in colour. In terms of an approximate material balance, the soil sample was divided into 5.0 mass% humic acid, 6.6 mass% fulvic acid and 88.4 mass% humin/inorganic.

3.3 DSC Sample Preparation

<u>3.3.1 Method</u>

Each sample tested in the DSC was weighed to 0.001 mg on a Mettler microbalance Model UMT2. The solid soil fraction was distributed over the base of

the aluminum crucible to ensure good contact between the DSC thermocouples and the sample. The liquid contaminant was dissolved in methylene chloride and injected with a syringe over the soil fraction in order to ensure even distribution. The sample crucibles were cold welded with their covers using a mechanical crucible sealer. A similarly sealed empty aluminum crucible was used as the reference in all the experimental tests. The samples were then stored at 4°C for a sorption time of normally 24 hours.

3.3.2 Chemicals and Concentrations

In order for the chemical contaminants to be distributed evenly over the soil fraction, methylene chloride (MC) was used as a solvent. Naphthalene and fluorene were dissolved in MC in concentrations of 10,000 ppm (1 mass%), 50,000 ppm (5 mass%) and 100,000 ppm (10 mass%), while a concentration of only 10,000 ppm (1 mass%) anthracene was used because of its observed limited solubility in MC. The levels of contamination were chosen based on the sensitivity values of the DSC.

Lighty *et al.* (1988) confirmed that the time of adsorption of contaminant from 1. day to 1 year had no apparent effect on the desorption characteristics for the p-xylene contaminant in the tested soil. In preliminary tests of the present study, the DSC results did not show any apparent variation due to the time of adsorption between 24 to 168 h for the samples tested.

Lighty *et al.* (1988) determined that for a volatile contaminant such as pxylene, the desorption and diffusion rates are not a function of the sample preparation procedures tested. To ensure that methylene chloride was indeed an appropriate solvent to use, the mixtures of MC and contaminants at 10,000 ppm were tested on the DSC with glass beads (35-40 mesh). Figure 3.2 shows two DSC tests for 1 mass% fluorene with MC. The dashed line shows the melting (first peak) and boiling (second peak) of pure fluorene (i.e. unmixed), whereas the solid line shows the thermogram of the MC and fluorene mixture. The boiling peak of the mixture is difficult to view due to the relatively large magnitude of the MC boiling peak at 40°C, but the melting peak coincides with that of the pure fluorene. Therefore, it is concluded that no substantial interaction between MC and fluorene occurred. Experiments with naphthalene and anthracene produced similar results. Also, in order to obtain consistent boiling peaks (i.e. return to baseline for the peaks coincide), a large enough mass (> 7 mg), similar to that tested for the pure chemical, is required to ensure reproducible DSC results.

3.3.3 Soil Fraction and Contaminant Mixtures

Three concentrations (0.8, 4.0 and 7.0 mass%) of naphthalene with each soil fraction and three concentrations (0.8, 3.0 and 4.0 mass%) of fluorene with each soil fraction were prepared. Anthracene was tested only at a concentration of 0.8 mass% with each soil fraction. Pre-weighed amounts of soil (8.97 mg), and 15–20 μ L of the contaminant–MC solution were tested together. Table 3.4 lists the number and type of experiments completed. Although a 168 hour test was completed for the humin/ inorganic fraction, reproducible results could not obtained due to the high inorganic content as described later.



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Figure 3.2 DSC Thermogram Demonstrating the Negligible Interaction of Methylene Chloride with PAH

	Humic Acid	Fulvic Acid	Humin/Inorg.
Fluorene			
0.8 mass%	2 (24 h) 1 (168 h)	2 (24 h) 1 (168 h)	2 (24 h)
3.0 mass%	2	2	1
4.0 mass%	2	1	1
<u>Naphthalene</u>			
0.8 mass%	2 (24 h) 1 (168 h)	1 (24 h) 1 (168 h)	3 (24 h) 1 (168 h)
4.0 mass%	2	2	1
7.0 mass%	3	2	1
Anthracene			
0.8 mass%	3 (24 h) 1 (168 h)	2 (24 h) 1 (168 h)	2 (24 h) 1 (168 h)

Table 3.4	Number and	Type of	DSC Experimen	ts Completed
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	Tests
Pure Fluorene	2
Pure Naphthalene	· 2
Pure Anthracene	2
Pure HA	2
Pure FA	2
Pure Humin/Inorganic	2
MC & Fluorene (10 mass%)	2
MC & Naphthalene (10 mass%)	2
MC & Anthracene (10 mass%)	2
Mass-Loss Expts.	
Humic Acid	3
Fulvic Acid	3
Humin/Inorganic	3

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3.4 Instrumentation

All DSC experiments were performed on a Mettler differential scanning calorimeter, Model DSC-12E, linked with an IBM PC for data acquisition. The Mettler software package TA89E controlled the DSC microcontroller so the calorimetric signal could be recorded, stored, and ultimately analyzed off-line.

The DSC measuring cell was purged throughout the experiment with dry nitrogen. The system schematic is outlined in Figure 3.3. The temperature and heat flow measurements were calibrated using the melting point and enthalpy of high purity indium as per the procedures outlined in the users' manual.

3.5 Testing Procedures

The DSC was programmed to scan the sample at 10°C/min from 20 to 390°C, which was the upper temperature limit of the DSC. Tan *et al.* (1986) confirmed that this heating rate is within the optimum scanning range for thermal analysis methods for testing soils.

An entire test consisted of an initial two minute isothermal period at 20°C, then heating at 10°C/min from 20 to 390°C, followed by another isothermal period for 2 min at 390°C, and finally cooling at 10°C/min from 390 to 60°C. If any contaminant was still remaining in the sample, a solidification peak would occur in the cooling portion of the test, near the original melting point temperature in the heating portion of the test. This is discussed further in Section 5.4.



Measurement of the thermal e.m.f. U in μV

TOP VIEW



Figure 3.3 Schematic Representation of the DSC Measuring Cell

Due to the non-isothermal nature of the DSC tests, the recorded temperatures are corrected for thermal lag between the sample and the thermocouple measurement in the calorimeter furnace as detailed by Hammami (1994). The calculated thermal lag for these experiments, calculated as per the users' manual for a heating and cooling rate of 10°C/min, was found to be 0.2°C. The actual DSC readings obtained also had to be corrected. For instance, the DSC output with no corrections produced a readout in W/g as a function of temperature. Note that the actual DSC readout only takes the input mass value to be constant throughout the experiment. In these particular tests, since the samples were losing mass continually, the thermal lag and mass-loss with temperature were corrected after the test.

3.6 Soil Fraction Mass-Loss Experiments

Since a thermogravimetric analyzer was not available for this study, the soil mass-loss data were produced from simulated experiments of thermogravimetry utilizing the DSC furnace. The soil fractions were weighed at 20°C intervals from 20 to 390°C with a 2-min isothermal period after being weighed and before the next temperature increment. At least three tests were completed for each soil fraction and the values were averaged. The experimental mass-loss results over 20–390°C for the three soil fractions are shown in Figure 3.4.

In heating the sample from 20 to 390°C, humic acid fraction was found to lose the most mass of 14.2%, with fulvic acid fraction losing 8.1 mass%, and humin/ inorganic fraction losing less than 2 mass%. These results are consistent with those



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Figure 3.4 Percent Mass-Loss of Three Soil Fractions as a Function of Temperature

by Schnitzer and Hoffman (1961), where HA was generally found to lose more mass relative to fulvic acid.

