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STRUCTURAL INVESTIGATION OF ASPHALTENES FROM SAUDI ARABIAN CRUDE OILS

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To my beloved parents,
my wife Ruqayya
and
to my brothers and sisters

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ABSTRACT

A structural investigation has been made of asphaltenes obtained from Saudi Arabian crude oils. For this purpose, asphaltenes precipitated from Arabian Light (AL) and Arabian Heavy (AH) crude oils by the use of different carbon number n-alkane solvents (nC_5-nC_{10}) were characterized in terms of elemental analysis, molecular weight determination (vapour pressure osmometry), thermal gravimetric analysis, pyrolysis gas chromatography, nonaqueous potentiometric titrations and infrared and nuclear magnetic resonance spectroscopy.

The higher carbon number alkane solvents (nC_8-nC_{10}) precipitated lower amounts of asphaltenes than those obtained from the lower carbon number alkane solvents (nC_5-nC_7). These asphaltenes had higher molecular weights, higher concentrations of heteroelements and a higher degree of aromaticity than the lower alkane precipitated asphaltenes. Molecular weights of asphaltenes obtained from Arabian Heavy (AH) crude oil were determined by vapour pressure osmometry in five different solvents of varying dielectric constant (2.2 to 12.3). Lower molecular weights were recorded in the solvents with higher dielectric constant.

The asphaltenes were thermally reactive and released low molecular weight gases on pyrolysis at 350°C. The decomposition of asphaltenes at 520°C resulted in higher yields of gases, maltenes and coke and there was a marked tendency to concentrate nitrogen in the coke. The release of large amounts of oxygen-containing gases at the lower temperature (350°C) was attributed to the presence of carboxylic acid and ether-linkages on the periphery of the asphaltene structures. Retention of over 90% of the total nitrogen in the pyrolysis coke suggested that a major portion of the nitrogen functionalities belonged to those parts of the structure which tend to form coke.

Nonaqueous potentiometric titrations indicated the presence of very weak, weak and strong basic functionalities in the asphaltenes , which were due to indole, phenazine and pyridine groups, respectively. The proportion of these functionalities was higher in the higher alkane precipitated asphaltenes.

The data obtained from elemental analysis, molecular weight determination, and infrared and nuclear magnetic resonance spectroscopy were used to derive a series of structural parameters for an average asphaltene moiety. Gross differences in the structural parameters for asphaltenes precipitated from AH crude oil by the use of different alkane solvents were noted. These differences in the structures may possibly be responsible for their different behaviour on pyrolysis. The asphaltenes precipitated by the higher carbon number alkane solvents have higher numbers of aromatic and peripheral carbons, aliphatic carbon and aliphatic hydrogen. The substitution index is also higher for the higher alkane precipitated asphaltenes, whereas the aromaticity index, the condensation index, and the percentages of aromatic carbon, unsubstituted carbon, and nonbridge carbon are lower in the higher alkane precipitated asphaltenes.

CONTENTS

LIST OF TABLES

LIST OF FIGURES

1. INTRODUCTION AND OBJECTIVES

1.1 Introduction

The current trend and probable long term future outlook for the hydrocarbon conversion industry is to utilize the heavier and more carbonaceous feedstocks. Such feedstocks are characteristically more difficult to process because they contain substantial amounts of asphaltenes. In general, asphaltenes have higher aromaticity, heteroatom content, metal content and molecular weight as compared to lighter petroleum fractions and are thereby commonly presumed to represent the most refractory and difficult portion of the feedstocks to process. Operationally, the asphaltenes are defined by their insolubility in aliphatic hydrocarbon solvents and solubility in aromatic solvents.

Asphaltenes have very undesirable effects in petroleum refining. They cause coke formation on the walls of distillation vessels during distillation, which demands increasing heat input. Asphaltenes also carbonize the catalysts in reactors in two ways. In the first place, they are heat labile at the process temperature and secondly, they are large molecules which are adsorbed on to more than one catalyst site. Miscible flooding of petroleum reservoirs by fluids such as natural gas liquids has become an economically viable technique for enhanced oil recovery. Introduction of a miscible fluid in the petroleum reservoirs will in general produce a number of alterations. One such alteration is asphaltene precipitation. The kind of precipitates observed can vary from very minor to large amounts depending on the nature of the crude oil, the nature of the injection fluid and the operating temperature and pressure of the reservoir. In most of the instances observed, asphaltenes precipitation may result in plugging or wettability reversal in the reservoir. Also, it is a proven fact that precipitation of asphaltenes is generally followed by polymerization or flocculation of the resulting material, which produces an insoluble material in the original reservoir fluid.

In Figure 1.1, a ternary diagram, taken from Tissot and Welte (1984a), has been presented in order to demonstrate the gross composition of a large number of crude oils. According to this diagram, most of the crude oils contain significant amounts of asphaltenes and resins.

The word asphaltenes was coined in France by J. B. Boussingault in 1837 (Boussingault, 1837). He described the constituents of a number of bitumens. After separation of an asphalt by distillation, he named the alcohol-soluble, essence of turpentine-soluble solids, obtained from the distillation residue, asphaltenes. Nellensteyn (1924) defined asphaltenes as the solid residue remaining after the superheated steam distillation of petroleum, which is largely coincident with the present day nC_7 asphaltenes. He also defined the origin of asphaltenes as being formed by the condensation of smaller entities such as resins and hydrocarbons. Pfeiffer and Van Doormaal (1936) defined asphaltenes as hydrogen deficient macromolecular hydroaromatics. Louis and Tissot (1967) claimed that asphaltenes are produced by the thermal decomposition of kerogen. Observations by Byramjee and Bestougeff (1970) and Albrecht et al. (1976) also led to the same conclusions.

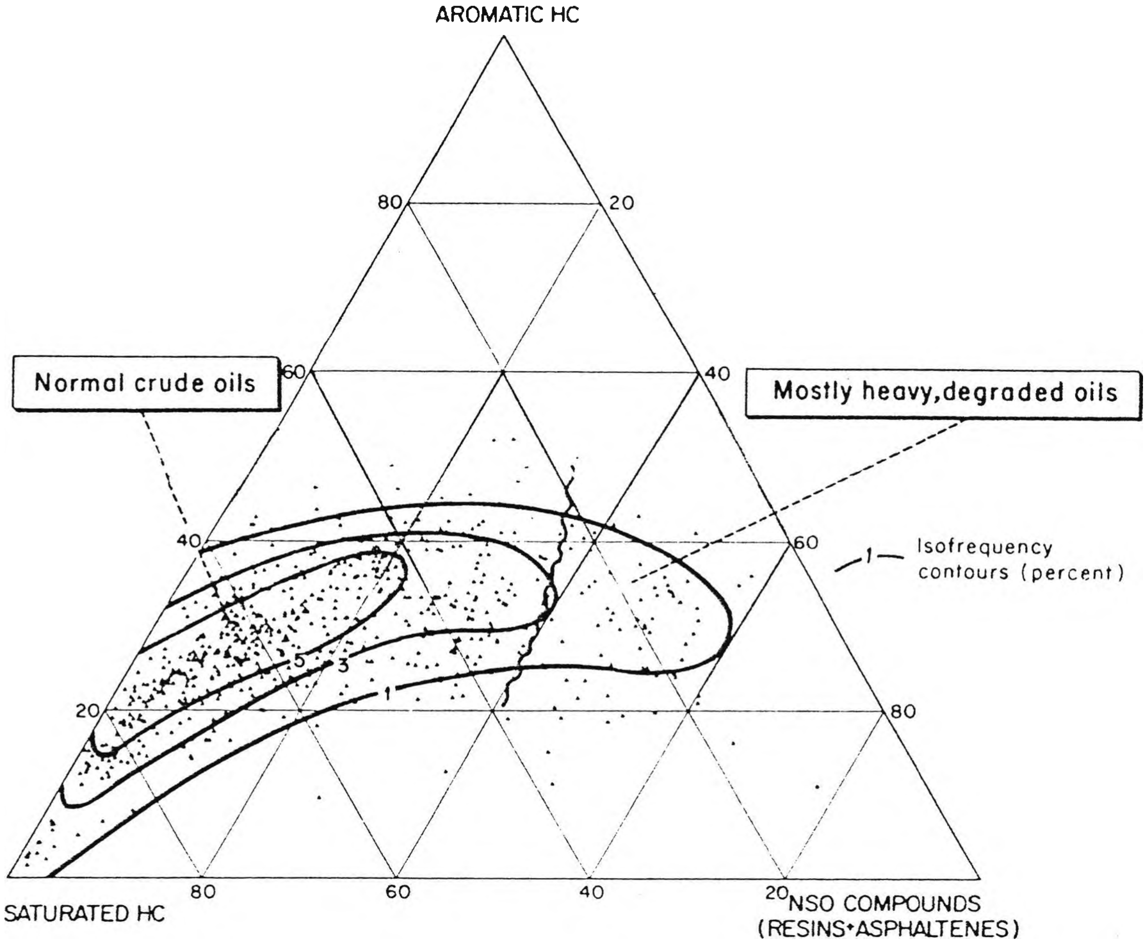

Fig 1.1 : Ternary diagram showing the gross composition of 636 crude oils: saturated hydrocarbons, aromatic hydrocarbons and resins plus asphaltenes as per Tissot and Welte (1984a).
(Reprinted with permission from Petroleum Formation and Occurrence by B. P. Tissot and D. H. Welte, page 380, copyright 1984, Springer-Verlag).

1.2 Objectives

The objective of this study was a structural investigation of the asphaltenes precipitated from Saudi Arabian crude oils. The structural data on asphaltenes obtained will provide some of the information which is necessary to develop processes that will contribute to more efficient utilization of the heavy ends of these crude oils.

For this purpose, asphaltenes precipitated from Saudi Arabian crude oils by the use of different alkane solvents have been investigated by analytical techniques such as elemental analysis, molecular weight determination, thermal gravimetric analysis, pyrolysis gas chromatography, nonaqueous potentiometric titration and infrared and nuclear magnetic resonance spectroscopy.

Solubility data of asphaltenes in different alkane solvents can be useful for researchers investigating in situ asphaltene deposition with different injection fluids and reservoir conditions.

In addition, the information obtained on the structure of asphaltenes will also be helpful to those involved in the geochemistry and exploration of crude oils, because the asphaltenes are more closely related to petroleum precursors than the other fractions of crude oil.

2. LITERATURE REVIEW

2.1 Introduction

The chemical structure of asphaltenes from petroleum has been a subject of active research during the past few years. A considerable amount of work has been done to define asphaltenes in terms of functional moieties. A number of significant details have emerged, but it is still not possible to deduce the precise chemical structure of this complex component of petroleum. Modern methods of physical and chemical analysis such as X-ray, IR and NMR spectroscopy and mass spectrometry, potentiometric titrations and their combination with traditional chemical methods of pyrolysis, hydrolysis, oxidation, etc. have been applied widely to the study of asphaltenes. These studies are frequently confounded by the properties of asphaltenes such as insolubility, high molecular weight, low volatility and strong intermolecular association. Nevertheless, the application of these techniques has brought to light some significant facts about asphaltene structure (Speight, 1972; Yen, 1972). The outcome of recent investigations has been the postulation of several average structures of asphaltene. These have varied from (a) a large polynuclear aromatic system (Speight, 1971) to (b) smaller, but linked polynuclear aromatic systems (Speight, 1975) and (c) linear polymer-type polynuclear aromatic systems (Suzuki et al., 1982). Asphaltenes have also been defined as sulphur polymers, consisting of relatively smaller molecules joined by sulphur bridges (Ignasiak et al., 1977a).

Attempts have also been made to describe the total structure of asphaltenes by the use of a group of structural parameters obtained by the application of nuclear magnetic resonance (NMR) and infrared (IR) spectroscopy and other analytical techniques. Figures 2.1 and 2.2 present the hypothetical structures for asphaltenes from different regions of the world. Figure 2.3 shows the macrostructure of petroleum asphaltene suggested by Yen (1981). This structure shows how the asphaltene particles and the asphaltene micelles are structured due to the formation of crystallites (A) of $\Pi - \Pi$ association among asphaltene molecules. On changing the conditions of solution, the particles may grow to micelles or the micelles may dissociate into particles. However, all the methods employed to postulate these structures are based on experimental data obtained for the more volatile portions of petroleum and the data are of questionable validity when applied to asphaltenes (Speight and Moschopedis, 1981).

The different techniques used for the structural characterization of asphaltenes and their achievements are reviewed in the following sections.

2.2 Precipitation and Isolation of Asphaltenes

The first step before the characterization of asphaltenes is their precipitation and separation from the crude petroleum. Several methods have been used as a means of asphaltene separation. However, each of these methods may suffer from a deficiency which renders it unsuitable for universal application. The nature of the precipitating solvent, solvent-to-oil ratio, ageing time and temperature are the important parameters which can greatly influence the characteristics of the asphaltenes isolated, not only on the yield but also upon the chemical nature of these complex materials. Although many

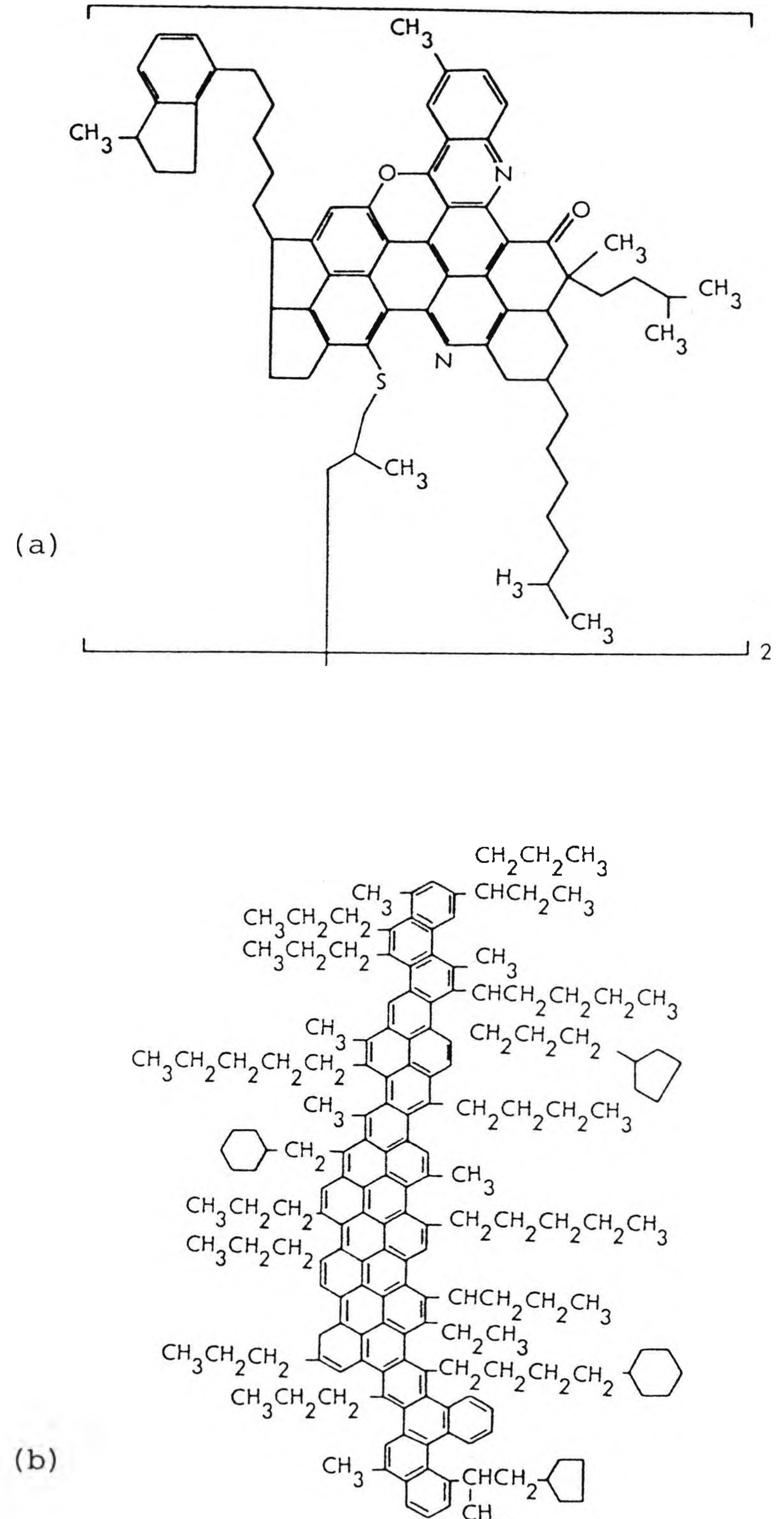

Fig 2.1 : Hypothetical structures of asphaltenes from (a) Californian crude oil and (b) Iraqi crude oil as per Speight (1980a).

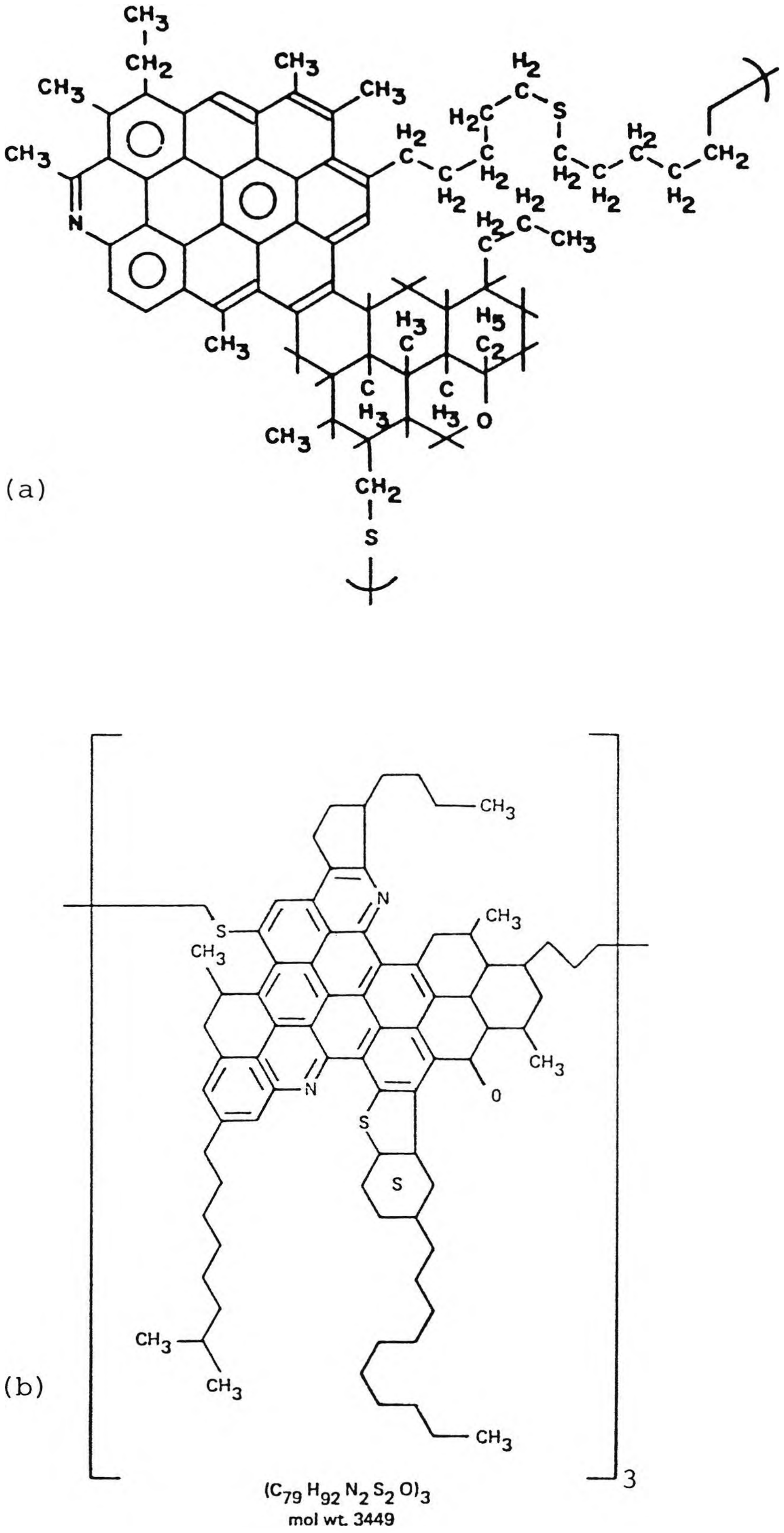

Fig 2.2 : Hypothetical structures of asphaltenes from
(a) Laquinillas crude oil as per Yen (1981)
(b) Venezuelan crude oil as per Speight and Moschopedis (1981).(Reprinted with permission from Chemistry of Asphaltenes by J. W. Bunger and N. C. Li, pages 4 & 43, copyright 1981, ACS).

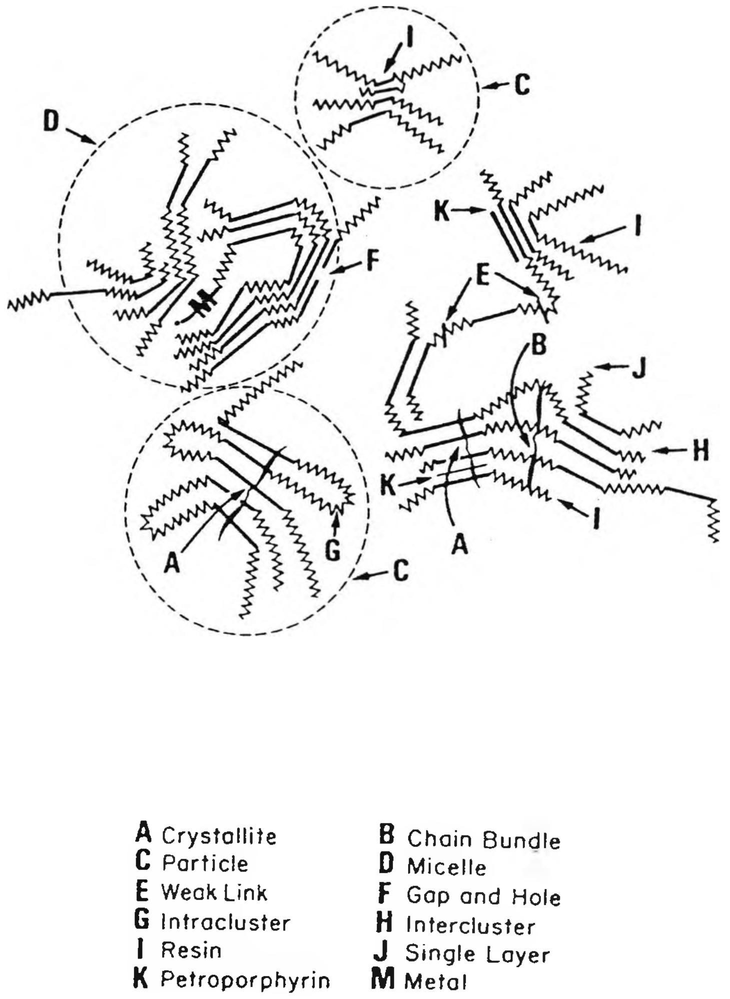

Fig 2.3 : Macrostructure of asphaltene as per Yen (1981)
(Reprinted with permission from Chemistry of Asphaltenes by J. W. Bunger and N. C. Li, page 45, copyright 1981, ACS).

attempts have been made there remain serious doubts about the methods employed for the separation of asphaltenes. Speight et al. (1984b) have reviewed the various parameters that can be applied to the separation of asphaltenes to bring attention to the general problem of asphaltene separation. They have concluded that asphaltenes are difficult to define even when a standard method of separation is used. The most important parameter in the separation of asphaltenes is the hydrocarbon employed for the precipitation. Normal pentane and normal heptane are the most common hydrocarbons employed in the several methods used for the separation of asphaltenes.

The Institute of Petroleum (IP) method, IP-143-57 (1984a) is one of the oldest methods recommended for the separation of asphaltenes by the use of normal heptane solvent. This method is mainly used for the separation of asphaltenes from air-blown asphalts. In this method one gram of sample, heated to about 60^{o}C, is mixed with 100 ml of normal heptane, followed by filtration through a Gooch crucible, and the asphaltenes are then dried at 107^{o}C. The method has been modified by reducing the volume of solvent from 100 to 30 ml and refluxing the mixture for 1h, followed by filtration through filter paper. The asphaltenes retained on the filter paper are dissolved in benzene or toluene and dried at 110^{o}C. Another early method used to isolate asphaltenes was to ultracentrifuge the crude or vacuum residue at a high speed followed by the separation of the precipitate into asphaltenes, oils and resins (Ray et al., 1957).

The American Society for Testing and Materials (ASTM) have recommended a method (ASTM D-893-80, 1983a) for the removal of insoluble material from lubricating oil by the use of normal pentane.

In this method, about 10 g of sample is heated to 65°C and mixed with a ten fold volume of normal pentane and the mixture is centrifuged for 20 minutes. After centrifuging, the mixture is decanted to 3 ml and again centrifuged for 20 minutes with 50 ml of the solvent. Finally the asphaltenes are dried at 105°C. Another method (ASTM D-2006-70, 1975), which is used for the hydrocarbon group type characterization of rubber extenders and processing oils, also uses normal pentane. The heated sample is mixed with five volumes of solvent and left for 15h, followed by filtration through filter paper. The filter paper is washed with three 10-30 ml portions of the solvent and the asphaltenes are dried at room temperature by aspirating air. Later this method was modified (ASTM D-2007-80, 1983b) by the use of fine porosity filter disks instead of filter papers.

There has been a growing tendency to classify asphaltenes by the particular paraffin used to precipitate the asphaltenes from the benzene-soluble portion. Thus there are pentane asphaltenes, hexane asphaltenes, heptane asphaltenes and so on. Lower yields of asphaltenes are reported (Bland and Davidson, 1967; Ali and Al-Ghannam, 1981; Corbett and Petrossi, 1978) with increasing carbon number of the precipitating solvent. For example, liquid propane precipitated approximately 50% of a natural bitumen as asphaltenes. The yields of asphaltenes precipitated with normal pentane, normal heptane and normal decane were 17%, 11% and 9% respectively (Mitchell and Speight, 1973).

Corbett and Petrossi (1978), in a study of the separation of the petroleum residue into hydrocarbon types using propane, normal pentane and normal heptane, suggested that the solvents cut deeper into the residue preferentially, removing saturated hydrocarbons and low molecular weight compounds first. This concentrates most aromatic and high molecular weight compounds in the precipitate. Propane precipitates a mixture of asphaltenes, polar aromatics and naphthene aromatics; pentane precipitates asphaltenes and polar aromatics, and heptane precipitates only asphaltenes.

Precipitation of asphaltenes and differences in yield with different solvents have been explained by McKay et al. (1978) as follows. Petroleum is a delicately balanced mixture of compounds that depend upon each other for solubility. When the composition of the mixture is changed by the addition of a normal alkane such as normal pentane, this balance is upset and some compounds precipitate. The two factors primarily responsible for maintaining the mutual solubility of compounds in a complex mixture are the ratio of polar to nonpolar molecules and the ratio of high molecular weight to low molecular weight molecules. In certain circumstances polar and nonpolar compounds are essentially immiscible. In a complex mixture like petroleum, polar and nonpolar compounds are miscible as long as the ratio of polar to nonpolar compounds is maintained. When this ratio is altered by the addition of a nonpolar solvent, polar molecules are less soluble. The polar molecules then form hydrogen bonded aggregates of non-uniform size and precipitate as asphaltenes. The ratio of high molecular weight molecules to low molecular weight molecules is another factor in maintaining solubility of all compounds in petroleum. The amount of asphaltenes also depends upon the change in the average molecular weight of the mixture after the addition of an alkane solvent. Thus the amounts of asphaltene precipitated from petroleum by pentane, hexane and heptane are different because the average molecular weight is different when these solvents are added to petroleum. Among these solvents pentane causes the largest amount of asphaltene formation because the average molecular weight of petroleum is lowered more than when the other solvents are used.

Striking differences in the volumes of the hydrocarbon used for the precipitation of the asphaltenes fraction have been found in the literature. Speight (1981) has stressed strongly that the addition of a minimum of forty volumes of the liquid hydrocarbon is required for complete precipitation of the asphaltene fraction. He reported that the use of a much lower proportion of the precipitating medium may lead to errors not only in the determination of asphaltene yield in the crude petroleum but also in the determination of compound type. Also, if an insufficient proportion of the precipitating medium is employed, resins are adsorbed on to the asphaltenes from the supernatant liquids and they can only be released by dissolving the asphaltenes in benzene followed by reprecipitation (Speight, 1984a).

On the other hand there are several reports in the literature in which lower proportions of solvent are used for precipitation of the asphaltenes fraction. For example, in a comprehensive study of asphaltenes from Wilmington crude oil, McKay et al. (1978) used only fifteen volumes of hydrocarbon for the precipitation of asphaltenes. Jacobs and Filby (1983) also used a lower proportion of the precipitating solvent. In their study asphaltenes from crude oil were isolated by stirring the crude oil with twenty volumes of the solvent for thirty minutes and then centrifuging the mixture for ninety minutes at 2000 rpm. The raw asphaltenes recovered from the bottom of the centrifuge tube were purified by extraction with the solvent in a Soxhlet extractor at room temperature.

Acevedo et al. (1985) have used twenty, forty and sixty volumes of normal heptane to precipitate asphaltenes from a heavy crude oil sample. After purifying the raw asphaltenes by exhaustive Soxhlet extraction they found that the differences in the yields of asphaltenes obtained by using different proportions of the precipitating solvent were insignificant.

Recently, Dolbear and Phan (1988) have proposed a method for the continuous isolation of asphaltenes. This method allows the isolation of large samples of asphaltenes by the use of a relatively smaller volume of solvent. The method gave reproducible yields of asphaltenes and the analysis of the product was identical to that of the asphaltenes isolated by a well studied batch precipitation technique.

The effect of temperature on the precipitation of asphaltenes has been studied by Ali and Al-Ghannam (1981). By conducting experiments for the yields of asphaltenes at cooling, ambient and reflux temperatures, they obtained higher yields at cooling and reflux temperatures as compared to ambient temperature. However, this trend was not observed for all the crude oils studied.

2.3 Elemental Analysis of Asphaltenes

Elemental analysis of hydrocarbons and their atomic ratios have great significance in characterizing petroleum compositions. The alkanes have a higher atomic H/C ratio than aromatics. Methane, the hydrocarbon with the smallest molar mass has the largest H/C ratio of 4.0 and the highly condensed aromatic systems with large molar masses have the smallest H/C ratios. Speight (1978) has carried out elemental analysis of a large number of asphaltene samples and has shown that the amount of hydrogen and carbon usually varies over a narrow range: 8.1 ± 0.7% hydrogen; 82 ± 3% carbon. These values correspond to an atomic H/C ratio of 1.15 ± 0.05. The near constancy of this property may be the reason for the general belief that asphaltenes from virgin petroleum may have a definite composition. This suggestion has been supported by a recent study by Acevedo et al. (1985). It has also been noted that the H/C ratios of resins are larger than those for the asphaltenes, indicating a higher degree of unsaturation in the latter materials. Speight (1978) also analysed asphaltenes for their nitrogen and sulphur contents and found that the amount of nitrogen varies from 0.6 to 3.3% and the atomic N/C ratios are usually about 0.015 ± 0.008. However larger variations were observed in the proportion of oxygen and sulphur. Oxygen contents vary from 0.3 to 4.9% and sulphur contents vary from 0.3 to 10.3%. On the basis of elemental analysis it has also been shown that the use of heptane as the precipitating medium yields a product which is substantially different from that obtained using pentane. For example the atomic H/C ratios of heptane precipitated materials are markedly lower than those of the pentane precipitated materials, indicating a higher degree of aromaticity in the heptane precipitated materials. Atomic N/C, S/C and O/C ratios are higher in the heptane precipitated materials indicating higher proportions of heteroatoms.

While studying a series of resin and asphaltene samples, Koots and Speight (1975) found a notable decrease in the H/C ratio of asphaltenes relative to the H/C ratio of resins and it was suggested that aromatization was more advanced in asphaltenes than in resins and, as suggested previously (Speight, 1971; Silverman, 1971), the asphaltenes may be the maturation products of resins.

Vercier (1981), in a study of the sulphur and nitrogen contents of different petroleum fractions, suggested that these elements present in the crude residues can be classified into two types: one part of the element is attached to the more volatile portion of the residue and the other part is more deeply buried in the structure of the less volatile portion of the residue, comprising asphaltenes and coke.

Speight and Long (1980b) have reported that asphaltenes have a varied distribution of heteroatom functionality; for example nitrogen in asphaltenes exists as various heterocyclic types. However, the presence of conventional primary, secondary and tertiary aromatic amines has not been established in petroleum asphaltenes. Oxygen has been identified in carboxylic, phenolic and ketonic locations (Ritchie et al., 1979; Nicksic and Jeffries-Harris 1968; Moschopedis and Speight, 1976a), but it is usually regarded as being located primarily in heteroaromatic ring systems. The presence of sulphur has been reported in the form of benzothiophene, dibenzothiophene and naphthenobenzothiophene (Speight and Pancirov, 1983; Nicksic and Jeffries-Harris, 1968; Clerc and O'Neal, 1961).

2.4 Molecular Weight Determination of Asphaltenes

Molecular weight is one of the principal characteristics of the chemical composition of asphaltenes. There is some controversy over the molecular weight of asphaltenes. The problem of determining their molecular weight has been discussed in detail by Speight and Moschopedis (1979). Several different methods have been used for the determination of the molecular weight of asphaltenes but the vapour pressure osmometric technique is the one which is most commonly employed. There have been fundamental criticisms of the application of the number average method in molecular weight measurements of asphaltenes. It has been suggested that vapour pressure osmometry (VPO) is not a precise or easy technique and requires significant care and attention in its execution (Larsen and Urban, 1979), but a number of reports have contributed to the improvement of VPO procedure (Speight, 1981; Chung et al., 1979; Dryden, 1979). The tendency of asphaltenes to associate, even in dilute solutions (Winniford, 1963; Speight and Moschopedis, 1977; Boduszynski et al., 1980) and the probable adsorption of resins on asphaltenes lead to discrepancies in molecular weight determination of these materials. For example ultracentrifugation studies (Witherspoon, 1958) gave molecular weights of up to 300,000, whilst an osmotic pressure method (Labout, 1950) indicated a molecular weight of the order of 80,000. However with other methods lower values have been obtained, such as 2500-4000 by the ebullioscopic method (Griffin et al., 1958), 900-7000 by viscosity determinations (Moschopedis et al., 1976), 1000-4000 by light absorption coefficient (Markhasin et al., 1969), and 1000-5000 by vapour pressure osmometry (Altgelt, 1968; Dickson et al., 1969; Koots and Speight, 1975; Larsen and Urban, 1979; Long and Vevrecka, 1981; Ali and Al-Ghannam, 1981).