For correcting the DSC results, the mass-loss data for each soil fraction were correlated as the fraction of initial mass remaining (w) at temperature (θ in °C):

Humic Acid Fraction:

$$w = 1.027 - 2.52 \times 10^{-3} \theta + 7.50 \times 10^{-5} \theta^2 - 8.60 \times 10^{-7} \theta^3 + 8.83 \times 10^{-11} \theta^4$$

Fulvic Acid Fraction:

 $w = 1.014 - 1.78 \times 10^{-3} \theta + 8.45 \times 10^{-5} \theta^2 - 2.08 \times 10^{-6} \theta^3 + 2.90 \times 10^{-8} \theta^4$

Humin/Inorganic Fraction:

 $w = 1.003 - 1.75 \times 10^{-4} \theta + 9.77 \times 10^{-7} \theta^2 - 1.02 \times 10^{-9} \theta^3 - 7.04 \times 10^{-12} \theta^4$

3.7 Evaluation of DSC Results

Now that the numerous possibilities of application for a DSC have been introduced, the method and basis for analysis for this research will be described. Both qualitative and quantitative analyses are possible with the results from a DSC

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experiment; hence, both aspects of these experiments will be discussed. Although this study does not go into the composition of humic substances in particular, the use of thermal analysis techniques such as the DSC is successful in providing insight into the interaction of PAHs with humic acid, fulvic acid and humin/inorganic fractions.

3.8 Qualitative Analysis of DSC Peaks

Qualitative identification of soil fraction and chemical contaminants is achieved by utilizing the DSC curves as "fingerprints" of the individual component samples being tested. A comparison between thermograms for pure (individual components) and mixtures of a soil fraction and contaminant can then be made.

3.8.1 Individual Component Analysis

The use of thermal methods such as the DSC for the analyses of organic fraction in soil has increased dramatically due to the improved knowledge on the procedures for the extraction and purification (if required) of humic and fulvic acids and related compounds from soils. As discussed earlier, due to the large variation in whole soil samples along with the complex mineralogy and organic matter content, an overall, soil thermogram or "fingerprint" was virtually impossible. Therefore, the extraction of organic mater into HA, FA, and humin/inorganic was useful in not only obtaining valuable information regarding the degree of interaction between organic matter in soils but also in obtaining overall "fingerprints" of the soil fractions for comparison in soil+contaminant mixtures. According to the results described by Tan *et al.* (1978), the DTA analysis, which is very similar to the DSC, is capable of distinguishing between humic and fulvic acid. In the DTA analysis, HA is characterized by a strong exothermic reaction at 400°C, whereas FA demonstrates this exothermic peak at 500°C. Although the overall curves vary from the thermograms obtained in this particular study, the additional peak near 150°C in fulvic acid, also observed by Tan *et al.* (1978), was consistent with the peaks obtained for our sample of fulvic acid.

Although the maximum temperature for the experiments was 390°C (due to instrument limitations), the thermograms obtained were still successful in differentiating between the HA, FA and humin/inorganic soil fractions. The pure chemicals and individual soil fractions were tested in order to achieve base curves as a means for comparison when testing the soil+contaminant mixtures. These individual component curves proved valid as base case comparisons since reproducible results for the soil fractions and chemicals were obtained.

3.8.2 Reproducibility - Pure Components

Figures 3.5 to 3.7 show two DSC runs each for fluorene, naphthalene and anthracene, proving that reproducible DSC thermograms are expected for these chemicals consisting of distinct melting (peak 1) and boiling peak (peak 2). The lack of any other major or minor exothermal peak in the thermograms, in Figures 3.5–3.7, also confirms that no detectable pyrolytic degradation of these compounds took place at temperatures up to 390°C. In fact, the PAHs tested are stable aromatic compounds.





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Figure 3.6 Two Reproducible DSC Runs for Pure Naphthalene



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In order to test for the boiling point correctly, the mass of the samples was to be sufficient enough to cover the base of the crucible. Note that the hole punctured in the crucible-lid was to be made as small as possible as outlined in the DSC users' manual. This ensured that the sample did not form a mixture with the nitrogen flowing through the cell or vaporize before its true boiling point. The melting and boiling temperatures were determined as being the return to baseline values and not the peak values as explained by Hammami (1994).

Two DSC thermograms for each of HA and FA are shown in Figures 3.8 and 3.9, respectively, and these are clearly reproducible. The shift in the HA and FA traces are due to the fact that although the components of each sample may be the same, they could still vary in relative amounts. The fact that even though the mass of each sample tested was near 8.97 mg, the masses between the two HA samples and the two FA samples could not be exactly the same; which could also account for the slight shift in the thermograms. Due to the heterogeneous inorganic content combined with the humin sample, this particular soil fraction was less likely to produce reproducible curves as demonstrated in Figure 3.10 showing three DSC traces.

3.8.3 Soil Fraction-Contaminant Binary Mixture Analysis

The experimental tests were performed on mixtures of one soil fraction and one contaminant at a time, because of the lack of data for even this level of (i.e. binary) interaction between PAHs and specific organic fractions in soils.



Figure 3.8 Two Reproducible DSC Runs for Humic Acid Fraction



Figure 3.9 Two Reproducible DSC Runs for Fulvic Acid Fraction



Figure 3.10 Three DSC Runs for Humin/Inorganic Fraction

Due to the requirement of the thermal desorption process to volatilize the chemical contaminants from the soil, the existence of the melting and boiling peaks and the temperatures at which they occurred for the chemicals when combined with the soil fractions were the focus when testing binary mixtures. Since the mass of contaminant was below the recommended levels for determining enthalpies of reaction for a DSC, quantitative results were limited and qualitative results and energy demands based on temperatures requirements to remove the chemical were mainly analyzed.

As a means for interpreting these DSC thermograms with more confidence, a thermodynamic model that simulated the DSC tests was developed. Temperatures at which the peaks' returned to the baseline were not the only variation but also the actual existence of peaks (e.g. liquid to vapour transition peaks). This raised the possibility of the binary mixtures behaving within the realm of a miscible to an immiscible system. The thermodynamic model and results are outlined in Chapter 4.

3.9 Quantitative Analysis - Peak Areas

As explained in Section 2.5, a differential scanning calorimeter can measure changes in enthalpy for thermal events such as reactions and phase-transitions. In the experiments described below, a transition or phase change is being focused upon in terms of the energy and the temperature at which the contaminant is volatilized from the system.

A quantitative analysis can be completed for a transition or reaction where an enthalpy change occurs by determining the area with respect to a baseline for the generated DSC curve. When the baseline is shifted at the end of the thermal event, such as when a mass loss, phase or composition change is experienced, a straight line approximation is not considered to be accurate (Brennan *et al.*, 1969). Therefore, the iterative method proposed by Brennan *et al.* (1969) was used to obtain an improved approximation of the true baseline; the procedure requires three trials:

1) An initial isothermal portion to establish a baseline.

2) A second portion to scan the temperature range of interest.

3) A final isothermal portion to locate the final baseline.

When the results of these three runs are superimposed, a basic DSC curve is obtained with an initial and final baseline on either side of the actual thermal event or peak. In the calculations completed specifically for this study, the initial and final baselines were simply extrapolated from the actual DSC curve obtained experimentally in one run from 20-390°C. Over this entire temperature range, all these steps could be viewed allowing for the calculation of the heats of fusion and enthalpy based on the area of the peak with the corrected baseline.

Equations for the initial and final baselines were obtained from a linear regression of the DSC data, which provided the values of heat capacity (C_p) for the reactant and the product as a function of temperature. These equations were then utilized in a Fortran program for the iterative calculations (Brennan *et al.*, 1969), until the baseline values remained virtually constant.

The DSC melting thermogram of the pure naphthalene used in experiments is shown in Figure 3.11(a), whereas the boiling thermogram is shown in Figure 3.11(b).



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Figure 3.11 Baseline Correction for (a) Naphthalene Melting Peak, and (b) Boiling Peak

Figure 3.11(a) demonstrates the iterative calculation results for determining the true baseline for the melting peak of naphthalene and clearly shows that since there is no mass loss during this event, a straight-line approximation is acceptable. The boiling thermogram in Figure 3.11(b), however, shows that when a mass loss is experienced within the temperature range of 205 to 220°C for naphthalene, a noticeable baseline shift is observed. The iterative procedure in this case converged in one iteration where both baseline runs are reproducible.