The precise mechanism of intermolecular association in asphaltenes has not been established conclusively but hydrogen bonding and charge complexation have been cited as being responsible for intermolecular association (Yen, 1974; Speight and Moschopedis, 1981). These concepts have been supported (Acevedo et al., 1985) by the results obtained from methylation experiments conducted on asphaltenes.

Moschopedis et al. (1976) have conducted a detailed study of the determination of the molecular weights of asphaltenes by vapour pressure osmometry and viscosity measurement techniques. They showed that the molecular weights of asphaltenes by VPO are dependent not only on the nature of the solvent but also on the solution concentration and the temperature at which the measurements are made. They found that values of molecular weight determined by VPO decrease with an increase in the dielectric constant of the solvents in which the measurements are made. It was concluded that solvents of high dielectric constant such as pyridine might be able to bring about dissociation of asphaltene agglomeration. Based on the data obtained for molecular weight determination of model aromatic compounds by viscosity measurements, it was noted that the method is suspect, due to the fact that the data obtained for different solvent/solute systems were not consistent and hence were unacceptable. Use of a solvent of low dielectric constant such as benzene does not cause any variation in the molecular weight when the concentration of asphaltenes ranges from 2 to 7% (Speight, 1981).

Application of field ionization mass spectrometry (FIMS) for the molecular weight determination of asphaltenes (Boduszynski, 1981) has indicated that the molecular weight data obtained by FIMS are much lower than those obtained by VPO, presumably due to the elimination of intermolecular association in the FIMS technique.

Gel permeation chromatography (GPC) has also been used for the molecular weight determination of asphaltenes (Acevedo et al. 1985; Boduszynski, 1981). The molecular weight data obtained by GPC were much lower than those obtained by VPO; moreover, the data obtained by two different detectors, ultraviolet and refractive index, were inconsistent, probably due to dependence of UV absorbance on molecular type (Acevedo et al., 1985).

2.5 Thermal Decomposition of Asphaltenes

The thermal decomposition of asphaltenes, coke and related materials is of considerable practical interest. The concept of an integrated technique for the study of petroleum asphaltenes is viable and can offer valuable information about the structure type and distribution within the volatile products obtained from the thermal decomposition of asphaltenes. Several asphaltene pyrolyses have been oriented towards either elucidation of the structure of asphaltenes or the identification of fragmentation products and the dependence of their yields on pyrolysis temperature. Pyrolysis kinetics related to product fractions and the variation of yields of the individual constituents of the product fractions with both temperature and time have also been reported.

The importance of asphaltene pyrolysis was recognized previously by Speight (1970), who examined changes during the destructive distillation of asphaltenes and observed that about 50% of the material was converted to volatile oils, resins and gases.

Moschopedis et al. (1978) have studied the thermal decomposition of asphaltenes over the temperature range 200-600°C. They inferred that the thermal decomposition of asphaltenes at relatively low temperature is due to the elimination of groups situated on the peripheral sites of the asphaltenes whereas more extensive degradation of asphaltene structure occurs at elevated temperatures.

Ritchie et al. (1978) have studied the pyrolysis products of bitumen by gas chromatography, and have shown that at temperatures below 500°C the evolution of volatile products is dominated by a distillation process. At higher temperatures deep-seated degradation to gases and light ends is dominant. In a separate study Ritchie et al. (1979) compared the product types obtained by the pyrolysis of Athabasca tar-sand asphaltenes at different temperatures. They claimed that no distinct differences in product types were detectable with variation in temperature. More aromatic and highly condensed structures were observed at high temperatures. It was concluded that the aromatic hydrocarbons are produced both by the thermal scission of primary aromatic structures and the dehydrogenation of cyclic alkanes.

Application of pyrolysis gas chromatography-mass spectrometry to study the thermal chemistry of asphaltenes by Speight and Pancirov (1983) indicated the preponderance of single ring species and the dominance of saturated material over aromatic material. Heteroatoms such as those in nitrogen- and sulphur-containing compounds were not estimated in this study.

Savage et al. (1985) have conducted a detailed analysis of the pyrolysis products from asphaltenes in terms of the variation of yields of individual constituents with both time and temperature. Primary pyrolysis products were found to include light heteroatomic and hydrocarbon gases, alkanes, cycloalkanes and single ring aromatics, from which the presence of corresponding moieties in the asphaltene was inferred. The temporal variations of the product fractions were found to be consistent with an asphaltene structure containing a hydrogen deficient, condensed aromatic core.

In a kinetic study of the volatilization of tar-sand and its derived fractions at temperatures up to 210°C, (Strausz et al., 1977), a range of alkanes up to C_5 was detected along with acetaldehyde and a number of other noncondensible gases. It was pointed out that these products had arisen from low temperature thermal degradation.

The pyrolysis gas chromatography-mass spectrometry technique has been used by Gallegos (1978, 1981) in a structural study of coals. He reported the presence of several homologous series of n-alkylbenzenes. Detailed analysis of the homologous series of alkylbenzenes isolated from three coal samples suggested that the alkylbenzenes are derived from carotenes and were found to decrease with increasing coal rank. In another investigation of kerogens from Green River shale using pyrolysis gas chromatography-mass spectrometry, Gallegos (1975) observed the pyrolytic release of many identifiable terpanes and steranes.

Gould and Gorbaty (1981) have investigated the effect of heat treatment during distillation on the quantity and physical and chemical properties of asphaltenes. Cold Lake crude, which is known to be thermally sensitive, was chosen for this study. Differential scanning calorimetry and thermogravimetric analysis, as well as rapid pyrolysis, were employed along with other analytical techniques to investigate the differences between the asphaltene obtained from crude oils and that obtained from crude oil residues. These techniques indicated essentially no discernible difference between the two asphaltenes.

More recently, Soodhoo and Philips (1988) have reported the product distribution during non-catalytic hydrocracking of Athabasca asphaltenes. Primary hydrocracking products were found to include light hydrocarbon gases, alkanes, sulphur compounds and coke. Secondary reactions included fission of the resins to lower molecular weight aromatic hydrocarbons. It was shown that the heteroatomic components, viz. oxygen and sulphur, are the most thermally labile constituents of the asphaltene fraction. The results have also indicated that the alkyl chain substituents are chemically bonded to the asphaltene molecule and not just physically associated with its structure.

Thermal gravimetric study of asphaltenes from Mexican Maya crude oil, one of the largest reserves of heavy crude oils in the world, indicated that these asphaltenes have a wide temperature range of their fusion and that their oxidation takes place at temperatures above 400°C under an oxygen atmosphere (Ayala et al., 1984).

Thermal gravimetric analysis has also been applied to pitch (Sekhar and Ternan, 1978) and shale samples (Wen and Yen, 1978) to investigate the thermal behaviour of these materials in order to find means of their better utilization.

Pelet et al. (1985) have conducted a study on resins, asphaltenes and kerogens from the Paris basin to investigate the generation and migration of petroleum. By using a pyrolysis technique followed by a detailed mass spectrometric analysis, they reported that petroleum asphaltenes are reservoired source rock kerogen moieties along with all the corresponding geochemical consequences. Asphaltenes and source-rock kerogen appeared to be geochemically equivalent to a large extent.

Organometallic compounds present in crude oil residues and asphaltenes play an important role during petroleum refining and are also important for the geochemical study of crude oils. Hernandez and Choren (1979) employed a thermal gravimetric technique to analyse asphaltenes from Venezuelan oils, with the purpose of establishing their contribution to the volatile and residual parts of the organometallic compounds. TGA analysis up to 550°C followed by vanadium content determination on the residue indicated that in some of the asphaltenes up to 50% of the total vanadium content can volatilize at 550°C.

2.6 Nonaqueous Potentiometric Titrations

Potentiometric titration is a versatile analytical technique. The titration of acids and bases in nonaqueous solvents compares favourably with aqueous titrations in terms of speed, accuracy and convenience. Moreover, the solubility of organic compounds is rarely a problem with nonaqueous solvents. The potential ranges attainable in organic solvents are much greater than in water. This makes it possible to titrate each compound in a mixture to a separate end point, provided there are significant differences in acidic and basic titratable compounds (Fritz, 1973).

A linear relationship exists between the half neutralization potentials for a large number of bases when titrated in nonaqueous solvents and their ionization constants in water. There are exceptions of course, but the linear relationship appears to be a good approximation for most of the compounds, and it holds good for bases which are not levelled by a particular solvent.

It is assumed that nitrogen in asphaltenes and related materials contributes to the basic functional groups in these materials. Similarly oxygen contributes to the acidic functional groups.

Nonaqueous potentiometric titrations have been used by several researchers to determine nitrogen and oxygen functional groups in petroleum- and coal-derived asphaltenes and related materials. As a result of such studies the presence of several nitrogen- and oxygen-containing compounds have been indicated. For the titration of bases perchloric acid in dioxane or acetic acid has usually been used. Acetic acid has a levelling effect on mixtures of certain bases and in such cases perchloric acid in dioxane proves to be a good titrant. For the titration of acids, tetra-n-butylammonium hydroxide in methanol has been commonly used as titrant.

Fritz (1953) titrated several aliphatic and aromatic amines in acetonitrile as solvent and found that this solvent meets the requirements of a good differentiating solvent for amines. Kolthoff et al. (1967) also used acetonitrile as the solvent for the titration of mixtures of aliphatic and aromatic nitrogen bases. The titrant used was perchloric acid in acetic acid containing 2% of acetic anhydride.

Streuli (1958) employed acetic anhydride as solvent to titrate neutral nitrogen bases with perchloric acid and demonstrated that a linear relationship exists between the pK_a values in water and the half neutralization potential in acetic anhydride. He found also that anions are stronger bases in acetic anhydride than in water as compared to the neutral nitrogen bases. In another study, Streuli (1959), used nitromethane as a solvent for the titration of amines and amides and other organic nitrogen bases with perchloric acid. It was observed that nitromethane is an excellent solvent for the titration of weak organic bases such as amides, amines and ureas. These nitrogen compounds show relatively greater basicity in this solvent than they do in water.

Wimer (1958) also used acetic anhydride as the medium for the titration of aliphatic amines and amides with perchloric acid. He found that these titrations were rapid and reproducible and permitted the determination of amides and amines in complex mixtures. Acetylation of the amines was prevented by titrating at 0°C.

Buell (1967) employed nonaqueous potentiometric titrations for the estimation of nitrogen compounds in petroleum and its fractions. Primarily, based on pK_a values, he modified the titration procedures used by Fritz (1953) and Wimer (1958) by using benzene-acetic anhydride or benzene-acetonitrile as solvent. He titrated a series of pure nitrogen compounds with perchloric acid and classified them into different classes based on their pK_a values and titration in different solvents. All compounds which were titrated in acetic acid or acetonitrile were called basic nitrogen compounds and those which were titrated in acetic anhydride, but not in acetonitrile, were classified as very weak bases.

Darlage et al. (1978) applied the nonaqueous potentiometric titration technique to coal-derived asphaltenes for the estimation of nitrogen-compounds. A number of model nitrogen-containing compounds were divided into five classes based on the half neutralization potentials obtained in acetophenone and nitrobenzene. Titration data of asphaltenes indicated the presence of two classes of nitrogen-containing compounds: a titratable class of the pyridine ring or aniline type and a non-titratable class. Approximately 50% of the total nitrogen in the asphaltenes was found to be sufficiently basic to titrate in acetophenone or nitrobenzene.

Pietrzyk (1967) has studied the acidic behaviour of perchloric acid and several substituted benzenesulphonic acids in acetic acid-acetic anhydride solvent mixtures. It was demonstrated that the presence of acetic anhydride in the acetic anhydride-acetic acid mixture increases the potential range in both acidic and basic directions. Solvent mixtures containing greater than 50% acetic anhydride proved to be a better differentiating solvent for strong acids than methyl isobutyl ketone or acetic acid.

McKay et al. (1976) have employed nonaqueous potentiometric titration and quantitative infrared spectroscopy to characterize four basic nitrogen compound types in high-boiling petroleum distillates. The data obtained by the two methods were quite comparable. The bases were titrated potentiometrically with perchloric acid dissolved in dioxane, using acetic anhydride/benzene (2:1) as solvent. Bases having half neutralization potential (HNP) of 350 mv or less were classified as strong bases; those with an HNP greater than 350 mv were classified as weak bases.

In a more recent study by Heppner and Homes (1983), nitrogen-rich fractions from retorted and hydroprocessed shale oil were analyzed by nonaqueous potentiometric titration. The results obtained by this method were compared to the results obtained by high resolution mass spectrometry. The results showed good agreement except in fractions where pyrroles and arylamine compound types were concentrated.

Dutta and Holland (1983) have applied nonaqueous potentiometric titration to coal-derived liquids to distinguish and determine carboxylic acid and phenolic groups in these materials. A model system consisting of carboxylic acids, phenols and indoles and their derivatives was titrated and the acidic compounds were divided into three groups of different pK_a values. Samples of coal and coal-derived liquids were titrated as pure and spiked with benzoic acid, phenol and indole. The titrant used was methanolic tetra-n-butylammonium hydroxide in toluene, and pyridine was used as the titration solvent. Data obtained for phenolic groups by potentiometric titrations were comparable to those obtained by a combination of nuclear magnetic resonance spectroscopy and gas chromatography-mass spectrometry.

In another study Dutta and Holland (1984) investigated acidic and basic groups in petroleum asphaltenes by the use of differential potentiometric titration. The acids and bases were split into differing pK_a values by the addition of model compounds. Structural information about the nature of the groups titrated was obtained from the study of many model systems. The strong, medium and weak acids were due to carboxylic, phenolic and indolic functionalities, respectively. The strong bases titrated were due to pyridine groups, the medium strength bases were due to pyrazines and sulphoxides and the very weak bases were due to indoles and amides. A mixture of chlorobenzene and acetic anhydride (9:1) was used as the solvent and perchloric acid in dioxane was used as the titrant for the bases. The study suggested the presence of functionalities with acidic and basic strengths corresponding to carboxylic acids, phenols, indoles, amides, pyrazines, sulphoxides and pyridine type structures in asphaltenes. The quantities of strongly basic and strongly acidic functionalities in asphaltenes were low.

2.7 Spectroscopic Techniques of Analysis of Asphaltenes

Among the varieties of available spectroscopic techniques, nuclear magnetic resonance (NMR) and infrared (IR) spectroscopy are probably the most important in the structural characterization of fossil materials such as asphaltenes. IR spectroscopy has been widely used to identify oxygen and nitrogen functionalities in asphaltenes, both qualitatively and quantitatively. The most commonly identified functionalities include free and hydrogen bonded OH and NH groups, carbonyls, carboxylic acids, pyridines, pyrroles, amides and other linkages.

Moschopedis and Speight (1976a) have conducted a study to investigate the oxygen functions in the hydrogen bonding which occurs between asphaltenes and resins from bitumen. By employing IR and NMR spectroscopy, it was possible to show a feasible representation of the manner by which asphaltenes are peptized by the resins. In another study Moschopedis and Speight (1976b) employed

IR spectroscopy to investigate oxygen functions in Athabasca asphaltenes. Acetylation of asphaltenes showed that 40-50% of the oxygen present in the asphaltenes was accessible to acetylation. IR spectra of the products indicated that this oxygen exists as phenolic and hydroxyl groups and that a considerable portion of these groups may occur either as a collection of two or more functions on the same aromatic ring or on adjacent peripheral sites, or sites adjacent to carbonyl functions in a condensed aromatic system.

Petersen and co-workers (Petersen et al., 1971) have investigated the molecular interactions of bitumen samples by IR spectroscopy. The results indicated a high degree of association and the formation of strong hydrogen bonds. They also obtained evidence from IR spectroscopy that 2-quinolones and carboxylic acids are highly associated in neat bitumen samples. The ability of two solvents, methylene chloride and tetrahydrofuran, to break up hydrogen bonded molecular complexes was also shown. Petersen (1975) also proposed a method for the quantitative estimation of the compounds absorbing in the carbonyl region in bitumen samples. The technique was based on differential IR spectroscopy combined with base hydrolysis and silylation reactions. Ketones and dicarboxylic acids were found in the oxidized bitumen. The formation of 2-quinolone was not observed during the oxidation.

Bockrath et al. (1979) have employed IR spectroscopy to characterize asphaltenes isolated from coal-derived liquids. The functional group contents of the whole asphaltenes were roughly comparable to those obtained for gel permeation chromatography and acid/base fractions of asphaltenes. In a recent study Gawel (1987) compared the composition and chemical structure of asphaltenes isolated from different asphalt samples by IR and proton NMR spectroscopy. The results of this investigation showed that the methods used for the production of the asphalt influences its chemical structure. The greatest differences in composition of chemical structure appeared between air-blown and distilled asphalt. The predominant structural difference in asphaltenes from blown asphalt was a 14 ring basic unit and the average asphaltene molecule consisted of three to five such units.