The calculated area for the melting peak provides the value for the heat of fusion, and the area for the boiling peak with its corrected baseline provides the heat of vaporization values as given in Table 3.5.

Since the straight line approximation is valid for the melting peak thermogram, the heat of fusion values were calculated directly from the DSC since it determines the area based on a straight line baseline only. The heat of vaporization values, however, must be calculated using the corrected baseline as described previously. Since the DSC produces a thermogram on a W/g basis and since there is a mass loss, the experimental heat of vaporization values are not within 3% of the literature values. Furthermore, the literature heat of vaporization values are for one temperature, while the values reported here were calculated over a temperature range. These differences may account for the discrepancies in Table 3.5.
Table 3.5	Heats	of Fusion	and	Vaporization
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	Heat of Fusion (J/g) Experimental	Heat of Fusion (J/g) Reported	Deviation (%)
Naphthalene	-145	-150.7ª	3.81
Anthracene	-159	-162.03ª	1.87
Fluorene	-117	-117.78 ^b	0.66
	Heat of Vaporization (J/g) Experimental	Heat of Vaporization (J/g) Reported	Deviation (%)
Naphthalene	-265	-337.5 ^b	21.5
Anthracene	-250	-317.0 ^b	21.1
Fluorene	-238	-319.5 ^b	25.5

^a Perry's Chemical Engineers' Handbook (Perry *et al.*, 1984)
^b DIPPR database (Daubert and Danner, 1989)

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CHAPTER 4

THERMODYNAMIC MODELLING FOR INTERPRETATION OF DSC CURVES

4.1 Introduction

The experimental results of this study, particularly for contaminated soil fractions, can be best introduced with a discussion on the behaviour of ideal, equilibrium vapour–liquid binary mixtures. In order to understand the DSC results, thermodynamic calculations were performed to simulate the experimental thermograms as a means for qualitatively comparing the trends between ideal, equilibrium extremes of miscible to immiscible binary systems.

4.2 Experimental System

Before detailing the steps involved in the thermodynamic model, the actual system being modelled with its accompanying assumptions must be explained further. As previously mentioned, the DSC directly measures the difference in energy change required to allow a sample and reference to maintain the same temperature while a programmed temperature scan rate (i.e. 10° C/min heating or cooling) is experienced by the sample and the reference. The DSC provides a measure of the differential change in energy, *dH*, with respect to time, *t*, in terms of the heat flow, *Q*, i.e.

$$dH/dt = Q \tag{4.1}$$

The actual results obtained from the DSC are converted to this form of heat flow as a function of temperature.

The following thermodynamic calculations give the heat flow as a function of temperature for an equilibrium, ideal binary system. This will ultimately provide data to compare the -dQ/dt (heat flow) versus temperature of the actual experimental DSC thermograms to simulated curves. Note that the negative sign is based purely on the DSC convention in which a negative peak indicates an endothermic reaction and a positive peak demonstrates an exothermic reaction. The peaks observed in these experiments were endothermic and will therefore be simulated accordingly.

The actual experimental tests were completed on binary mixtures of contaminant (fluorene, naphthalene, or anthracene) with a soil fraction (humic acid, fulvic acid or humin/inorganic). The aluminum pan holding the sample was punctured in order to ensure that any vapour being formed was removed from the sample pan, and allowed the sample to remain at atmospheric pressure. This process will result in a decrease in the sample mass being heated and is modelled accordingly. The energy balance coupled with this mass balance will produce a cumulative energy graph, Q, that corresponds to the difference in energy per time (-dQ/dt) versus temperature relationship required for interpreting the experimental DSC thermograms.

4.3 Energy Balance

For an ideal solution with no heat of mixing, the energy required to vaporize a liquid at constant pressure can be shown in three steps:

- 1) Taking one mole of liquid and heating it from an initial temperature T_o to the boiling point (or bubble point) of the liquid, T_b .
- 2) Next, the liquid is totally vaporized at T_b .
- 3) Finally, the vapour is heated from T_b to a final temperature T_{f} .

The energy required to increase the temperature from T_o to T_f would be the total energy, E, of the three steps:

$$E = C_{pL} (T_b - T_o) + \Delta H_v + C_{pV} (T_f - T_b)$$
(4.2)

If the vapour phase is not heated (as in this study due to puncturing of the DSC crucible lid), Equation (4.2) can be written as:

$$E = C_{pL} \left(T_b - T_o \right) + \Delta H_v \tag{4.3}$$

For a binary mixture, the energy required to heat a liquid to the bubble point includes the same steps, and it was calculated with the following equations (Smith and Van Ness, 1975):

$$Q = H_T = \overline{H}_L + \overline{H}_V \tag{4.4}$$

Liquid Enthalpy:

$$\bar{H}_L = \sum x_i \bar{H}_L \tag{4.5}$$

$$\bar{H}_{L_i} = \int C_{pL_i} dT \tag{4.6}$$

Vapour Enthalpy:

$$\bar{H}_{V} = \sum y_{i} \bar{H}_{V_{i}} \tag{4.7}$$

$$\bar{H}_{V_i} = \sum y_i \Delta H_{V_i} \tag{4.8}$$

As in Equation (4.3), the third term for heating of the vapour is not considered once again; therefore, the total energy required for the binary system is now written as follows:

$$\Delta H = Q = \sum x_i \overline{H}_{L_i} + \sum y_i \overline{H}_{V_i}$$
(4.9)

and subsequently as:

$$Q = \sum x_i \int C_{pL_i} dT + \sum y_i \Delta H_{V_i}$$
(4.10)

4.4 Material Balance

It is clear from Equation (4.10) that x_i and y_i values are required as a function of temperature. These values were obtained from the modelled phase diagrams described in the following sections for the miscible and immiscible scenarios. These liquid (x_i) and vapour (y_i) mole fractions were then used to determine the vapour fraction and ultimately the overall material balance over small temperature increments.

The overall description of the system is outlined with reference to Figure 4.1. At some temperature T_o (e.g. at the bubble point), a liquid feed of mole fraction, Z_0 , of component 'a' flashes into a vapour phase of composition Y_1 and a liquid phase of composition X_1 . For our experimental system, only the remaining liquid of composition X_1 is heated to the next temperature T_1 . At temperature T_1 , vapour with composition Y_2 and liquid composition of X_2 are produced, with the similar process being followed at each subsequent increment of temperature. This scenario for the varying feed composition is demonstrated in Figure 4.2, showing the corresponding miscible phase diagram.



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Figure 4.1 Basis for Thermodynamic Model



Figure 4.2 Miscible Phase Diagram Demonstrating the Steps Shown in Figure 4.1

Depending on the initial feed, the bubble-point temperature also varies along with the vapour fraction for each temperature interval for a miscible system. For an immiscible system, the scenario would be much simpler since the bubble-point temperature remains the same regardless of the feed concentration. The vapour fraction can be calculated using the lever rule at temperature T_1 :

$$VF = (Z_0 - X_1)/(Y_1 - X_1)$$
(4.11)

where, VF = vapour phase mole fraction

 Z_0 = initial mole fraction of component 'a' in feed

 X_1 = liquid phase mole fraction of component 'a' at temperature T_1

 Y_1 = vapour phase mole fraction of component 'a' at temperature T_1

For subsequent stages, the feed value of Z_0 in Equation (4.11) will be equal to the liquid phase mole fraction from the previous stage, as shown in Figure 4.1. Referring to Figure 4.1, the material balance therefore is calculated as follows:

$$F_i = L_i + V_i \tag{4.12}$$

The vapour phase mole fraction is:

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or,

$$VF_i = V_i / F_i \tag{4.13}$$

and the liquid phase mole fraction is:

$$LF_{i} = L_{i}/F_{i} = 1 - VF_{i}$$
(4.14)

Therefore, the ratio of vapour to liquid mole fraction is:

$$VF_{i}/LF_{i} = (V_{i}/F_{i})/(L_{i}/F_{i})$$
 (4.15)

$$VF_i/LF_i = VF_i/(1 - VF_i)$$

$$(4.16)$$

Therefore, the moles of vapour phase are given as:

$$V_i = (L_i VF_i)/(1 - VF_i)$$
 (4.17)

and the moles of liquid phase as:

$$L_{i} = F_{i} (1 - VF_{i})$$

$$L_{1} = F_{0} (1 - VF_{1})$$

$$L_{2} = F_{0} (1 - VF_{1}) (1 - VF_{2})$$

$$L_{k} = F_{0} (1 - VF_{1}) (1 - VF_{2}) \dots (1 - VF_{k})$$
(4.18)

The overall energy balance calculations for the system require the composition, vapour fraction and the amount of liquid phase for each stage.

4.5 Soil Fraction–Contaminant System

In order to extend the vapour-liquid flash calculations to the soil fraction-contaminant system, vapour pressure correlations, heat of vaporization equations along with the liquid heat capacities as a function of temperature for the three contaminants (i.e. fluorene, naphthalene and anthracene) were obtained from the DIPPR database (Daubert and Danner, 1989) and are listed in Table 4.1.

Modelling the soil fraction, however, required certain assumptions and approximations due to the lack of sufficient information. The soil fraction was modelled as one pseudo-component, which was the same for humic acid, fulvic acid and humin/inorganic fractions, since the specific differences between each fraction were difficult to ascertain.

The following empirical correlation by Ghuman and Lal (1985) for the heat capacity of sand/silt/organic matter of the soil was used:

That is,

	Eq.	A	В	С	D	E		
Vapour Pressure								
Naphthalene	1	8.529E1	-9.0662E-3	-9.0648E0	3.5805E-6	2.000		
Fluorene	1	1.2909E2	-1.2347E4	-1.6059E1	1.0522E-2	1.000		
Anthracene	1	7.6938E1	-1.1106E4	-7.3878E0	1.5665E-18	6.000		
Soil Fraction	1	3.0951E1	-7.717E3	-1.1296E0	2.6938E-7	2.000		
Heat of Vaporization								
Naphthalene $T_c = 748.35$ K	2	7.5E7	1.0330	-1.2300	6.6400E-1			
Fluorene $T_c = 870 \text{ K}$	2	7.872E7	3.69E-1					
Anthracene $T_c = 873 \text{ K}$	2	7.99E7	3.074E-1		•			
Soil Fraction $T_c = 1735$ K	2	6.92E7	3.551E-1					
Liquid Heat Capacity								
Naphthalene	3	-7.9729E5	6.345E3	-1.2981E1	8.8981E-3			
Fluorene	3	1.0614E5	4.8476E2					
Anthracene	3	1.6700E5	4.0510E2					
Soil Fraction	3	3.1106E4	-1.453E1	1.2908E-2				
Equation (1): Y (in Pa) = exp($A + B/T + C \ln T + DT^E$)								
Equation (2): Y (in J/kmol) = $A(1 - T_r)(B + CT_r + DT_r^2 + ET_r^3)$								
Equation (3): Y (in J/kmol·K) = $A + BT + CT^2 + DT^3 + ET^4$								

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Table 4.1 Model Constants and Equations (Daubert and Danner, 1989)

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$$\ln C = -0.003 X - 1.071 \tag{4.19}$$

where C = heat capacity, and X = total of sand, silt and organic carbon contents (in mass%) as given in Table 3.2. Equation (4.19) predicted the soil heat capacity to be 0.2767 cal/(g.°C) or 1.95×10⁶ J/(kmol·K).

Since vapour pressure of the soil fraction as a function of temperature was difficult to estimate, a substance that had a boiling point below 390°C and above the boiling temperature of the contaminants was chosen; which, for the qualitative study here, was selected to be mercury. The heat of vaporization and the vapour pressure for this compound were used to simulate the soil fraction.

In order to determine the soil mole fraction in the feed, the molar mass of humic acid as 1684 kg/kmol (Schnitzer *et al.*, 1982) was used in all calculations. It is important to note, however, that the molar mass of fulvic acid as 669 kg/kmol is known to be lower than that of humic acid, but for the purpose of calculations considered here, the difference is not important. Listings of the equations and constants used for all components in this model are provided in Table 4.1.

4.6 Soil Fraction–Contaminant Vapour–Liquid Systems

Overall, binary vapour-liquid systems at equilibrium can show a range of behaviours. The temperature-composition diagrams (constant pressure) being used to interpret the DSC thermograms included the one extreme, where the two chemical species are completely miscible in the liquid phase, to the other extreme, where the two liquids are totally immiscible. Although partial miscibility of components to varying degrees is a distinct possibility, only the two extreme cases of miscible and immiscible were focused on.

Before proceeding with the model calculations for the miscible (case 1) and immiscible (case 2) binary soil fraction-contaminant system, additional assumptions were required. In order to comprehend the possibility of two liquids being present in the system of HA, FA, or humin/inorganic and the contaminant (fluorene, naphthalene, or anthracene), the mass-loss experiments for the soil fractions explained in Chapter 3 need to be discussed further.

Due to the large number of components in humic substances, the mass-loss experienced by each soil fraction (as the temperature is increased linearly) was assumed to be similar to that by a contaminant (i.e. fluorene, naphthalene or anthracene). Humic acid and the contaminants go from the solid to liquid and finally to the vapour phase at which time they would be removed from the system. Since only 14.2 mass % of the humic acid, 8.1% of the fulvic acid, and <2% of the humin/inorganic were removed over the temperature range of 20 to 390°C, only these percentages of the soil fractions can be considered as going through any phase change (i.e. solid to liquid to vapour). Consequently, only these percentages of the soil fractions were modelled as being in the liquid phase with the liquid contaminant in either a miscible or immiscible system.

4.6.1 Two Completely Miscible Liquids (Case 1)

The temperature–composition phase diagram for the soil fraction–contaminant mixture was for atmospheric pressure and at temperatures well above the freezing points of both components. The following simplifying assumptions were made in order to complete the thermodynamic model for this complex binary system:

- 1) Vapour phase is an ideal gas,
- 2) Raoult's law applies, i.e.

$$y_i = x_i P_i^{sat} / P_T \tag{4.20}$$

where,

 P_T = Total pressure

 P_i^{sat} = pure component vapour pressure

 $x_i =$ liquid mole fraction

 y_i = vapour mole fraction

- 3) Ideal solution,
- 4) No heat of mixing.

Specifically for the binary system comprising a soil fraction as one pseudocomponent and the second component being a chemical contaminant, the general equations for an overall mass balance and to construct a T-X-Y diagram are as follows (Smith and Van Ness, 1975):

Application of Raoult's law to each component yields:

$$y_a = x_a P_a^{sat} / P_T \tag{4.21}$$

$$y_{\rm b} = x_{\rm b} P_{\rm b}^{\ sat} / P_T \tag{4.22}$$

therefore,

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$$y_{\rm b}/y_{\rm a} = (x_{\rm b} P_{\rm b}^{sat})/(x_{\rm a} P_{\rm a}^{sat})$$
 (4.23)

With

$$\beta = P_a^{sat} / P_b^{sat} \tag{4.24}$$

$$x_{\rm a} + x_{\rm b} = 1 \tag{4.25}$$

$$y_{a} + y_{b} = 1$$
 (4.26)

we get

$$(1 - y_a)/y_a = (1 - x_a)/x_a\beta$$
 (4.27)

Rearranging Equation (4.27) gives:

$$y_{\rm a} = x_{\rm a}\beta/[1 + x_{\rm a}(\beta - 1)]$$
 (4.28)

$$y_{\rm b} = 1 - y_{\rm a}$$
 (4.29)

In addition,

$$P_T = x_a P_a^{sat} + x_b P_b^{sat}$$

$$(4.30)$$

or,

$$P_T = x_a P_a^{sat} + (1 - x_a) P_b^{sat}$$
(4.31)

$$P_T = x_a P_a^{sat} + P_b^{sat} - x_a P_b^{sat}$$
 (4.32)

$$P_T - P_b^{sat} = x_a (P_a^{sat} - P_b^{sat})$$
 (4.33)

With the pressure being constant, the composition varies with temperature, while P_a^{sat} , P_b^{sat} and β not being constant. Therefore, the procedure followed was to choose temperatures between the two saturation temperatures of components 'a' and 'b' for the miscible system. In order to obtain the liquid phase composition values of x_a and x_b :

$$x_{\rm a} = (P_T - P_{\rm b}^{\ sat}) / (P_{\rm a}^{\ sat} - P_{\rm b}^{\ sat})$$
(4.34)

$$x_{\rm b} = 1 - x_{\rm a} \tag{4.35}$$

with the corresponding y_a and y_b values given by Equations (4.28) and (4.29).