Barbour and Petersen (1974) have investigated the hydrogen bonding basicity of asphalt and its fractions by an infrared technique. Phenol was used as the hydrogen bonding solvent. The data indicated that asphalts contain molecular systems exhibiting strong hydrogen bonding basicity. Air oxidation of asphalts at elevated temperatures caused an increase in the measured hydrogen bonding basicity.

Boduszynski et al. (1980) have reported a quantitative differential infrared spectroscopy method for the estimation of -OH and -NH groups and carbonyl compounds in asphaltene fractions. The IR analysis showed that pyrroles and phenols were the predominant compound types identified in asphaltenes. Small amounts of carboxylic acids, amides and 2-quinolones were also found. However, the amount of nitrogen-containing compound types identified in asphaltenes by the IR technique did not account for the total nitrogen present in the fractions.

Jacobs and Filby (1983) have characterized liquid chromatographic fractions of petroleum asphaltenes by IR and NMR spectroscopy. The data indicated that about 50-60% of asphaltenes consist~~s~~ of low functionality components in which heteroatoms are located primarily in ring structures or in nonpolar peripheral groups. Two distinct molecular types were present in asphaltenes, namely lower functionality species with lower heteroatom content and the higher functionality species with higher heteroatom content. Most of the fractions were predominantly polynuclear aromatics with alkyl substituents and probably bridged by cycloalkanes.

McKay et al. (1978) have separated asphaltenes into acidic, basic and neutral nitrogen compounds and saturated and aromatic hydrocarbons by ion-exchange and coordination chromatography. Compound classes such as carboxylic acids, phenols, amines, carbazoles and pyridine benzologues were identified by IR spectroscopy in acidic and basic fractions. Some of these compound types were also found in high-boiling distillates and the residue from the same crude oil. Brown et al. (1977) also separated coal-derived asphaltenes into acid and base fractions to investigate the functionalities in the asphaltenes. IR and NMR spectra of the TMS derivatives of the whole asphaltenes confirmed the presence of OH groups. IR spectra of dilute solutions of the acid fraction in carbon disulphide indicated that hydrogen bonding was intermolecular in character.

Ignasiak et al. (1977b) have investigated the oxygen distribution in Athabasca asphaltenes by IR spectroscopy. The data obtained indicated that approximately 75% of the oxygen was present in the form of hydroxyl groups. They also inferred that the hydroxyl groups exist almost entirely as a hydrogen bonded complex, which was not observed in carbon tetrachloride solution. The decrease in the molecular weight of acetylated, methylated and silylated asphaltenes suggested that the hydrogen bonding was intermolecular in character. IR spectra of asphaltene fractions extracted with polar solvents showed the presence of free OH, NH and carboxylic groups.

Recently, Jacobson and Gray (1987) have proposed a method combining quantitative IR spectroscopy and nitrogen titration data for the structural group analysis of bitumen samples. Incorporation of data obtained by the two techniques into the structural group analysis of Peace River bitumen significantly improved the profile of the heteroatomic groups and allowed better representation of the hydrocarbon groups. The method determines directly the concentration of certain heteroatomic groups and thus eliminates the extensive class separation which is otherwise needed for the assignment of heteroatomic structures.

Proton and ^{13}C nuclear magnetic resonance spectroscopy have also been used to derive a series of parameters of an average molecule which characterize multicomponent complex mixtures such as asphaltenes. These structural parameters include aromatic, aliphatic, methyl and ring carbons, average chain length and percent straight chain, etc. Reduction of long spin-lattice relaxation time of quaternary carbons by using relaxation agents and the elimination of nuclear Overhauser effect (NOE) by setting the instrument in a gated decoupling mode has established ^{13}C NMR spectroscopy as a very useful technique for structural characterization of complex materials.

Today, ^{13}C NMR spectra of solids are approaching the quality of the high resolution of the ^{13}C NMR spectra of liquids, due to techniques such as high-power proton decoupling (elimination of ^{1}H – ^{13}C dipole-dipole coupling), ^{1}H – ^{13}C cross-polarization (increasing signal sensitivity) and magic angle spinning (removing the broadening effect due to chemical shift). Ali and Al-Ghannam (1981) have compared asphaltenes precipitated with different alkane solvents and at different temperatures by means of their NMR structural parameters. The results showed that as the temperature of asphaltene precipitation increases, the naphthenic carbon content in the separated asphaltenes tends to increase.

Dereppe et al. (1978) have conducted an investigation of asphaltenes from the Paris basin to develop a method for the derivation of structural parameters by the use of proton and ^{13}C NMR spectroscopy. The variation of parameters such as aromaticity factor, degree of substitution and number of aromatic and naphthenic cycles per structural unit were studied as a function of depth of burial for the rock samples from different origin.

Kemp-Jones et al. (1977) have used IR, UV and NMR spectroscopy to compare natural asphaltenes and asphaltenes produced synthetically by the reaction of cholesterol with sulphur. The results indicated striking similarities between natural and synthetic asphaltenes. Reduction of these asphaltenes with lithium aluminium hydride provided experimental evidence that asphaltenes could be formed in nature by the reaction of similar molecules, either of biological origin or already present in petroleum, with sulphur at moderate temperatures.

Yen et al. (1977) have employed IR and proton NMR spectroscopy for the structural investigation of three shale oil asphaltene samples. A number of similar well defined bands were found in the IR spectra of all of these samples. A broad absorption band at 3220 cm^{-1} was attributed to hydrogen bonded OH and NH groups. The proton NMR spectra of shale oil asphaltenes were similar to those of petroleum asphaltenes and coal-derived asphaltenes.

Koots and Speight (1975) have compared a number of asphaltenes and resin samples in terms of chemical and structural analysis by NMR spectroscopy and other analytical techniques. They claimed that resins associate with asphaltenes in the manner of an electron donor-acceptor system and that there could well be several points of structural similarities between asphaltenes and resins.

Qian et al. (1984) have proposed a method combining proton NMR and relative IR spectroscopic data to evaluate the molecular structure of heavy petroleum feed stocks. By comparing proton NMR/IR, ^{13}C coupled proton NMR and Brown-Ladner procedures, it was shown that the most precise analytical procedure is ^{13}C coupled proton NMR analysis. Brown-Ladner procedure, which is used to calculate the aromaticity index, substitution index and condensation index, was found to be suitable for the structural analysis of feed stocks containing long straight-chain alkyl substituents and low aromaticity.

Recently Cyr and Selucky (1985) have suggested a new technique to study asphaltene structural parameters with dipolar dephasing NMR spectroscopy. The apparent carbon aromaticities of asphaltenes measured by NMR spectroscopy in solution were compared with those obtained by cross polarization magic angle spinning (CP/MAS).

From proton NMR solution spectra and ^{13}C solid NMR spectra of asphaltenes some skeletal features were also suggested. Such information was not obtainable by solution spectra alone. More recently Cyr and co-workers (Cyr et al., 1987) have conducted a ^{13}C NMR study of asphaltenes and their gel permeation chromatography (GPC) fractions. It was shown that Athabasca asphaltenes consist largely of long alkyl chains and some methyl branches attached to aromatic and naphthenic cores. Among the GPC fractions the longest chains were found in the highest molecular weight fractions. Also these fractions contained the highest proportions of naphthenic carbons.

Suzuki et al. (1982) have investigated the chemical structure of tar-sand bitumens and their fractions, including asphaltenes, by ^{13}C and proton NMR spectroscopic methods. The most probable average structural parameters were calculated without making any assumptions. The average structural parameters for asphaltenes of both the original bitumen and the vacuum residue were the same except for the difference in molecular weight. The vacuum residues of tar-sand bitumens contained relatively longer paraffinic straight-chains than the original bitumens.

Bouquet and Bailleul (1986) have proposed a routine method for the quantitative estimation of the structural hydrocarbon pattern in petroleum fractions, including asphaltenes. Measurements for hydrocarbon group distribution were taken with the aid of an improved combination matrix: inverse gated decoupling and gated spin-echo ^{13}C NMR experiments. Emphasis was placed on the experimental and practical running of the method and its convenience for routine industrial research experiments.

2.8 Mass Spectrometry and Combined Gas Chromatography/Mass Spectrometry

Gas chromatography/Mass spectrometry (GC/MS) is a very effective analytical technique for obtaining information about the structure, molecular weight profile and hydrocarbon group types of complex organic mixtures. In the 1960s, high resolution mass spectrometry was introduced for the group type analysis of petroleum fractions. New rapid scan techniques coupled with high resolution gas chromatography have, so far, greatly surpassed any other method or a combination of methods for the analysis of complex organic mixtures. During recent years, this technique has been applied for group type and z-number analysis of fossil materials such as coal and asphaltenes and their GPC fractions.

Aczel et al. (1979) have used low resolution and high resolution mass spectrometry, along with other analytical techniques, for the structural investigation of asphaltenes from coal liquids. More than 1200 individual components were identified as carbon number homologues. Excellent agreement was observed between composites calculated from the detailed MS data and the average structural parameters determined by IR, NMR and elemental analysis. The results indicated that coal asphaltenes are extremely complex mixtures of hydrocarbons and heterocyclic compounds with an average molecular weight of 500-800. Basic structural units were found to contain two to eight ring condensed aromatic hydrocarbons, associated with one to three functional groups. Average aromatic ring condensation ranged from four to five.

Scheppele et al. (1979) have separated coal-derived asphaltenes into fractions containing acids, bases and neutral compounds by ion-exchange chromatography, and the fractions were subjected to high resolution GC/MS. The results indicated that the asphaltenes contain higher molecular weight homologues and different compound types compared to the corresponding oils. However, compound types with equivalent molecular formulae, and hence presumably similar structure were observed in both the asphaltenes and oils. The results suggested that a number of physical/chemical phenomena such as coprecipitation, molecular inclusion and intermolecular electronic interactions are involved in the solvent extraction of asphaltenes.

Dooley et al. (1978) have illustrated that low/high resolution mass spectrometry is a very effective method for establishing the various hydrocarbon types present in GPC fractions of synthetic crude oil. Sixty pure compounds were subjected to GPC separation to establish a relationship between pure compounds and/or mixtures, elution volume and molecular structure. The correlations provided a basis for direct application of the GPC column for both separation and characterization of petroleum polyaromatic concentrates. Heppner and Homes (1983) analyzed nitrogen rich concentrates from shale oil by high resolution mass spectrometry. The results obtained by this method were similar to those obtained from titrimetric measurements on the samples except for the fractions where the pyrroles and arylamine compound types were concentrated.

Speight and Pancirov (1983) have developed a method for the analysis of asphaltene pyrolysis products by GC/MS. The technique offers an attractive on line method for the study of structural types in asphaltenes. The concept of deducing average structure of asphaltenes has been discussed. Several saturates, mono- and polycyclic aromatic compounds were identified in Athabasca asphaltenes.

Gallegos (1978) has reported a detailed structural investigation of several coal samples by GC/MS. Several compound types such as alkanes, alkylbenzenes, phenols, sesquiterpanes and pentacyclic triterpanes were found in coal with a tendency for a decrease in their concentration with the maturity of the coal. In contrast, naphthalenes, phenanthrenes, anthracenes, fluorenes and polyaromatics were found to increase in concentration with the maturity of the coal. The practical ability of the GC/MS data system to provide qualitative and quantitative information on a complex material such as coal was demonstrated. In another GC/MS study Gallegos (1981) analysed several coal samples for alkylbenzenes. Seven homologous series of alkylbenzenes ranging in carbon numbers from C_{10} to C_{35} were tentatively identified in Tertiary, Cretaceous and Carboniferous coals.

Ritchie et al. (1979) have also employed GC/MS for the analysis of pyrolysis oils from Athabasca tar-sand asphaltenes. Straight chain alkanes up to C_{34} were identified in the pyrolysates and were thought to reflect the presence of such chains in the original asphaltenes. The range of aromatic hydrocarbons present included benzene, toluene and xylenes. Sulphur was found to be widely distributed in the fractions studied, principally in the form of thiophenes and condensed thiophene types. Savage et al. (1985) also used GC/MS for the analysis of the pyrolysis oils from petroleum asphaltenes. The study furnished information on the quantitative variation of product yield with both time and temperature, which provided an insight into the asphaltene structure. The temporal variation of products also allowed discernment of primary and secondary reaction pathways. The results suggested that catalyst deactivation during the hydroprocessing of heavy oils can be partially attributed to the precipitation and deposition of asphaltenes and their aromatic core.

Pelet et al. (1985) have investigated the origin of asphaltenes by comparing the GC/MS analysis of several asphaltene samples from crude oils and source rocks. The asphaltene samples were pyrolysed at 550°C and the products were analyzed for hydrocarbon types by GC/MS. It was concluded that the asphaltenes and source rocks are geochemically equivalent to a large extent. Borwitzky and Schomburg (1979) developed a method for the qualitative analysis of coal tar using capillary GC combined with mass spectrometry. Based on a comparison of retention times of model nitrogen compounds, over 140 compounds were identified.

Yoshida et al. (1981) have employed field ionization and field desorption mass spectrometry for the analysis of GPC fractions of coal-derived liquids. The molecular weight profiles obtained for the fractions and the average molecular weights calculated were close to those obtained by VPO measurements.

3. EXPERIMENTAL

3.1 Materials

3.1.1 Crude Oils

Arabian Heavy (AH) and Arabian Light (AL) crude oils were obtained from the Arabian American Oil Company, Dhahran and were stored at -10°C prior to analysis. Arabian Heavy (AH) is a medium gravity paraffinic crude oil comprised of oil produced from the Safaniyah offshore oil field, which is located at about 200 kilometres northwest of Ras Tanura, the oil exporting terminal of Saudi Arabia on the Arabian Gulf coast. The Safaniyah oil field, discovered in 1957, is considered to be the largest offshore oil field in the world. AH crude oil is produced from Cretaceous sandstone reservoirs. Arabian Light (AL), a moderately high gravity paraffinic crude oil, is produced from Ghawar trend and Abqaiq oil fields, which are major oil fields of the Upper Jurassic Arab Zone reservoirs. Ghawar trend is one of the largest oil fields in the world. It is about 200 kilometres long and has six culminations: Ain Dar, Uthmaniyah, Hawiyah, Haradh, Shedgum and Ghawar. The AL crude oil accounts for over 65% of the total oil production of Saudi Arabia.

3.1.2 Reagents

Normal alkane solvents, viz. pentane, hexane, heptane, octane, nonane and decane, used for the precipitation of asphaltenes were of reagent grade, obtained from Fisher Scientific. These solvents were used without further purification.

Benzil used for the calibration of the vapour pressure osmometer (VPO) was of high purity grade (> 98%), obtained from BDH Chemicals. Toluene, chloroform, carbon tetrachloride, chlorobenzene and pyridine, used for the determination of the molecular weights of asphaltenes by the vapour pressure osmometer method, were spectroscopic grade solvents, also obtained from BDH Chemicals.

Acetanilide, benzoic acid and dibenzyl disulphide, used as standards for elemental analysis, were organic analytical standard (OAS) grade chemicals from BDH Chemicals.

Alumina, used as reference material for the thermal gravimetric analysis of asphaltenes, was of high purity grade (Al_2O_3 > 99%), obtained from BDH Chemicals.

The standard gas mixture used for the identification and quantification of the gases evolved during the pyrolysis of asphaltenes was supplied by ECM Special Gases, England.

The model nitrogen compounds used in the nonaqueous potentiometric titrations were obtained from Fluka AG and their purities were 99% or better. Chlorobenzene, acetic anhydride, dioxane, perchloric acid, pyridine and other solvents were of analytical grade from BDH Chemicals. Potassium hydrogen phthalate and benzoic acid were organic analytical standard (OAS) grade chemicals from BDH Chemicals.

3.2 Determination of Crude Oil Properties

Crude oil is made up of many different individual chemical substances including gases, liquids and solids ranging from methane to asphalt. Although most of the constituents of crude oil are hydrocarbons, there are significant amounts of compounds containing sulphur, oxygen and nitrogen. The individual members of a crude oil which form an uninterrupted chain of compounds differ only a little from one another in their properties, and their physical data actually overlap at times.

There is no overall and generally acceptable method for classifying crude oils. However, the ultimate methods of analysis used for their principal elements, viz. carbon, hydrogen, sulphur, oxygen and nitrogen and the chemical composition of the paraffin, naphthene and aromatic types of compounds present are used as an index of the usefulness of a crude oil and the suitable conditions for its refining. Based on such analysis, the crude oils are divided into four broad types: (i) paraffin-base, (ii) mixed-base, (iii) naphthene-base and (iv) aromatic-base.

However, these analyses furnish little information about the quality and quantity of different products which can be obtained from a crude oil and the data needed for the optimal refining conditions. Such information is obtained by crude oil assay and inspection which include true boiling point (TBP) distillation and determination of properties such as American Petroleum Institute (API) gravity, viscosity, pour point, sulphur, ash content, carbon residue and metal analysis.