4.6.2 Two Completely Immiscible Liquids (Case 2)

An important property of an immiscible system is that each component in the liquid phase exerts its own vapour pressure regardless of the amount of the other component present, i.e.

$$y_a P_T + y_b P_T = P_T$$
 (4.36)

Figure 4.3 is a generalized temperature-composition diagram for two immiscible components 'a' and 'b'. If the mixture is initially in the liquid phase, as in the case of the soil fraction-contaminant system, this would be represented by point P in Figure 4.3. Upon heating at a constant pressure as with the miscible system, when the temperature T is reached, the partial pressure of component 'b' in the vapour phase will equal the vapour pressure of pure 'b'. At this temperature T, pure liquid 'a', pure liquid 'b' and vapour of composition W are in equilibrium at the three-phase temperature T, the bubble point temperature of the immiscible system. The temperature will remain constant at temperature T until the vapour phase disappears. The remaining liquid (in this case pure component 'a') will be heated until it is completely vaporized at its boiling point. If the initial feed composition had been H, the sequence of events would have been identical; however, pure liquid 'a' would have vaporized first, at temperature T, and the partial pressure of 'a' in the vapour would become equal to the vapour pressure of pure component 'a'.



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Figure 4.3 Generalized Temperature Composition Diagram for an Immiscible System of Components 'a' and 'b'

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As in the case of miscible liquids, the data required to obtain Figure 4.3 for the soil fraction-contaminant can be obtained from the vapour pressure correlations for the two liquids when the vapour phase is an ideal gas. The point where both components 'a' and 'b' start to vaporize from a liquid mixture and the vapour composition at point W, is at the temperature where the sum of the vapour pressures is equal to the total pressure (atmospheric). The partial pressures of the components (p_a, p_b) are:

$$y_a P_T = p_a \tag{4.37}$$

$$y_{\rm b} P_T = p_{\rm b} \tag{4.38}$$

therefore,

$$y_{\rm a} P_T + y_{\rm b} P_T = P_T$$
 (4.39)

Next, the composition of the vapour phase is:

$$y_{\rm b} = P_{\rm b}/P_T, \ y_{\rm a} = 1 - y_{\rm b}$$
 (4.40)

Thus, point E is located with the temperature and composition, and this fixes the horizontal line (the three-phase line) below which a vapour phase cannot exist. To locate points on the dew point line WB, temperatures are chosen between the three-phase temperature T and the boiling point of pure component 'b', and the compositions are calculated using Equation (4.40). A similar calculation is completed for the dewpoint line EA between temperature T and the boiling point of pure component 'a'.

Once the miscible and immiscible phase diagrams were obtained, the energy balance for both systems was completed. The cumulative energy, Q, was determined along with the change in energy with time as a function of temperature. Noting that the temperature in the DSC experiments was increased at a constant rate of 10°C/min;

therefore, the results for the rate of change in energy with temperature or time are related directly.

4.7 Discussion of Model Predictions

The model calculations for obtaining simulated DSC curves for contaminant and soil fraction systems were completed for the miscible and immiscible scenarios. Only the liquid/vapour transition temperatures (bubble points) of the components were focused on, since the solid/liquid transition temperatures were not affected in all the actual DSC tests.

4.7.1 Fluorene-Soil Fraction Binary System

Figure 4.4 shows the miscible phase diagram obtained for the fluorene-soil fraction mixture initially in the liquid phase. The temperature range from the boiling point of pure fluorene (297°C) to the designated boiling point of the soil pseudo-component (356°C) was the range in which the DSC behaviour was simulated.

The feed mole fraction of fluorene was varied in order to determine the effect of concentration. The amount of soil was kept constant in the sample as 8.97 mg (= 5.3266×10^{-9} kmol, for a molar mass of 1684 kg/kmol). From Figure 4.4, it is clear that as the mole fraction of fluorene (component 'a') is decreased, the bubble point temperature increases.

Figure 4.5(a) for the fluorene-soil system, shows the cumulative heat energy required to raise the temperature from 297°C (boiling point of fluorene) to 356°C



Figure 4.4 Model Miscible Phase Diagram for Fluorene (a)–Soil Fraction (b) with Example Fluorene Feed Mole Fractions





(boiling point of soil pseudo-component). The effect of varying the feed, and subsequently the bubble point as already discussed, is clearly seen at the higher-end feed concentrations (i.e. at 0.85, 0.80, 0.55 mole fractions of component 'a'). A linear increase of energy requirement is predicted in Fig. 4.5(a) until the bubble point temperature is reached, followed by a sudden increase due the addition of the vapour enthalpy. There would be a drop in energy required for the system as the mass is volatilized, which explains the levelling out of the curves in Figure 4.5(a) for the 0.85, 0.80, 0.75 and 0.55 curves in Figure 4.5(a).

The feed with 0.05 mole fraction of fluorene is probably the most relevant to the present study, because the concentrations of fluorene, naphthalene and anthracene tested with DSC were 0.06 mole fraction or lower. The curve for 0.05 mole fraction of component 'a' in Figure 4.5(a) demonstrates no observable shift in the cumulative energy since the bubble point temperature is reached near the end of the temperature range being considered.

Figure 4.5(b) is the simulated DSC curve within the boiling ranges of the two components. It is clear that regardless of the feed concentration of fluorene with soil, the DSC curve should demonstrate no peaks within the boiling points of two miscible components. The only peaks seen in Figure 4.5(b) are as a result of the numerical analysis when the bubble point temperatures are reached (corresponding to the sudden increases seen in Figure 4.5(a)). On the basis of Figure 4.5(b), if fluorene is miscible with the soil fraction (in the range of 297–360°C), there should be no visible peaks in the experimental DSC results.

<u>4.7.2 Fluorene–Soil Fraction Immiscible Model Results</u>

Figure 4.6 shows the immiscible phase diagram at the feed concentrations of 0.85, 0.55 and 0.10 mole fraction of fluorene (component 'a'). Note that the bubblepoint temperature at 275°C (i.e. the three-phase temperature) does not vary with concentration. If the concentration is above the three-phase composition of 0.74 (e.g. with 0.85 feed mole fraction), the soil fraction would vaporize first followed by fluorene which would vaporize at its boiling point temperature. If the concentration is below the three-phase composition of 0.74, as is the case for the 0.55 and 0.10 mole fraction curves, an opposite sequence is predicted in Figure 4.6.

Figures 4.7(a) and 4.7(b) show the cumulative energy and -dQ/dt versus temperature relationships, respectively, for the fluorene-soil immiscible system. Figure 4.7(a) shows how the cumulative energy increases abruptly at the three-phase temperature for all three feed concentrations. However, for the 0.85 mole fraction feed, there is an additional increase at the boiling point of pure 'a', whereas for the 0.55 and 0.10 feeds, a second increase is seen at the boiling point of component 'b'. Fig. 4.7(b) gives the corresponding effects of these abrupt energy changes that result in distinct peaks at the three-phase temperature, and at the pure boiling points of fluorene (for the 0.85 curve) and of the soil component (for the 0.55 and 0.10 curves). As the concentration is decreased, the magnitude of these peaks also decreases (note that certain peaks have been truncated in plotting the data).