True boiling point (TBP) distillation of crude oils is carried out under specified conditions of temperature, pressure and separation efficiency on a laboratory scale distillation column. The distillation, which is carried out first at atmospheric pressure and then at reduced pressure, provides a relationship between the total percent distilled and the corresponding temperature at the top of the fractionating column. American Petroleum Institute (API) gravity is a factor which governs the quality of crude oil. The price of crude oil is fixed on the basis of API gravity. Carbon residue gives an indication of the composition and the presence of heavy asphaltic components in a crude oil. Viscosity and pour point are the most important physical parameters of a crude oil as far as production and transportation are concerned. The viscosity of a crude oil is influenced by the abundance of resins and asphaltenes. Sulphur, the third most abundant atomic constituent of crude oils after carbon and hydrogen, is an index of sulphur levels in the products of a crude oil. Metals such as nickel and vanadium are undesirable in crude petroleum because they cause corrosion and catalyst poisoning problems.

Table 3.1 shows the tests and test methods used in the present work for the determination of the general properties of crude oils. All tests were performed in accordance with the Institute of Petroleum (IP) and the American Society for Testing and Material (ASTM) procedures. The metals were determined by atomic absorption spectrophotometry.

TEST	TEST METHOD	
	IP	ASTM
1. API gravity	-	ASTM D-287 (ASTM, 1988a)
2. Pour point	IP-15/(IP,1984b)	ASTM D-97 (ASTM, 1988a)
3. Viscosity, kinematic	IP-71/(IP,1984b)	ASTM D-445 (ASTM 1988a)
4. Carbon residue	IP-13/(IP,1984b)	ASTM D-189 (ASTM, 1988a)
5. Sulphur	IP-61/(IP,1984b)	ASTM D-129 (ASTM, 1988a)
6. Ash content	IP-4/(IP,1984b)	ASTM D-482 (ASTM, 1988a)
7. Distillation	-	ASTM D-2892 (ASTM, 1988b)
8. Nitrogen	CHN Analysis	
9. Iron	Atomic absorption spectrophotometry	
10. Nickel	Atomic absorption spectrophotometry	
11. Vanadium	Atomic absorption spectrophotometry	

Table 3.1 : Tests and test methods used for the general properties of crude oils and the residua.

3.3 Preparation of 370°C+ Residue

3.3.1 True Boiling Point Distillation

3.3.1.1 Introduction

True boiling point distillation is a common procedure for the distillation of stabilized crude petroleum. This method offers a compromise between efficiency and time in order to facilitate the distillation of crude petroleum on the laboratory scale. First, the distillation is carried out at atmospheric pressure and then the pressure is reduced in stages to allow the high boiling components to be distilled at temperatures low enough to avoid thermal degradation. A curve showing the relationship between the weight percent distilled and the corresponding temperature is called the TBP Distillation Curve.

3.3.1.2 Instrumentation

The apparatus used for the true boiling point distillation of the crude oil was an all-glass semi-cal series 3650 TBP apparatus made by Podbielniak Inc., Illinois, U.S.A., and the method adopted was ASTM D-2892 (ASTM, 1988b). Figure 3.1 illustrates the true boiling point distillation apparatus. The apparatus consists of a charge flask of 5.0 litre capacity which is provided with two side arms. One side arm is a thermowell provided with a sensor for measuring the temperature of the boiling liquid. The second side arm is equipped with a stopcock for connection to one side of a manometer or pressure transducer to be used for pressure drop control. The flask is covered with two heating mantles to provide steady full boil up at all pressure levels and it is connected to a fractionating column. The

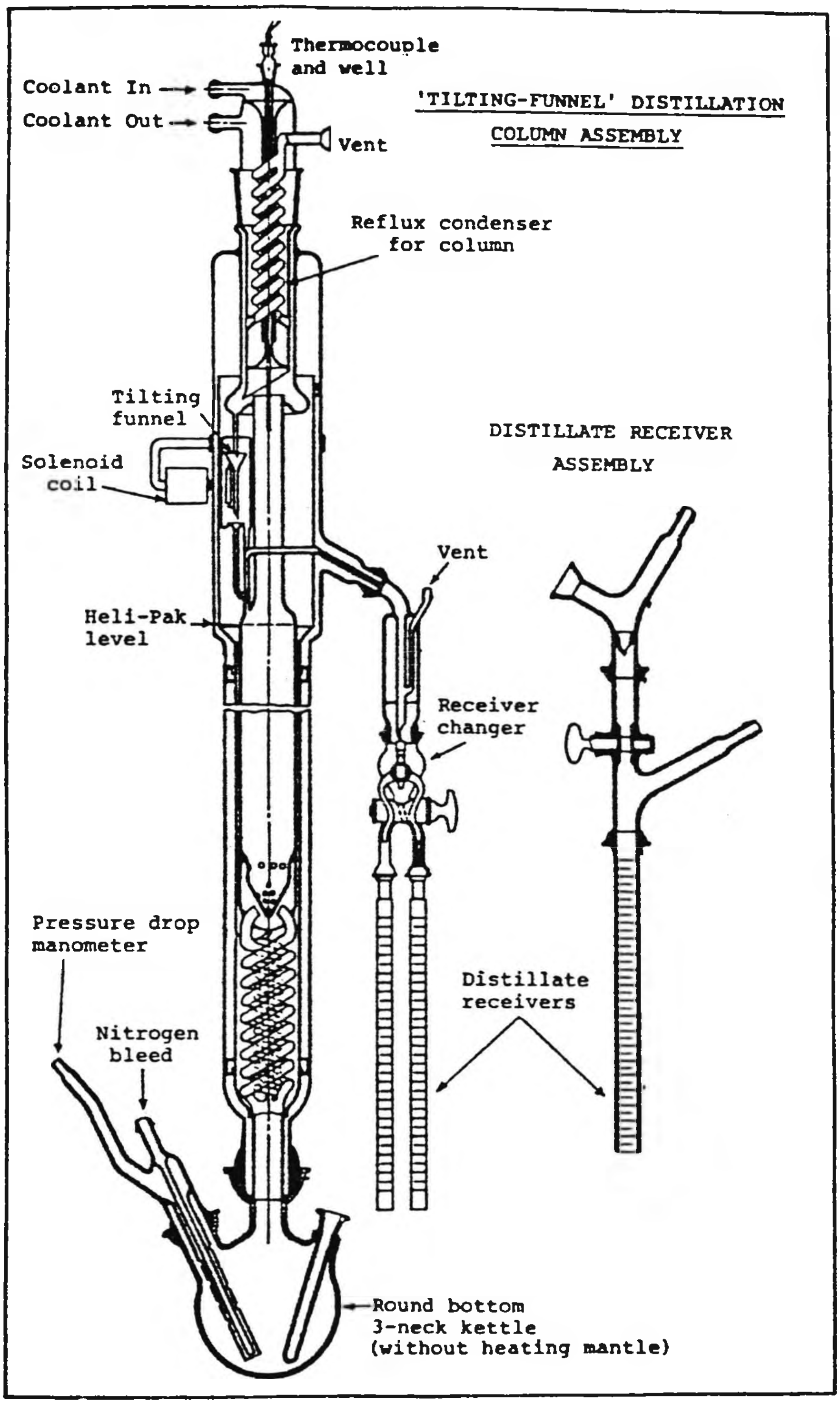

Figure 3.1 : True boiling point distillation apparatus.

fractionating column is 1.0 metre long with an internal diameter of 25.4 mm and it is packed with Nichrome Heli-Pak 2917 (2.5 x 2.5 x 1.3 mm) packing. The fractionating column has an efficiency of 15 theoretical plates and it contains an adjustable reflux divider capable of dividing the condensate. The column also contains a condenser, cold trap and gas collector. Graduated cylinders are attached to the column to receive the distillate. A vacuum pump is used to reduce the pressure of the system below atmospheric pressure.

3.3.1.3 Procedure

A 3.0 litre sample of the crude oil was charged to the kettle and the kettle was connected to the fractionating column. For atmospheric pressure distillation the kettle was heated at a suitable rate and the distillates were collected at a reflux ratio of 5:1. The distillation was continued until a vapour temperature of 200°C was reached. At that point, the distillation was halted and the kettle was cooled slightly. The pressure of the system was reduced to 5.32 kPa and the distillation was continued to 300°C. Then the pressure was reduced to 1.32 kPa to remove distillate boiling up to 320°C. Nitrogen gas was allowed to bubble through the oil to facilitate boiling and to remove the traces of oxygen present in the oil.

3.3.2 Wiped Film Molecular Distillation

3.3.2.1 Introduction

TBP distillation was not used to distil the crude oil beyond 320°C to prevent thermal cracking of the oil, which would occur due to prolonged heating of the oil in the TBP apparatus at higher temperature. Further distillation to obtain the 370°C+ residue was done on a wiped film molecular still. This technique allows the oil to stay in the heated zone for a very short period of time. The pressure of the still can be reduced low enough to allow the volatile components to leave the hot surface and condense on a nearby cold surface. This technique is widely used for high temperature distillations (Coleman et al., 1973).

3.3.2.2 Instrumentation

Figure 3.2 illustrates the wiped film molecular still. It is an all-glass apparatus consisting of a feed and degassing flask at the top of the apparatus, which is connected to the main body of the still (evaporator) through a narrow tube provided with a valve which is used to control the flow of the feed to the evaporator. The evaporator consists of a set of three carbon wipers placed on a vertical axis and connected to a drive unit which rotates these wipers at a constant speed. The evaporator is provided with two receiving flasks at the bottom, one for the distillate and the other for the residue. A high efficiency vacuum system consisting of a rotary pump and a diffusion pump is used to reduce the pressure of the system.

3.3.2.3 Procedure

All the joints were greased with a low vapour pressure grease and the apparatus was assembled as shown in Figure 3.2. 1.0 litre of the 320°C+ residue prepared on the TBP apparatus was charged to the feed and degassing flask. The evaporator and the feed and

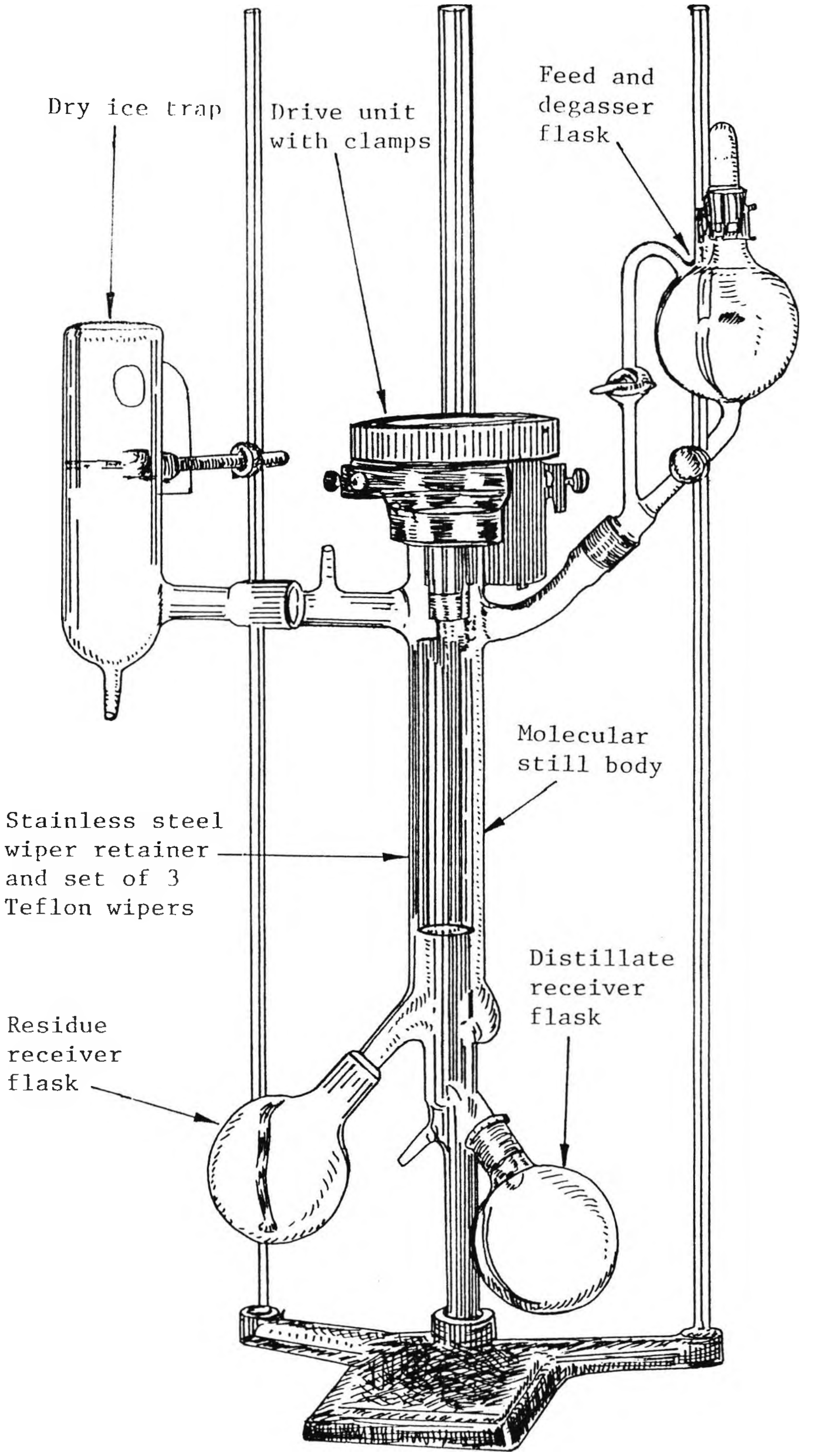

Figure 3.2 : Wiped wall molecular still

degassing flask were covered with heating mantles from all sides to achieve uniform and constant heating. A thermocouple was provided between the heating mantle and the evaporator to record the temperature of the evaporator. The vacuum pumps were started to reduce the pressure of the system. Heating of the feed and degassing flask was also started and the system was left at low pressure to degas the feed. After obtaining a constant pressure ($\approx 2.7 \times 10^{-2}$ kPa), the temperature of the evaporator was raised to 150°C, which is the temperature corresponding to 370°C at atmospheric pressure.* At this point, the drive mechanism for the wipers was started, the degassing valve was closed and the oil was allowed to flow slowly through the evaporator by opening the valve on the feed and degassing flask. The wipers spread the oil as a thin film on the hot walls of the evaporator. The portion of the oil which was volatile at 150°C, the evaporator temperature corresponding to 370°C at atmospheric pressure, vaporized and condensed on the inner cold surface of the condenser and was collected in one of the receiving flasks as distillate. The 370°C+ residue left on the walls of the evaporator was wiped downward and was collected in the other flask. The distillation was continued until all the oil charged into the feed and degassing flask had passed through the evaporator column. The 370°C+ residua obtained from the two crude oils, were also tested for properties like API gravity, pour point, viscosity, sulphur, carbon residue, ash content

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* UOP Method 56-77 (UOP Laboratory Test Methods for Petroleum and its Products, 1984, Illinois: UOP) was used to convert 150°C recorded at 0.2 mm Hg ($\approx 2.7\text{x}10^{-2}$ kPa) to the corresponding temperature of 370°C at atmospheric pressure.

and metals. The test methods used for these determinations are shown in Table 3.1.

3.4 Isolation of Asphaltenes

Asphaltenes were isolated from the AH 370°C+ residue by digesting 45 g of residue with 1350 ml (30 fold volume) of the alkane solvent (nC_5 – nC_{10}). The mixture was stirred for 90 minutes at 1500 rpm and then it was allowed to stand for 16 hours. It was then transferred into 100 ml centrifuge tubes and centrifuged for 60 minutes at 1600 rpm. The supernatant liquids (maltenes) were decanted, and the mixture was recentrifuged with fresh volumes of the alkane solvent to wash the asphaltenes. Asphaltenes were collected from the bottom of the centrifuge tubes and were purified by extraction for 24 hours with the respective alkane solvent on a Soxhlet extractor at ambient temperature, followed by drying in a vacuum oven at 50°C and 2.5 kPa pressure. The same procedure was used to precipitate asphaltenes from AL 370°C+ residue by the use of normal pentane as solvent (Jacobs and Filby, 1983).

Asphaltenes were also precipitated from Arab Heavy crude oil by the use of different solvent-to-oil ratios. Twenty, forty and sixty fold volumes of normal heptane solvent were added directly to the crude oil and the rest of the procedure followed was the same as that described above. In one of the experiments, the heptane precipitated asphaltenes were purified by dissolving them in toluene followed by reprecipitation with normal heptane (Speight, 1984a).

3.5 Elemental Analysis

Elemental analyses of asphaltene samples were done on an Elemental Analyzer model 1106 from Carlo Erba. The technique for CHN analysis is based on a modification of the classical Pregl and Dumas method. The sample (0.5 to 1.5 mg), held in a light weight tin container, was dropped into a vertical quartz tube maintained at 1030°C, through which a constant flow of helium was run. When the sample was introduced, the helium flow was temporarily enriched with pure oxygen. Flash combustion took place due to the oxidation of the container. Quantitative combustion was achieved by passing the mixture of gases over Cr_2O_3. The mixture of combustion gases was then passed over copper at 650°C to remove the excess of oxygen and reduce oxides of nitrogen. It was then passed through a chromatographic column of Porapak-QS heated to approximately 100°C. The individual components were separated and eluted as N_2,CO_2 and H_2O. These components were measured by a thermal conductivity detector. The instrument was calibrated by the use of standard compounds. For the determination of sulphur, the quartz tube was maintained at 1010°C. Quantitative conversion of sulphur to SO_2 was achieved by passing the gases over WO_3. After the elimination of oxygen by passing the gases through a heated reduction tube containing copper, the mixture entered a chromatographic column at 80°C.

3.6 Determination of Molecular Weights

3.6.1 Instrumentation

The apparatus used for the determination of the molecular weights of asphaltenes was a Knauer vapour pressure osmometer model 11.00. The apparatus consists of two matched thermistors in a vapour saturated cell. The cell temperature is electronically thermostatted at a very high temperature stability. Temperature equilibrium is achieved between the two thermistors, from each of which a solvent drop hangs. When one of the solvent drops is replaced by a drop of the sample solution, solvent vapours condense on the thermistor surface as a result of the lower solvent vapour pressure. The heat resulting from condensation enthalpy raises the temperature of the solution drop. The resulting temperature difference between the two thermistors, which is proportional to the osmolal concentration of the sample solution, is converted to an electrical output signal by incorporation of the thermistors into a Wheatstone bridge arrangement and the value of the signal is recorded on a digital meter.

3.6.2 Procedure

First, the apparatus was calibrated by the use of a series of solutions of benzil in toluene of known molality. By dividing the value recorded on the digital meter by the molal concentration of the standard solution, a value was obtained which represented the calibration constant for the particular solvent-solute system, the sensitivity setting of the apparatus and the temperature. Asphaltene solutions were also prepared in toluene in the concentration range of

20-80 g/kg and were run in essentially the same manner as the calibration solutions. The data obtained for sample solutions were also divided by the concentration to obtain the measurement constant. The ratio of calibration constant and measurement constant gave the molecular weight. Since the solution systems do not behave ideally at increasing concentrations, at least four concentration levels were used both for calibration and sample measurements, and the data obtained for different solutions were plotted against the concentration. These curves were extrapolated to zero concentration to eliminate the non-ideal behaviour of solute-solvent system (ASTM D-3592-77, 1987a).

VPO molecular weights of asphaltenes were also determined in solvents of different dielectric constant, viz. carbon tetrachloride, chloroform, chlorobenzene and pyridine, by preparing both standard and asphaltene solutions in the same solvent. The VPO determinations were made at 40, 60 and 80°C (Moschopedis et al., 1976c).

3.7 Thermal Analysis

3.7.1 Introduction

Thermal analysis is a group of techniques in which physical properties of a substance are measured as a function of temperature while the substance is subjected to a controlled temperature programme. Characteristic parameters of a physical or chemical nature which change under thermal treatment are measured and recorded together with temperature. In this way additional information on the thermal behaviour of the material is obtained and conclusions as to its composition and predictions about its characteristics become possible. In thermogravimetric analysis (TGA), the change in the mass of a substance is measured as a function of temperature. The differential thermal analysis (DTA) technique is a means of measuring the amount of heat evolved or absorbed and the temperature at which these changes take place within the material. In this technique, the temperature difference between a substance and reference material is measured as a function of temperature. In addition to the traditional thermogravimetric analysis and differential thermal analysis, this field now includes evolved gas detection and analysis, emanation thermal analysis, thermoparticulate analysis and thermoelectrometric analysis (ASTM E-473-80, 1987b).

3.7.2 Instrumentation

The equipment used for the thermal analysis of asphaltenes was a Simultaneous Thermal Analyzer model STA-429, manufactured by Netzsch, West Germany, which performs thermogravimetry and differential thermal analysis simultaneously. Figures 3.3 and 3.4 illustrate the functional details of the Thermal Analyzer for thermogravimetry and differential thermal analysis, respectively. The cabinet of the measuring unit houses a microanalytical balance with electromagnetic compensation. The temperature of the sample is measured by thermocouples of platinum and platinum plus 10% rhodium. The furnace temperature is programmed and controlled by a microprocessor temperature control system. The parameters such as temperature, change in weight, derivative of change in weight and difference in temperature between sample and reference are recorded simultaneously. The

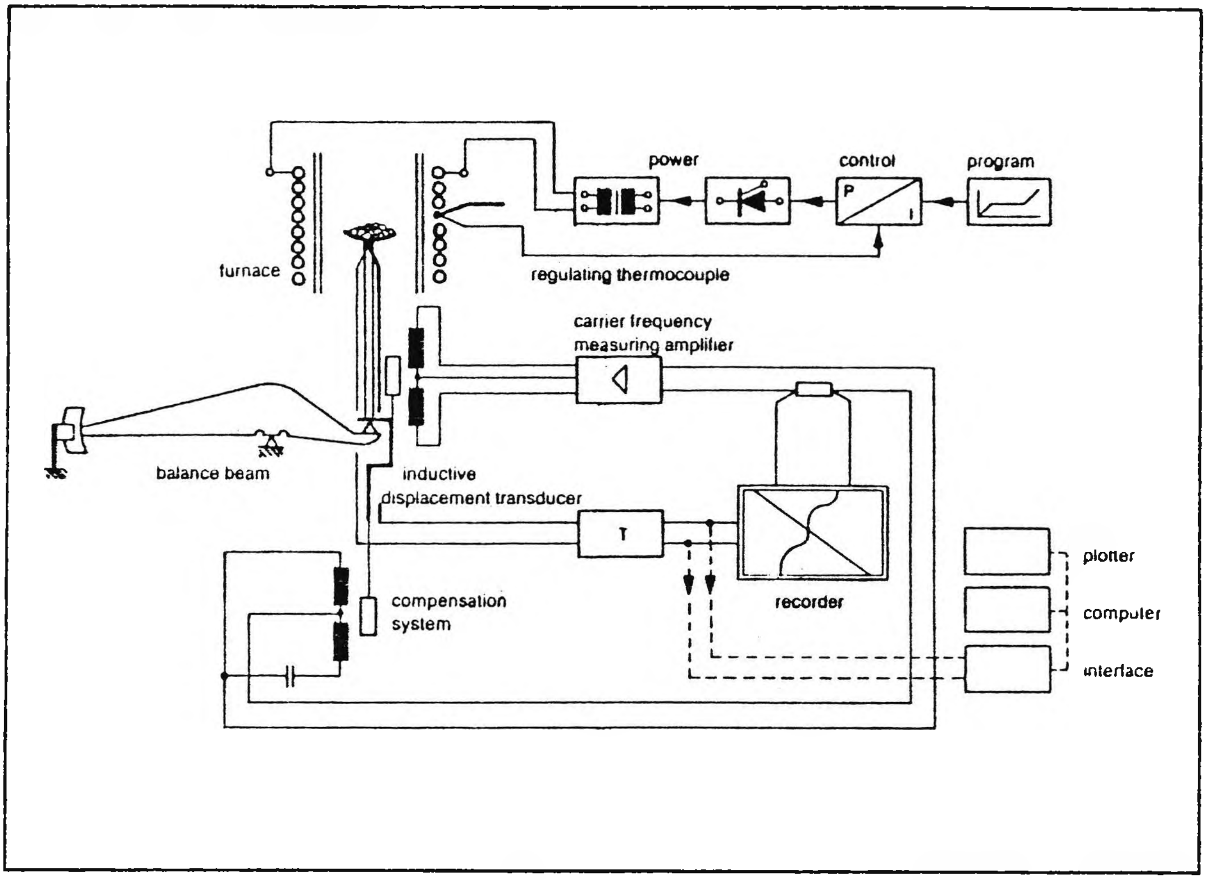

Fig 3.3 Block diagram for thermogravimetric analysis.

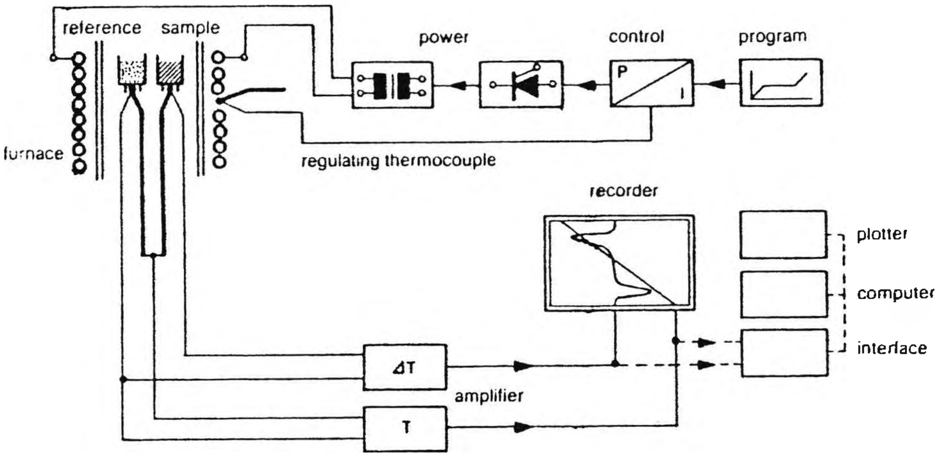

Fig 3.4 Block diagram for differential thermal analysis.

equipment consists of two main sections for measurement and control. A microprocessor controlled data acquisition system is used to couple the recording and control cabinets to a computer system (ASTM E-472-79, 1987c).

3.7.3 Procedure

The asphaltenes sample (≈50 mg) ground to 125 mesh size was placed in an alumina crucible. The same weight of aluminium oxide, which undergoes no thermal change in the temperature range of the experiment, was placed in an identical alumina crucible as a reference sample. By the use of a sample carrier system, which has two sets of thermocouples, the sample was placed in the middle of the vertical furnace. The temperature was raised at a uniform rate of 20^0C/min. The analyses were made over the temperature range of 25-920^0C in a dynamic atmosphere of nitrogen flowing at a rate of 40 ml/min. In the thermogram, the weight loss, the differential temperature and the temperature of the sample were plotted simultaneously. The endothermic peaks are shown downward and the exothermic peaks are shown upward with respect to the base line.

3.8 Pyrolysis Gas Chromatography

3.8.1 Instrumentation

The pyrolysis apparatus consisted of a 20 mm O.D. quartz tube of 450 mm length horizontally aligned in a tubular furnace of 280 mm length. The non-condensible gases collected during pyrolysis were analyzed on a Hewlett-Packard model HP 5880 gas chromatograph equipped with two columns: one 91 cm x 3.2 mm O.D. stainless steel, packed with Molecular Sieve 13X, 45/60 mesh and the other 305 cm x 3.2 mm O.D. stainless steel packed with Porapak-N, 80/100 mesh. (Ritchie et al., 1979).

3.8.2 Procedure

Pyrolysis of asphaltenes was carried out at 350°C and 520°C. The apparatus was flushed with nitrogen before the furnace was heated to the desired temperature. A weighed amount of asphaltene sample (≈300mg) contained in a 10 cm long quartz boat was inserted into the hot zone by moving the section of the quartz tube containing the sample boat into the hot zone. Pyrolysis was continued for two hours at 350°C and one hour at 520°C. Condensible products of pyrolysis were trapped using a liquid cooling bath maintained at -10°C. The pyrolysis residue and the sample boat were extracted with the respective alkane solvent to determine the yield of unreacted asphaltenes. The unreacted asphaltenes were further extracted with benzene to determine the quantity of coke formed. The non-condensible gases collected at the end of the cold trap were injected into the gas chromatograph. The column oven of the gas chromatograph was programmed between 35°C and 175°C, increasing at the rate of 15°C/minute, after an initial hold-up time of 6 minutes. Argon was used as the carrier gas in conjunction with thermal conductivity and flame ionization detectors. Component gases were identified and quantified by comparison of retention times with those for a standard gas mixture (Moschopedis et al., 1978; Savage et al., 1985).

3.9 Nonaqueous Potentiometric Titrations of Asphaltenes

It is assumed that basic functional groups in asphaltenes and related materials are due to the presence of nitrogen and acidic functional groups are due to the presence of oxygen. Nonaqueous potentiometric titration allows for the differentiation of acids and bases as well as the estimation of very weak acids or bases. In the present work, differential nonaqueous potentiometric titration has been used for the estimation of various basic functionalities present in the asphaltenes isolated from Saudi Arabian crude oils by a careful comparison with model compounds. Due to the complex nature of asphaltenes , the end points were usually diffuse. Therefore, the basicities of asphaltenes were classified into distinct pK_a ranges by the addition of known bases of established pK_a values and determination of the bases that titrate along with them.

3.9.1 Instrumentation

All titrations were carried out with a semiautomatic Metrohm Potentiograph (E-576) in conjunction with an automatic titrant feeding unit Metrohm Dosimat model E-575. The electrode system consisted of a glass indicating electrode and a calomel reference electrode. The filling solution of the calomel electrode was a saturated solution of lithium chloride in acetic acid. The titrations were followed potentiometrically and the results were recorded to obtain the end points or half neutralization potentials (HNP).

3.9.2 Titration Procedures

3.9.2.1 Basic Functionalities

After examining a variety of solvents for solubility and titration characteristics for the model compounds and the asphaltene samples, a mixture containing chlorobenzene and acetic anhydride in the volume ratio of 9 to 1 was chosen as the titration medium for basic functionalities. The use of acetic anhydride as a titration medium in conjunction with another solvent has been noted by Gremillion (1955). The titrant used was 0.05M perchloric acid, prepared by diluting the required amount of 72% perchloric acid with dioxane. Potassium hydrogen phthalate in acetic acid was used as the primary standard for the standardization of the titrant.

The amounts of solid model basic compounds ranged from 20 to 40 mg. The liquid model compounds were added to the titration solvent by the use of 20 lamda disposable micro pipettes. The tips of the pipettes were placed beneath the surface of the solvent to prevent evaporation of the compound being added. The sample sizes for the asphaltenes were in the range of 50 to 70 mg.

3.10 Fourier Transform Infrared Spectroscopy of Asphaltenes

3.10.1 Introduction

Fourier transform infrared (FT-IR) spectroscopy offers potential advantages compared with conventional dispersion infrared spectroscopy, namely, (a) a higher signal-to-noise ratio for spectra obtained under conditions of equal measurement time and (b) a higher accuracy in frequency for spectra taken over a wide range of frequencies. The improved signal-to-noise ratio is achievable as a consequence of the larger throughput of the interferometer relative to that of a grating spectrometer.

An FT-IR spectrometer consists basically of two parts: (i) an optical system which uses an interferogram and (ii) a dedicated computer which controls optical components, collects and stores data, performs computations on data and displays spectra. FT-IR spectrometers differ in the design of their interferometers and the manner in which they are operated. They may be operated either by scanning in a discontinuous, step-wise manner, a slow continuous manner with chopping of the IR beam or rapidly without chopping of the IR beam.

3.10.2 Instrumentation and Procedure

Infrared spectra of the asphaltenes were recorded on a Perkin Elmer high resolution rapid scanning Fourier transform infrared spectrometer model 1760. The spectrometer was equipped with a Perkin Elmer model 1700 Michelson interferometer and a computer model 7700. The interferogram was aligned automatically and the optical system of the instrument contained a multicoated potassium bromide beam splitter. The wave number range of the instrument was 7200 cm^{-1} to 370 cm^{-1} with 0.5 cm^{-1} to 64 cm^{-1} resolution.

In a rapid scanning FT-IR spectrometer, the light beam from an infrared source is collimated and sent to the beam splitter of a Michelson interferometer. The beam is divided, part going to the moving mirror, and part going to the fixed mirror. The return beams combine at the beam splitter undergoing interference. The reconstructed beam is then directed through the sample and focussed on to the detector. The motion of the mirror results in a signal on the detector which varies with wavelength. A laser beam undergoing the same change of optical path as the infrared beam serves to reference the position of the mirror during the scan and indicates the collection of data points from the signal of the infrared detector at uniform intervals of mirror travel. The data points are digitized and are recorded as an interferogram.

Infrared spectra of the asphaltenes were recorded using potassium bromide pressed discs. A 15-20 mg portion of the finely-ground asphaltene was added to a known amount (approximately 300 mg) of high purity potassium bromide. Mixing was effected by thorough grinding in a smooth agate mortar. The mixture was pressed in a special die under a pressure of 10,000 pounds per square inch into a transparent pellet of 1.5 mm thickness and 13 mm diameter. The pellets were dried for 24 hours in a vacuum desiccator before recording the spectra. A total of 50 scans (interferograms) of nominal resolution of 4 cm^{-1} were recorded in the wavenumber range 4000-400 cm^{-1}, from which a reference spectrum of potassium bromide was subtracted to yield the sample spectrum.

3.11 Nuclear Magnetic Resonance Spectroscopy of Asphaltenes

3.11.1 Introduction

The use of nuclear magnetic resonance (NMR) spectroscopy for structural investigations in the petroleum industry was reviewed as early as 1955 (Williams, 1955); however, the actual NMR spectra were not reported until 1957 (Williams, 1957; Zimmerman and Lasater, 1957). The heavy fractions of petroleum such as asphaltene are inherently complex and contain many aliphatic, aromatic and heteroatom moieties. Various structural parameters of such materials like percentages of aliphatic carbons, aromatic carbons, and methyl carbons, numbers of aromatic and naphthenic rings, paraffinic chain length, etc., can be obtained by the use of multinuclear NMR spectroscopy.