Figure 4.6 Model Immiscible Phase Diagram for Fluorene (a)–Soil Fraction (b) with Example Fluorene Feed Concentrations



Figure 4.7 Predicted Results for Fluorene–Soil Fraction in an Immiscible System

4.7.3 Naphthalene–Soil Fraction Model Results

Figures 4.8 and 4.9 show the miscible and immiscible phase diagrams, respectively, for the naphthalene–soil fraction system. The feed mole fractions of naphthalene for the miscible system were 0.85, 0.80, 0.75, 0.20 and 0.10, and for the immiscible system these were 0.97, 0.85, 0.55 and 0.10.

Overall, as in the fluorene-soil system, there are no visible peaks due to vaporization for the miscible case in Figure 4.10(b). On the contrary, the peaks are quite distinct for the immiscible case in Figure 4.11(b) due to reasons given in Section 4.6.1 for the fluorene-soil fraction system.

Although the case of 0.97 feed mole fraction (naphthalene) is not useful for the thermal desorption process, it demonstrates the behaviour corresponding to a naphthalene content higher than the three-phase composition of 0.96 at 216°C. Note that the bubble point temperature and the peak at the boiling point of naphthalene overlap due to the their proximity.

4.7.4 Anthracene-Soil Fraction Model Results

Figures 4.12 and 4.13 show the predicted phase diagrams for anthracene in a miscible and immiscible system with the soil fraction, respectively. Figures 4.14(a) and 4.15(a) show the cumulative energy results, and Figures 4.14(b) and 4.15(b) show the -dQ/dt versus temperature results for the miscible and immiscible cases, respectively.



Figure 4.8 Model Miscible Phase Diagram for Naphthalene (a)–Soil Fraction (b)

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Figure 4.9 Model Immiscible Phase Diagram for Naphthalene (a)-Soil Fraction (b)



Figure 4.10 Predicted Results for Naphthalene–Soil Fraction in a Miscible System



Figure 4.11 Predicted Results for Naphthalene–Soil Fraction in an Immiscible System



Figure 4.12 Model Miscible Phase Diagram for Anthracene (a)–Soil Fraction (b)



Figure 4.13 Model Immiscible Phase Diagram for Anthracene (a)–Soil Fraction (b)



Figure 4.14 Predicted Results for Anthracene–Soil Fraction in a Miscible System



Figure 4.15 Predicted Results for Anthracene–Soil Fraction in an Immiscible System

The peaks observed for the miscible case in Figure 4.14(b) are, once again, due to numerical calculations when the bubble point temperature is reached for each feed concentration. The results in Figure 4.15(b) for the immiscible system demonstrate that distinct peaks should be expected, with the first peak for all feed compositions corresponding to the three-phase temperature. The second peak for the feed composition of 0.85 (which is higher than the three-phase composition of 0.57) occurs at the boiling point of anthracene. For feed compositions of 0.55 and 0.10, the second peak occurs at the boiling point of the soil fraction pseudo-component.

4.8 Summary of Model Calculation Results

The purpose of thermodynamic calculations presented here was to investigate the likelihood of the existence of liquid–vapour transition peaks in DSC experiments with some soil fraction–contaminant mixtures and not with others. However, due to low contaminant concentrations used in obtaining experimental DSC thermograms, the two peaks in an immiscible system may not be as distinct as predicted by the thermodynamic model. Furthermore, due to a number of simplifying assumptions made, the model predictions should be used only for qualitative interpretations. Overall, the results presented in this chapter provide important guidelines for interpreting experimental DSC thermograms for binary mixtures of contaminants and soil fractions, which will be presented in Chapter 5.

CHAPTER 5

DSC RESULTS FOR MIXTURES OF SOIL FRACTIONS AND CONTAMINANTS

The DSC experimental results presented in this chapter demonstrate how different concentrations of fluorene, naphthalene or anthracene are removed from humic acid, fulvic acid, or humin/inorganic fractions of the whole soil. Since the reproducibility of results is a major concern when working with soil samples, the experiments were repeated at each contaminant concentration. The results for each binary mixture are compared on the same graph to the corresponding pure chemical thermogram along with what will be referred to as the "pure" soil fractions as the base case curves discussed previously in Section 3.8.2.

5.1 Experiments with Fluorene–Soil Fraction Mixtures

5.1.1 Humic Acid Fraction

Figures 5.1, 5.2 and 5.3 show the 10°C/min DSC thermograms for 0.8, 3.0 and 4.0 mass% fluorene, respectively, mixed with the humic acid fraction. Also plotted, for comparison, are the pure fluorene and "pure" humic acid traces. Five important features are observed in these plots:

- (i) The DSC thermograms at each concentration are reproducible.
- (ii) The dashed-curve in Figure 5.1 for 0.8 mass% fluorene represents the sample with a sorption time of 168-hours, and it demonstrates no effect of sorption



Figure 5.1 DSC Thermograms for 0.8 mass% Fluorene (MC) in Humic Acid Fraction


Figure 5.2 DSC Thermograms for 3.0 mass% Fluorene (MC) in Humic Acid Fraction



Figure 5.3 DSC Thermograms for 4.0 mass% Fluorene (MC) in Humic Acid Fraction

time when compared to the two 24-hour runs also shown in Figure 5.1. This observation supports the findings of Lighty *et al.* (1988), who had reported a similar observation based on the p-xylene and soil thermal desorption experiments after 1 day, 6 months and 1 year.

- (iii) The melting peaks in the thermograms for all fluorene concentrations coincide with the melting point peak of pure fluorene.
- (iv) Although the fluorene melting peak is visible in the binary mixture of fluorene and humic acid, the overall shape of the curves for 0.8, 3.0, and 4.0 mass% are similar to that of "pure" humic acid.
- (v) Most importantly, there is no liquid-vapour transition observed at or near theboiling point of pure fluorene for all concentrations tested.

The lack of a bubble point peak in all of the mixture traces in Figures 5.1-5.3 is qualitatively similar to the results shown in Figure 4.5(b) in Section 4.7.1 for the fluorene-soil fraction predictions for the miscible system. It is, therefore, concluded that, at the concentrations tested, fluorene in humic acid forms a miscible mixture.

5.1.2 Fulvic Acid Fraction

Figures 5.4 and 5.5 show the DSC thermograms for fluorene at 0.8 and 4.0 mass% concentrations in fulvic acid. The results for the higher concentration are similar to that for the 4.0 mass% results; therefore, only two concentrations are discussed in detail. Once again, the following observations are made:



Figure 5.4 DSC Thermograms for 0.8 mass% Fluorene (MC) in Fulvic Acid Fraction



Figure 5.5 DSC Thermograms for 3.0 mass% Fluorene (MC) in Fulvic Acid Fraction

- (i) The DSC thermograms for 0.8 and 3.0 mass% concentrations are reproducible.
- (ii) The dashed-curve in Figure 5.4 once again shows that the time of sorption from24 hours to 168 hours does not alter the DSC thermograms.
- (iii) The melting peaks coincide with the melting peak temperature of pure fluorene at all concentrations.
- (iv) Although the bubble point peak is not clearly apparent in the 0.8 mass% cases in Figure 5.4, the higher concentration of 3.0 mass% shows its existence near the return-to-baseline temperature of 280°C, which is slightly below the boiling temperature of pure fluorene. This can be viewed as the bubble point temperature of the binary system.

The characteristic bubble point peak, obtained experimentally near 280°C, is similar to the 284°C peak in the model predictions in Section 4.7.2 for the fluorene–soil immiscible system. Hence, it is concluded that fluorene and fulvic acid form an immiscible system with the characteristic bubble point and boiling temperature depending on the fluorene concentration.