Before the introduction of ^{13}C NMR spectroscopy, complex hydrocarbon fractions of petroleum were often characterized in terms of average structural parameters derived mainly from proton NMR spectroscopy. However, to determine the nature of carbon backbones of the molecule, it was necessary to make several assumptions about the aliphatic groups present. The recent routine availability of ^{13}C NMR spectrometers has made it possible to obtain information directly about the average carbon skeletons of the molecules present in a hydrocarbon mixture. As in other fields, the use of NMR spectroscopy in the analysis of heavy fractions of petroleum has expanded considerably during the past decade with the introduction of improved instrumentation, enabling a wide range of pulsed Fourier transform methods to be applied to both liquid and solid fuels.

In the Fourier transform (FT) mode, the relation between the intensities obtained in the NMR spectrum and the number of nuclei at resonance is influenced by a number of factors such as (i) spin-lattice relaxation times compared to pulse repetition rates, (ii) non-linearity in the recording system, (iii) the effect of limited pulse strength and (iv) the nuclear Overhauser effect (NOE). The most serious problem comes from the slow pulse repetition rate required by the long relaxation time characterizing certain types of carbon nuclei such as quaternary carbons. In such cases, the analysis time could become prohibitive and it becomes necessary that the experimental conditions should be such that all carbon nuclei must have fully relaxed and returned to their equilibrium state before a repetitive pulse is applied. One of the most widely used methods for decreasing the relaxation time is the addition of a relaxation agent such as ferric acetylacetonate. The non-linearity of the measuring system can be eliminated by calibrating the response of the spectrometer with a known sample. The NOE effect, which arises via dipole-dipole interactions between different types of carbon nuclei, can be avoided by recording the spectra in the gated decoupling mode while still providing the spectral simplification afforded by decoupling. Rather than leaving the decoupling radio frequency source engaged continuously, it is switched (gated) for a minimum time necessary to achieve decoupling, i.e. only during the actual acquisition of the spectrum and not during any delay between successive acquisitions.

3.11.2 Instrumentation and Procedure

Proton and ^{13}C NMR spectra of asphaltenes were recorded on a Varian XL-200 high resolution pulsed Fourier transform nuclear magnetic resonance spectrometer, which has a computer controlled system with a high capacity hard disk storage unit. The acquired and processed data, as well as the programs are stored on dual disk cartridges with a storage capacity of 5 mega words. The spectra are displayed on a cathode ray tube for visual inspection and interaction, data manipulation and monitoring of the experiment in progress. The system contains a 47 kilogauss, wide-bore (50 mm) superconducting solenoid surrounded by a low-loss Dewar vessel containing liquid helium or nitrogen.

Solution state proton NMR spectra of the asphaltene samples were recorded at 200 MHz as concentrated solutions (20 mg asphaltene in 0.5 ml of d-chloroform) in 5 mm sample tubes. The experimental conditions used were as follows : spectral width, 2800 Hz; data points 15680; pulse width, 3.5 μs (45° pulse); pulse repetition time, 25 seconds and number of transients, 60. Tetramethylsilane (TMS) was used as an internal standard.

Proton decoupled ^{13}C NMR spectra were recorded in the pulsed Fourier transform mode at 50.3 MHz in 10 mm sample tubes. Solutions were prepared by dissolving 0.5 g of asphaltene in 2.5 ml of d-chloroform containing 15 mg of ferric acetylacetonate as a relaxation agent. Tetramethylsilane was used as an internal standard. The solvent, d-chloroform, also provided an internal deuterium lock signal. The nuclear Overhauser effect was suppressed by operating the spectrometer in the gated decoupling mode. The decoupling radio frequency source was switched on during the actual data acquisition time. The experimental conditions used were: spectral width, 10,000 Hz; data points, 24,000; pulse width, 12 μs (45° pulse); pulse delay, 10 seconds and number of transients, 5000.

4. RESULTS AND DISCUSSION

4.1 Properties of Crude Oils

The general properties of the Arabian Light (AL) and Arabian Heavy (AH) crude oils as recorded in the present work are shown in Table 4.1. Both of these oils with specific gravity >0.85 and sulphur content >1.0%, are aromatic intermediate types of crude oil. The resin and asphaltene contents of such crude oils amount to ca 10-30%. In Figure 4.1 a ternary diagram, taken from Tissot and Welte (1984b), is presented to demonstrate the composition of different classes of crude oils. A strong correlation between sulphur content and aromatics, resins and asphaltenes (Deroo et al., 1974) suggests that the amounts of resins and asphaltenes will be higher in the AH crude oil compared with the AL crude oil. Carbon residue, which is directly related to gravity and sulphur content, is also higher for the AH crude oil. This implies that coke-forming tendency will be higher in the AH crude oil compared with the AL crude oil. AH crude oil is also significantly higher in metal content than AL crude oil. This indicates that the AH crude oil will contain a higher concentration of organometallic compounds which are extremely difficult to remove from the feed stocks.

4.2 Properties of 370°C+ Residua

Table 4.2 presents the general properties of the 370°C+ residua obtained from the AH and AL crude oils. The residua make up sig-

TEST	ARABIAN LIGHT CRUDE OIL	ARABIAN HEAVY CRUDE OIL
1. Gravity, API	33.1	27.5
2. Gravity, specific @ 15.56/15.56°C	0.8597	0.8899
3. Total sulphur, wt%	1.81	2.82
4. Carbon residue, wt%	3.8	7.2
5. Viscosity, kinematic centistokes @ 37.8°C	7.0	27
6. Pour point, °C	-20	-28
7. Ash content, ppm	58	121
8. Nitrogen, wt %	0.11	0.17
9. Iron, ppm	0.9	1.1
10. Nickel, ppm	3.9	19.5
11. Vanadium, ppm	14	45
12. Distillation yield, wt % on crude oil		
100°C	8.2	7.0
200°C	24.3	18.9
300°C	42.1	33.6
370°C	54.0	44.7

Table 4.1 : General properties of Arabian Light and Arabian Heavy crude oils.

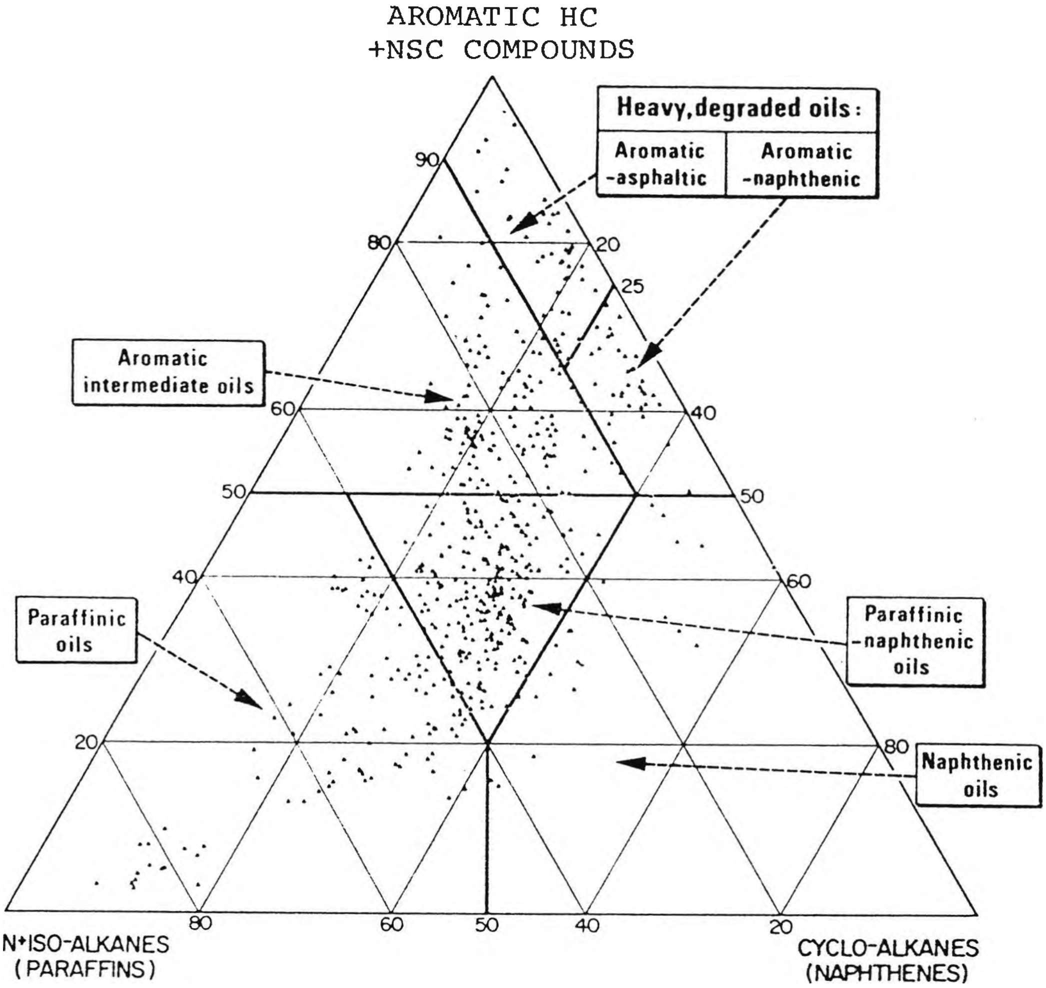

Fig 4.1 : Ternary diagram showing the composition of six classes of crude oils from 541 oil fields as per Tissot and Welte (1984b).
(Reprinted with permission from Petroleum Formation and Occurrence by B. P. Tissot and D. H. Welte, page 419, copyright 1984, Springer Verlag).

	TEST	ARABIAN LIGHT 370°C+ RESIDUE	ARABIAN HEAVY 370°C+ RESIDUE
1.	Gravity, API	14.5	10.4
2.	Gravity, specific @ 15.56/15.56°C	0.9692	0.9972
3.	Total sulphur, wt%	2.91	4.48
4.	Carbon residue, wt%	8.2	14.9
5.	Viscosity, kinematic, centistokes @ 99°C	25	88
6.	Pour point, °C	+11	+21
7.	Ash content, ppm	120	350
8.	Nitrogen, wt %	0.18	0.26
9.	Iron, ppm	16.5	29.5
10.	Nickel, ppm	8.5	20.5
11.	Vanadium, ppm	32	85
12.	Yield, wt % on crude oil	46.0	55.3

Table 4.2 : General properties of Arabian Light and Arabian Heavy residua.

nificant portions of the crude oils. A comparison of the properties of the residua with those of the respective crude oil (see Table 4.1) indicates that the residua are much higher in properties such as gravity, sulphur content, carbon residue and metal content. The higher concentrations of nickel and vanadium in the AH residue indicate that both porphyrin-bonded and nonporphyrin-bonded metals will be higher in the AH residue.

4.3 Isolation of Asphaltenes

Yields of impure and purified asphaltenes isolated from the AH 370^0C+ residue by the use of normal heptane as the precipitating solvent in different solvent-to-oil ratios are presented in Table 4.3. Initial inspection of the data shows that the yield of impure asphaltenes is decreasing with an increase in the solvent-to-oil ratio. This suggests that larger amounts of resins are coprecipitated when lower solvent-to-oil ratios are employed. This is confirmed by a considerable reduction in the yields of asphaltenes after purification by Soxhlet extraction. Similar observations were reported by Acevedo and coworkers (Acevedo et al., 1985).

It is known that resins, which provide a transition between the non-polar oils and the polar asphaltenes, always coprecipitate with the asphaltenes, if lower solvent-to-oil ratios are employed. Therefore, it was proposed that a minimum of forty volumes of the precipitating solvent should be used to ensure complete precipitation of asphaltenes and also to prevent coprecipitation of resins (Speight, 1981). However, the present study reveals that the asphaltenes precipitated from the AH residue by the use of a sixty fold volume of

VOLUMES OF NORMAL HEPTANE TO ONE VOLUME OF CRUDE OIL	YIELD OF ASPHALTENES (WT %) IMPURE	PURIFIED
20	8.8	5.0
20(*)	8.8	4.9
30	8.2	4.9
40	7.0	4.9
60	5.7	4.9

(*) dissolved in toluene and reprecipitated before Soxhlet extraction.

Table 4.3 : Yields of asphaltenes from AH crude oil with different solvent-to-oil ratios.

the precipitating solvent also contain coprecipitated resins. This is indicated by a decrease in the yield of asphaltenes after Soxhlet extraction.

Equal yields of purified asphaltene were obtained for thirty, forty and sixty fold volumes of the precipitating solvent. This indicates that thirty volumes of the precipitating solvent and sixteen hours contact time, followed by Soxhlet extraction are suitable parameters to obtain stable yields of asphaltenes from the AH crude oil. Figure 4.2 shows the correlations between solvent-to-oil ratio and the yields of impure and purified asphaltenes.

Asphaltenes were also precipitated from the AH 370°C+ residue by the use of six normal alkane solvents, namely, pentane, hexane, heptane, octane, nonane and decane, and from the AL 370°C+ residue by the use of normal pentane as precipitating solvent. These asphaltenes were coded as AH5, AH6, AH7, AH8, AH9, AH10 and AL5 respectively. The number immediately following the crude oil designation (AH or AL) indicates the carbon number of the precipitating solvent. A solvent-to-oil ratio of 30:1 was used for these precipitations. The yields of purified asphaltenes obtained by the use of different alkane solvents are presented in Table 4.4. In one of the experiments, the impure asphaltenes were purified by the procedure of Speight (1984a), by dissolving the impure asphaltenes in a small portion of toluene ($\approx$ 1:1) followed by reprecipitation. The difference in the yields of asphaltenes purified by the two procedures was insignificant. The yield of asphaltenes (Table 4.4) decreased with an increase in the carbon number of the precipitating alkane solvent.

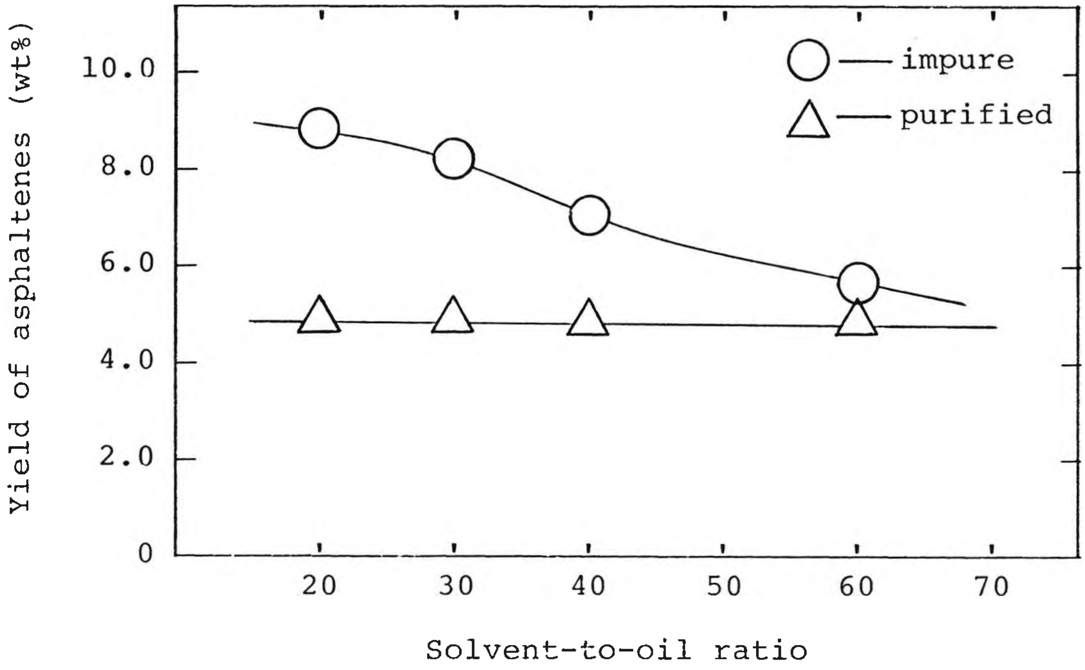

Fig 4.2: Effect of solvent-to-oil ratio on the yield of asphaltenes.

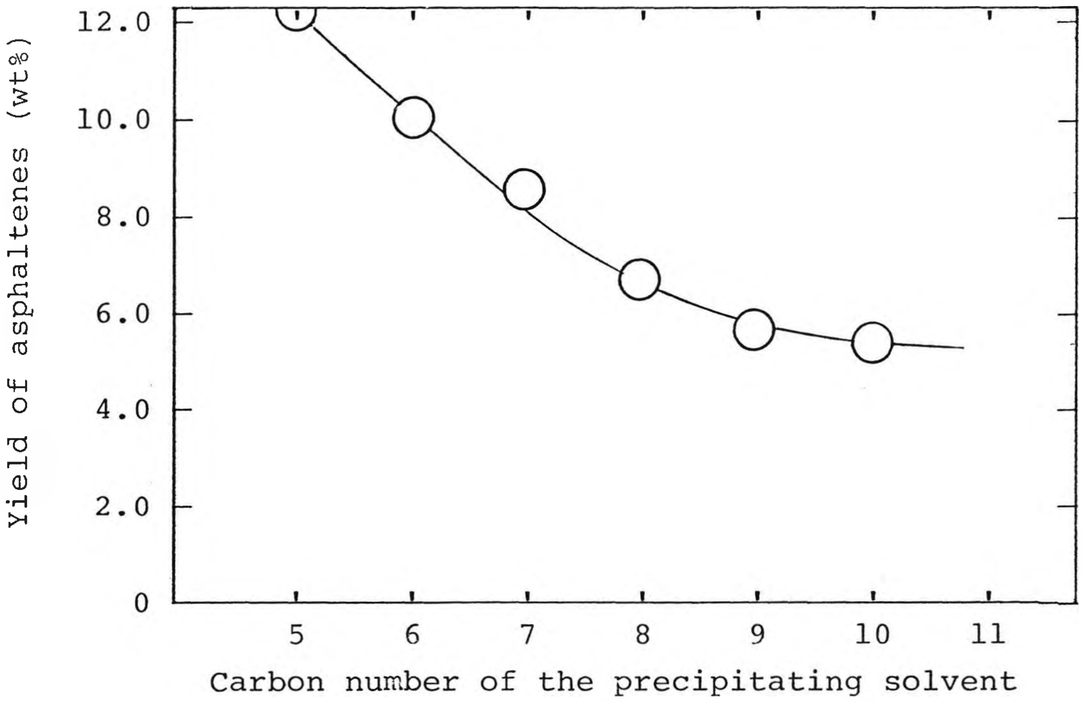

Fig 4.3: Effect of carbon number of the precipitating solvent on the yield of asphaltenes.