5.1.3 Humin/Inorganic Fraction

The DSC thermograms in Figures 5.6 and 5.7 for fluorene-humin/inorganic soil fraction are qualitatively similar to those for fluorene-fulvic acid mixtures. Although at each concentration, the melting peaks coincide for all of the DSC tests and the results being reproducible, the boiling peak only becomes apparent for the



Figure 5.6 DSC Thermograms for 0.8 mass% Fluorene (MC) in Humin/ Inorganic Fraction



Figure 5.7 DSC Thermograms for 3.0 mass% Fluorene (MC) in Humin/ Inorganic Fraction

concentration of 3.0 mass% in Figure 5.7, with identical results for 4.0 mass%. Therefore, these results indicate the behaviour of fluorene-humin/inorganic mixtures to be like an immiscible system rather than the miscible system, and similar to the model predictions shown in Figure 4.7(b).

The predicted bubble point peak at 284°C demonstrates that at this temperature, the partial pressure of fluorene is equal to its vapour pressure. The remaining material being the soil components is then heated until it vaporizes (boils) at 360°C. In reality, since there is a range of temperatures at which the soil components would vaporize (with some soil components vaporizing at much higher temperatures), a distinct second peak (boiling peak) would not be observed experimentally at the low tested concentrations of fluorene.

5.1.4 Concentration Effects

Figure 5.8 clearly demonstrates the effect of fluorene concentration on the DSC results. Also included in Figure 5.8 are the traces for the pure fluorene and "pure" humic acid. In Figure 5.8, it is readily observed that regardless of the contaminant concentration, the boiling peak is not visible and the magnitude of the existing peak increases with concentration.

In Figure 5.9 for fluorene and fulvic acid mixtures, the boiling peaks are distinctly present for the two higher contaminant concentrations, with only a small peak in the 0.8 mass% case. An important feature to note in Figure 5.9, however, is the shift to lower temperatures as the contaminant concentration is decreased. This



Figure 5.8 DSC Thermograms for the Effect of Contaminant Concentration in Fluorene–Humic Acid Mixtures



Figure 5.9 DSC Thermograms for the Effect of Contaminant Concentration in Fluorene–Fulvic Acid Mixtures

could be due to the use of a lower mass of fluorene in the sample being volatilized before reaching its boiling point. The DSC users' manual, for instance, recommends the use of a sample mass of 5-10 mg of the chemical for an accurate measurement of its boiling point temperature.

The results for fluorene-humin/inorganic mixtures in Figure 5.10 are identical to that for the fulvic acid results, with a similar shift in the return-to-baseline values for the boiling peaks.

5.1.5 Summary of Fluorene-Soil Fractions Results

The observations that the fluorene-humic acid mixtures behave like a miscible system and that the mixtures of fluorene and fulvic acid or humin/inorganic behave like an immiscible system are based on a comparison with the thermodynamic model predictions in Chapter 4. These results are consistent with the degree of partitioning expected for hydrophobic contaminants in humic acid compared to fulvic acid, as pointed out by Kile and Chiou (1989). Since soil humic acids are known to have a much higher molecular weight than fulvic acids, and are also found to have a lower polar group content due to the lower oxygen content, humic acids should promote the partition interactions with non-ionic organic solutes to a larger extent compared to fulvic acids and, as shown by the experimental results, also with humin/inorganic fractions. This behaviour would point out the need for higher temperatures necessary for the removal of PAHs from humic acid compared to fulvic acid or humin/inorganic.



Figure 5.10 DSC Thermograms for the Effect of Contaminant Concentration in Fluorene–Humin/Inorganic Mixtures

5.2 Experiments with Naphthalene–Soil Fraction Mixtures

5.2.1 Humic Acid Fraction

Figures 5.11, 5.12 and 5.13 show the reproducibility of results for naphthalene– humic acid mixtures containing 0.8, 4.0 and 7.0 mass% naphthalene, respectively. Similar to the case of fluorene–humic acid mixture results in Section 5.1.1, the melting peak for mixtures is consistent with that of pure naphthalene, but the boiling peak is once again non-existent regardless of the concentration tested. Figure 5.14 gives the concentration comparison for the naphthalene–humic acid system. These results also show that naphthalene in humic acid, like fluorene in humic acid, resembles the miscible case predictions of Section 4.7.3 (e.g. Figure 4.10), where no peaks were observed within the boiling temperature range for the two model components.

5.2.2 Fulvic Acid Fraction

The DSC results for naphthalene–fulvic acid mixtures at all tested concentrations again showed a satisfactory reproducibility of the results; hence, it was decided to not include all the results in the thesis (to avoid the discussion from becoming repetitive). It is also pointed out that, unless stated otherwise, the results for all 168-hour tests compared well to the 24-hour tests, i.e. showing no noticeable difference between the two.

Figure 5.15 demonstrates that the distinct peaks for the melting and bubble points of naphthalene–fulvic acid mixtures become larger as the naphthalene concentration is increased. Due to the large magnitude of the pure naphthalene peak



Figure 5.11 DSC Thermograms for 0.8 mass% Naphthalene (MC) in Humic Acid



Figure 5.12 DSC Thermograms for 4.0 mass% Naphthalene (MC) in Humic Acid



Figure 5.13 DSC Thermograms for 7.0 mass% Naphthalene (MC) in Humic Acid



Figure 5.14 DSC Thermograms for the Effect of Contaminant Concentration in Naphthalene–Humic Acid Mixtures



Figure 5.15 DSC Thermograms for the Effect of Contaminant Concentration in Naphthalene–Fulvic Acid Mixtures

and the 7.0 mass% bubble point peak, they have been truncated to facilitate graphical comparison of results. Once again, as with the fluorene–fulvic acid results, a slight downward shift of the return-to-baseline temperatures for the boiling peak is apparent as the contaminant concentration is decreased.

By a qualitative comparison of the DSC thermograms with the predictions in Figure 4.11 (Section 4.7.3), it is concluded that the naphthalene–fulvic acid mixtures behave like an immiscible system. The most important point to note, however, is that the liquid-vapour transition peak obtained experimentally is lower than the boiling peak of pure fluorene, suggesting the existence of a bubble-point peak, as in the model predictions for the immiscible mixture case.

5.2.3 Humin/Inorganic Fraction

Figure 5.16 shows the DSC thermograms for the pure naphthalene, the naphthalene–humin/inorganic mixtures containing 0.8, 4.0 and 7.0 mass% naphthalene, and the "pure" humin/inorganic fraction. The existence of two peaks, corresponding to the naphthalene melting and bubble point temperatures, allows the mixtures to be characterized as an immiscible system, much like the naphthalene–fulvic acid mixtures.

5.3 Experiments with Anthracene–Soil Fraction Mixtures

As previously mentioned, due to the limited solubility of anthracene in methylene chloride diluent, only one concentration level (i.e. 0.8 mass% of anthracene) was tested with the three soil fractions.



Figure 5.16 DSC Thermograms for the Effect of Contaminant Concentration in Naphthalene–Humin/Inorganic Mixtures

5.3.1 Humic Acid Fraction

Figure 5.17 shows the four DSC thermograms for 0.8 mass% anthracene in the anthracene–humic acid mixture, including a 168-hour trace shown as the dashed-curve. Similar to the cases of fluorene and naphthalene as contaminants, no boiling peak is observed for the anthracene–humic acid mixture. However, unlike the other two contaminants, the anthracene–humic acid mixture does not show a distinct anthracene melting peak in any of the thermograms shown in Figure 5.17. Although an explanation for this anomaly cannot be offered at present, the results for the anthracene–fulvic acid and anthracene–humin/inorganic mixtures (both at the same contaminant concentration of 0.8 mass%) in the following section will be used to establish the validity of the experimental procedure, particularly in terms of preparing the contaminant solution in methylene chloride.

5.3.2 Fulvic Acid and Humin/Inorganic Fractions

In Figures 5.18 and 5.19, the DSC experimental results are shown for the 0.8 mass% mixtures of anthracene–fulvic acid and anthracene–humin/inorganic, respectively. Unlike the results in Figure 5.17 for the anthracene–humic acid mixture, Figures 5.18 and 5.19 show small, but readily noticeable, melting peaks which coincide with the pure anthracene melting peak. Similar to the results with the 0.8 mass% concentration of fluorene (in Figure 5.4) and naphthalene (in Figure 5.15) in fulvic acid, the possibility of the DSC simply not being sensitive enough to register the bubble point peak at the low contaminant concentration may explain the absence of the



Figure 5.17 DSC Thermograms for 0.8 mass% Anthracene (MC) in Humic Acid



Figure 5.18 DSC Thermograms for 0.8 mass% Anthracene (MC) in Fulvic Acid



Figure 5.19 DSC Thermograms for 0.8 mass% Anthracene (MC) in Humin/ Inorganic Fraction

bubble point peak. Since this was difficult to verify in the tests with anthracene at higher concentrations (due to its low solubility in methylene chloride, as explained before), an extrapolation of the results with the other two polyaromatic hydrocarbons tested (i.e. fluorene and naphthalene) would indicate that a bubble point peak for anthracene in these two soil fractions would be present at higher concentrations. In support of this, the model predictions for the immiscible case involving anthracene and soil fraction had indicated the existence of distinct phase transition peaks. Based on the above, it would be safe to conclude that all three polyaromatic hydrocarbons tested in this study form a predominantly immiscible mixture when combined with either fulvic acid or humin/inorganic soil fraction.

The anomaly in the experimental results, however, seem to exist for the 0.8 mass% anthracene-humic acid mixture in Figure 5.17. Since neither a melting nor a bubble point peak is observed in Figure 5.17, and since the same source of anthracene was used for all of the tests with fulvic acid, humic acid and humin/inorganic fractions, the presence of anthracene in the diluted sample cannot be questioned. The lack of the anthracene melting peak, therefore, may simply be attributed to the possibility of the small concentration of anthracene not being detectable by the Mettler DSC 12E.

5.4 Cooling Thermograms

In order to confirm that all of the contaminants in the sample had indeed been removed completely during the heating step in the DSC, corresponding crystallization (i.e. solidification) thermograms were completed with each sample following the heating process at a cooling rate of 10°C/min. It was reasoned that if any of the contaminants was still left in contaminant-soil fraction mixtures, it would recrystallize near the melting temperature of the heating thermogram, taking supercooling effects into account (Hammami, 1994).

Figure 5.20 shows examples of cooling thermograms corresponding to the highest concentration of naphthalene (7.0 mass%) tested in humic acid, fulvic acid and humin/inorganic fractions. Note that no crystallization (or positive exothermic) peaks are present in any of the curves in Figure 5.20. Moreover, the cooling thermograms are similar to those obtained for the 'pure' soil fractions. Similar observations were also made from the cooling tests with the other two contaminants tested, i.e. fluorene and anthracene.

To summarize, the non-existence of a peak corresponding to the melting/ solidification temperatures for the three PAHs in these cooling thermograms validates the model prediction that the three PAHs would be removed completely once the contaminated soil fractions are heated to a temperature of 390°C.

5.5 Summary

Overall, the experimental results on contaminant-soil fractions, presented in this chapter, confirm the model predictions in Chapter 4. Specifically, under the conditions of the DSC experiments, the humic acid fraction was found to be miscible in the liquid phase with the polyaromatic hydrocarbons tested (i.e. fluorene, naphthalene and anthracene) to a larger degree than the fulvic and humin/inorganic fractions. The latter



Figure 5.20 Cooling Thermograms for 7.0 mass% Naphthalene (MC) in Each Soil Fraction Tested

two soil fractions demonstrated immiscible characteristics with the three PAHs, which implies that these contaminants would be volatilized and removed from these soil fractions at temperatures lower than their boiling points. Due to the miscible behaviour demonstrated by the mixtures of PAHs with humic acid, temperatures higher than the boiling points of the contaminants would be required for their removal.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

Experimental differential scanning calorimetry (DSC) tests were completed on binary mixtures of each fraction of soil and each of the three PAHs (with methylene chloride as the diluent). It was shown that there is a distinct variation in the energy and temperatures required to volatilize polyaromatic hydrocarbons, namely fluorene, naphthalene and anthracene, from different fractions of humic substances such as humic acid, fulvic acid and humin/inorganic. Explanations were provided for the variations observed between the humic fractions for removing volatile PAHs by use of an equilibrium thermodynamic model developed for simulating the DSC results.

Due mainly to the sensitivity of the DSC, contaminant concentrations up to 7.0 mass% in the soil fractions were tested. Although these concentration levels are much higher than those expected actually in a contaminted soil sample, the method of analysis and the thermodynamic model presented here have successfully provided an important first step towards understanding the removal of PAHs from humic substances by use of the thermal desorption process.

The observed DSC thermal traces for heating the samples demonstrated reproducible results for the three contaminants with a double-peak feature that is characteristic of the solid–liquid and liquid–vapour transitions. The DSC results for the 'pure' humic fractions, namely humic acid and fulvic acid, demonstrated reproducible and recognizable differences in the heating traces between the HA and FA soil fraction that were utilized to identify the samples. Although the thermal traces for the "pure" humin/inorganic soil fraction were not as reproducible, the results indicated that there were no distinct peaks corresponding to the solid-liquid or liquid-vapour transitions of naphthalene, fluorene or anthracene, and could therefore be used as base case curves.

For the case of humic acid fraction combined with fluorene, naphthalene or anthracene, the thermodynamic model predicted a miscible system would be formed with humic acid components. For this case, no bubble point peak was observed in either experimental thermograms or simulated DSC results. The cooling DSC traces confirmed that volatile components were removed completely since no peaks for the solidification/crystallization of contaminants were present.

Conversely, the fulvic acid and humin/inorganic soil fractions combined with the contaminants demonstrated immiscible system characteristics. In the immiscible binary system, there are distinct bubble point and boiling point peaks in the simulation results. The experimental results showed a peak demonstrating a bubble point temperature of the respective contaminant–fulvic acid and contaminant– humin/contaminant mixtures. The boiling point peak was not observed because at the concentration of contaminant used in the experiments, the contaminants would be removed at the bubble point temperature.

When relating to the thermal desorption process, the miscible behaviour of humic acid with PAHs indicates that the temperature necessary for complete removal of the contaminant would be higher than its boiling point temperature. For the immiscible behaviour depicted by the contaminants mixed with fulvic acid and humin/inorganic fractions at the low contaminant concentrations normally experienced in soil remediation situations, reaching only the bubble point temperature would suffice for removing the contaminant.

Since all soils (comprising humic acid, fulvic acid and humin/inorganic fractions) contain some organic matter, an understanding of the extent of contaminant—soil fraction interaction will assist in improving the effectiveness and efficiency of remediation processes such as thermal desorption. This will aid in modelling and optimizing the temperature and/or energy requirements of the thermal desorption process.

6.2 Recommendations for Future Work

- 1. To more accurately complete the mass-loss measurements on the soil organic fractions, experiments involving the use of a thermogravimetrical analyzer in conjunction with the DSC should be undertaken.
- 2. The measurement of the vapour pressure of soil fractions will aid in developing a more accurate thermodynamic model for the miscible and immiscible binary systems for interpreting the DSC thermograms. One possible method would be to determine the actual components and their composition in the soil fractions, followed by the measurement of their vapour pressures.

3. The environmental problems related to soil contamination that are faced today are much more complex than just binary mixtures of contaminants and soil fractions. Although the present study presents is a crucial first step, additional experiments need to be completed with mixtures of more than one contaminant in soils in order to extend the database to more realistic situations. Since all soils contain varying fractions of humic acid components, the removal of contaminants from more complex mixtures by the thermal desorption process would require temperatures higher than the boiling point of the contaminants. That is, heating the contaminated soil to the boiling point of the contaminant may not be sufficient for its complete removal.

CHAPTER 7

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