RESIDUE	PRECIPITATING SOLVENT (*)	ASPHALTENE CODE	YIELD OF ASPHALTENES (WT %)
AH 370°C+	n-Pentane	AH5	12.2
AH 370°C+	n-Hexane	AH6	10.0
AH 370°C+	n-Heptane	AH7	8.5
AH 370°C+	n-Octane	AH8	6.7
AH 370°C+	n-Nonane	AH9	5.7
AH 370°C+	n-Decane	AH10	5.3
AL 370°C+	n-Pentane	AL5	2.9

(*) precipitated with 30:1 solvent-to-oil ratio

Table 4.4 : Yields of asphaltenes from Saudi Arabian crude oils with different alkane solvents.

These results are in agreement with those reported earlier for asphaltenes from different origins (Mitchell and Speight, 1973; Corbett and Petrossi, 1978; Ali and Al-Ghannam, 1981). Figure 4.3 shows the effect of the carbon number of the precipitating solvent on the yield of asphaltenes.

4.4 Elemental Analysis

Elemental analysis for carbon, hydrogen, nitrogen, sulphur and oxygen and the atomic H/C, N/C, S/C and O/C ratios for the asphaltenes precipitated from the two crude oils are recorded in Table 4.5. A careful inspection of the data shows that the amounts of carbon and hydrogen are decreasing whereas the heteroelements are increasing with an increase in the carbon number of the precipitating solvent. Accordingly, atomic H/C ratios have decreased and atomic N/C, S/C and O/C ratios have increased for the higher alkane precipitated asphaltenes. Comparatively lower values of the atomic H/C ratio and higher values of heteroelement atomic ratios for the higher alkane precipitated asphaltenes suggest that these asphaltenes have a higher degree of aromaticity and also have higher proportions of heteroelement compounds.

Higher values of atomic H/C ratios accompanied by higher yields for the lower alkane precipitated asphaltenes (Table 4.5) could also be due to coprecipitated resins, which have higher atomic H/C ratios than those of the corresponding asphaltenes (Koots and Speight, 1975) and cannot be removed even by Soxhlet extraction (Acevedo et al., 1985).

RESIDUE	PRECIPITATING SOLVENT	ELEMENTAL ANALYSIS (WT %)					ATOMIC RATIO			
		C	H	N	S	O(*)	H/C	N/C	S/C	O/C
AH 370°C+	n-Pentane	82.38	7.65	0.85	7.41	1.71	1.114	0.009	0.034	0.016
AH 370°C+	n-Hexane	82.40	7.61	0.91	7.30	1.78	1.108	0.009	0.033	0.016
AH 370°C+	n-Heptane	82.15	7.40	0.96	7.61	1.88	1.081	0.010	0.035	0.017
AH 370°C+	n-Octane	82.01	7.35	1.04	7.61	1.99	1.076	0.011	0.035	0.018
AH 370°C+	n-Nonane	81.68	7.32	1.19	7.71	2.10	1.075	0.013	0.035	0.019
AH 370°C+	n-Decane	81.39	7.30	1.31	7.79	2.21	1.076	0.014	0.036	0.020
AL 370°C+	n-Pentane	83.76	7.26	0.80	6.59	1.59	1.040	0.008	0.030	0.014
AH Crude oil	n-Heptane	81.90	7.35	0.95	7.85	1.95	1.077	0.010	0.036	0.018

(*) by difference.

Table 4.5 : Elemental analysis and atomic ratios of asphaltenes from Saudi Arabian crude oils.

Table 4.6 gives the empirical formulae for the asphaltenes precipitated from the AH residue computed from the elemental analysis data. The formulae have been normalized to 100 carbon atoms. The $\Sigma(N+S+O)$, total hetero atoms per 100 carbon atoms and $\Sigma(N+S)$, total nitrogen and sulphur atoms per 100 carbon atoms are also given in Table 4.6. Both $\Sigma(N+S+O)$ and $\Sigma(N+S)$ generally increase from normal pentane precipitated asphaltenes to normal decane precipitated asphaltenes .

4.5 Molecular Weights of Asphaltenes

The molecular weights of asphaltenes precipitated from the AH residue by the use of different alkane solvents were determined by vapour pressure osmometry (VPO). The asphaltenes were dissolved in toluene in the concentration range of 2-8% wt and the determinations were made at 40, 60 and 80°C. The results are shown in Table 4.7. Higher values of molecular weights were recorded for the higher alkane precipitated asphaltenes. An increase in the solution temperature caused a decrease in the observed molecular weight. Figure 4.4 shows the effect of solution temperature on the VPO molecular weight of asphaltenes. These results are in agreement with those reported earlier by Speight (1984a) for Athabasca asphaltenes but are in conflict with the findings of Ali and Al-Ghannam (1981), who have reported a decrease in the molecular weight for higher alkane precipitated asphaltenes from the Qaiyarah crude oil.

Lower values of molecular weight at higher solution temperatures, such as 9950, 8950 and 7900 at 40, 60 and 80°C, respectively for AH7 asphaltenes are presumably due to stripping or dissociation

PRECIPITATING SOLVENT	EMPIRICAL FORMULA (C=100)	Σ(N+S+O)	Σ(N+S)
n-Pentane	$C_{100}H_{111}N_{0.9}S_{3.4}O_{1.6}$	5.9	4.3
n-Hexane	$C_{100}H_{111}N_{0.9}S_{3.3}O_{1.6}$	5.8	4.2
n-Heptane	$C_{100}H_{108}N_{1.0}S_{3.5}O_{1.7}$	6.2	4.5
n-Octane	$C_{100}H_{108}N_{1.1}S_{3.5}O_{1.8}$	6.4	4.6
n-Nonane	$C_{100}H_{108}N_{1.2}S_{3.5}O_{1.9}$	6.6	4.7
n-Decane	$C_{100}H_{106}N_{1.4}S_{3.5}O_{2.0}$	6.9	4.9

Table 4.6 : Empirical formulae of asphaltenes from AH residue computed from the elemental analysis data.

	VPO MOLECULAR WEIGHT IN TOLUENE (*)		
TEMPERATURE (^{0}C)	40	60	80
Precipitating Solvent			
n-Pentane	7900	7150	6250
n-Hexane	8800	7900	7050
n-Heptane	9950	8950	7900
n-Octane	11200	10300	9800
n-Nonane	13050	12050	11500
n-Decane	14850	13900	13050

(*) accuracy ± 10%

Table 4.7 : VPO molecular weights of asphaltenes from AH residue at different solution temperatures.

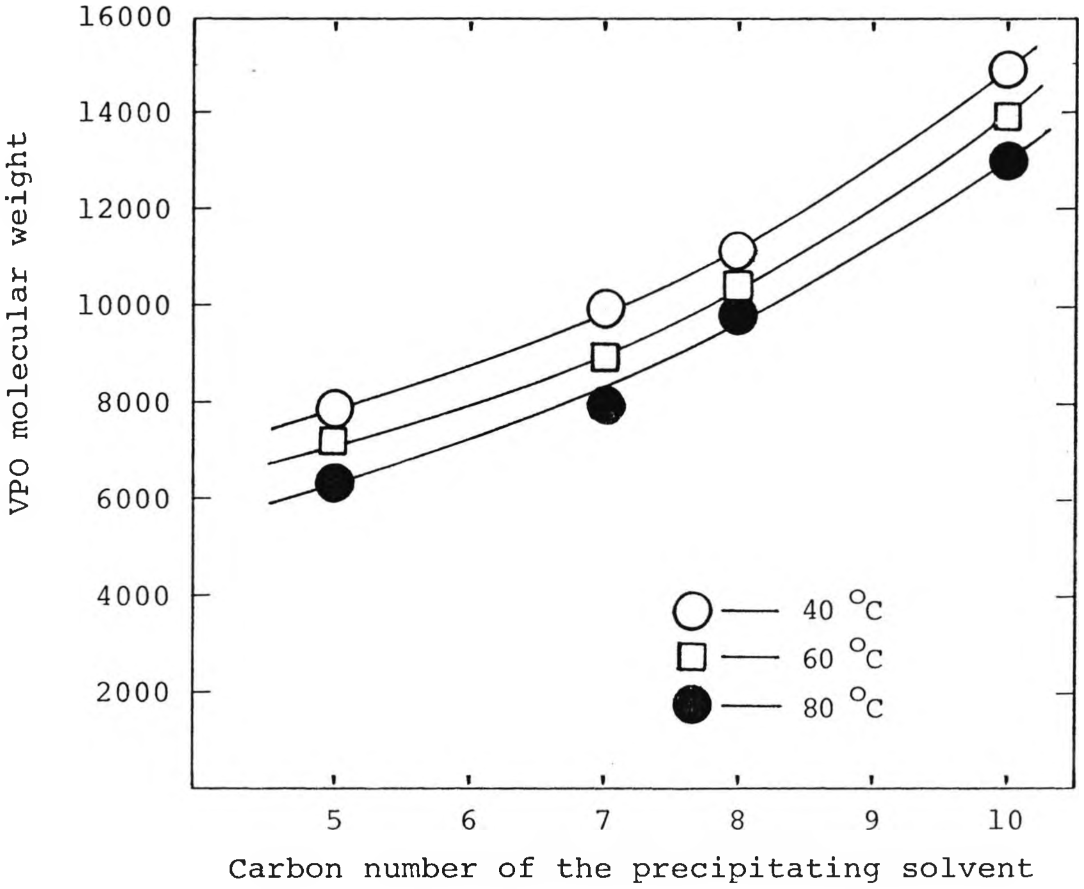

Fig 4.4: VPO molecular weight as a function of temperature for asphaltenes precipitated with different alkane solvents.

of some of the unit sheets from the asphaltene molecule (Mustafa et al., 1986; Boduszynski, 1981). Unit sheets are thought to be one of the three entities of asphaltenes , the other two being particles and micelles. The unit sheets are conceived as being held together in the particles by the intermolecular forces or by short aliphatic chains.

The VPO molecular weights of asphaltenes from the AH residue determined in solvents of different dielectric constant are given in Table 4.8. These asphaltenes are soluble in the solvents with low dielectric constant but are sparingly soluble in solvents with high dielectric constant such as pyridine, particularly the asphaltenes precipitated by normal heptane and higher alkane solvents. Lower values of molecular weight were obtained in the solvents with higher dielectric constant, e.g. pyridine.

The present data support the previous observations that the molecular weight of asphaltene material depends not only on the nature of the solvent (Speight, 1971; Moschopedis and Speight, 1971), but also on the temperature of the solution at which the determinations are made (Moschopedis et al., 1976). The effect of dielectric constant of the solvent on the VPO molecular weight is illustrated in Figure 4.5.

The higher molecular weights recorded in the solvents with low dielectric constant such as toluene are undoubtedly due to molecular association between the asphaltene nuclei, whereas the solvents with high dielectric constant such as pyridine are able to bring about dissociation of the asphaltene agglomerations (Acevedo et al., 1985).

	VPO MOLECULAR WEIGHT				
Solvent	Carbon Tetrachloride	Toluene	Chloroform	Chlorobenzene	Pyridine
Dielectric constant	2.24	2.37	4.81	5.71	12.30
Temperature (°C)	60	40	40	40	40
Precipitating Solvent					
n-Pentane	7300	7900	3400	3300	2850
n-Hexane	8100	8800	4200	4050	3250
n-Heptane	8700	9950	4550	4250	3450(*)
n-Octane	10600	11200	5200	5400	(**)
n-Nonane	11850	13050	6350	6300	(**)
n-Decane	13100	14850	7400	7250	(**)

(*) sparingly soluble. (**) insoluble.

Table 4.8 : VPO molecular weights of asphaltenes from AH residue in different solvents.

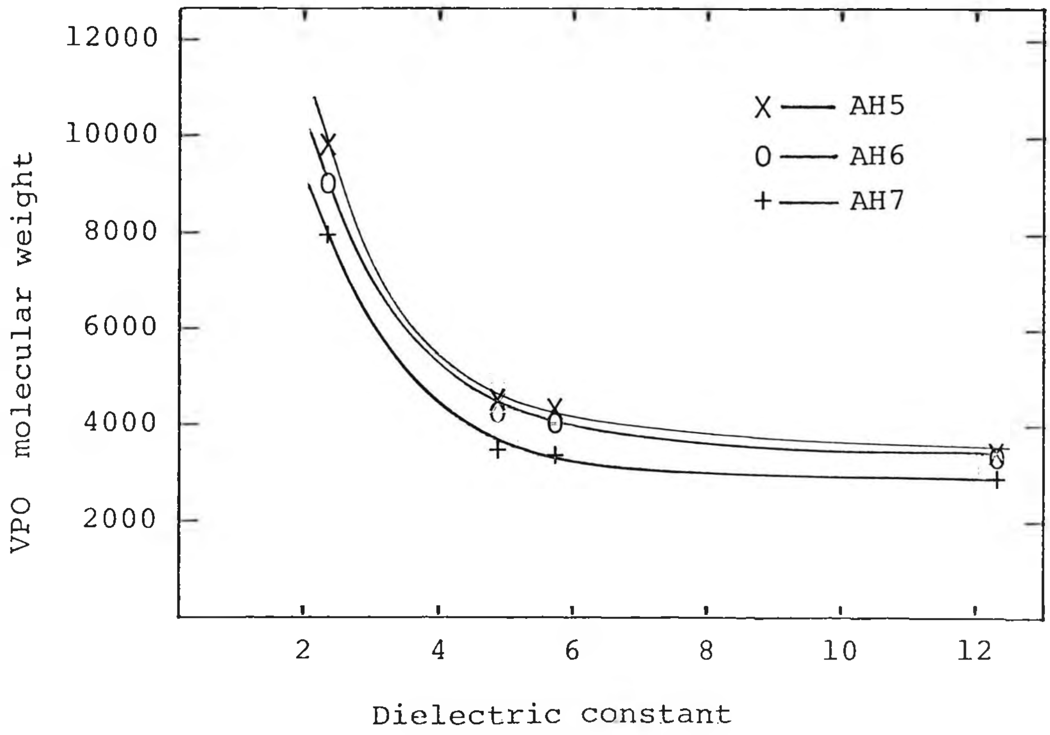

Fig 4.5: Effect of dielectric constant of the solvent used in the VPO method on the molecular weight of asphaltenes precipitated with different alkane solvents.

Normal octane and higher alkane solvents have been used to precipitate hard core asphaltenes which have poor solubility and have molecular weights of the order of > 10,000 (Mitchell and Speight, 1973).

4.6 Thermal Gravimetric Analysis of Asphaltenes

The general characteristics of the asphaltene samples subjected to thermal gravimetric analysis (TGA), i.e. AL5 asphaltenes isolated from Arabian Light residue (370°C+) and AH5, AH7 and AH10 asphaltenes isolated from Arabian Heavy residue (370°C+) are shown in Table 4.9.

Thermal gravimetric (TG) and differential thermal gravimetric (DTG) curves for the four asphaltenes are presented in Figures 4.6 (AL5 and AH5) and 4.7 (AH7 and AH10). The weights of the residues as a function of temperature are shown as TG curves. The rates of change in weight of the residues with temperature are shown as DTG curves. The temperature abscissa have a linear scale from ambient to 1000°C.

The TG curves indicate that very little reaction occurred up to approximately 400°C. The greatest changes in the residue weight occur between 400 and 520°C. Above 520°C, the change in weight was small. The rate of change in weight of the residue (DTG curves) shows that the pyrolysis reaction rate was slow up to a temperature of about 400°C. As the temperature was raised, the reaction rate went through a maximum near 500°C and then declined.

	ARABIAN LIGHT ASPHALTENE	ARABIAN HEAVY ASPHALTENE		
	AL5	AH5	AH7	AH10
Yield on residue (wt%)	5.7	12.5	8.5	5.3
Carbon (wt%)	82.37	82.38	82.15	81.39
Hydrogen (wt%)	7.85	7.65	7.40	7.30
Nitrogen (wt%)	0.78	0.85	0.96	1.31
Sulphur (wt%)	6.50	7.43	7.61	7.79
Oxygen (wt%)*	2.50	1.69	1.88	2.21
Mol.Wt (VPO, in Toluene @ 60°C)	6250	7150	8950	13900

* by difference

Table 4.9 : General characteristics of asphaltenes from Saudi Arabian crude oil 370°C+ residua.

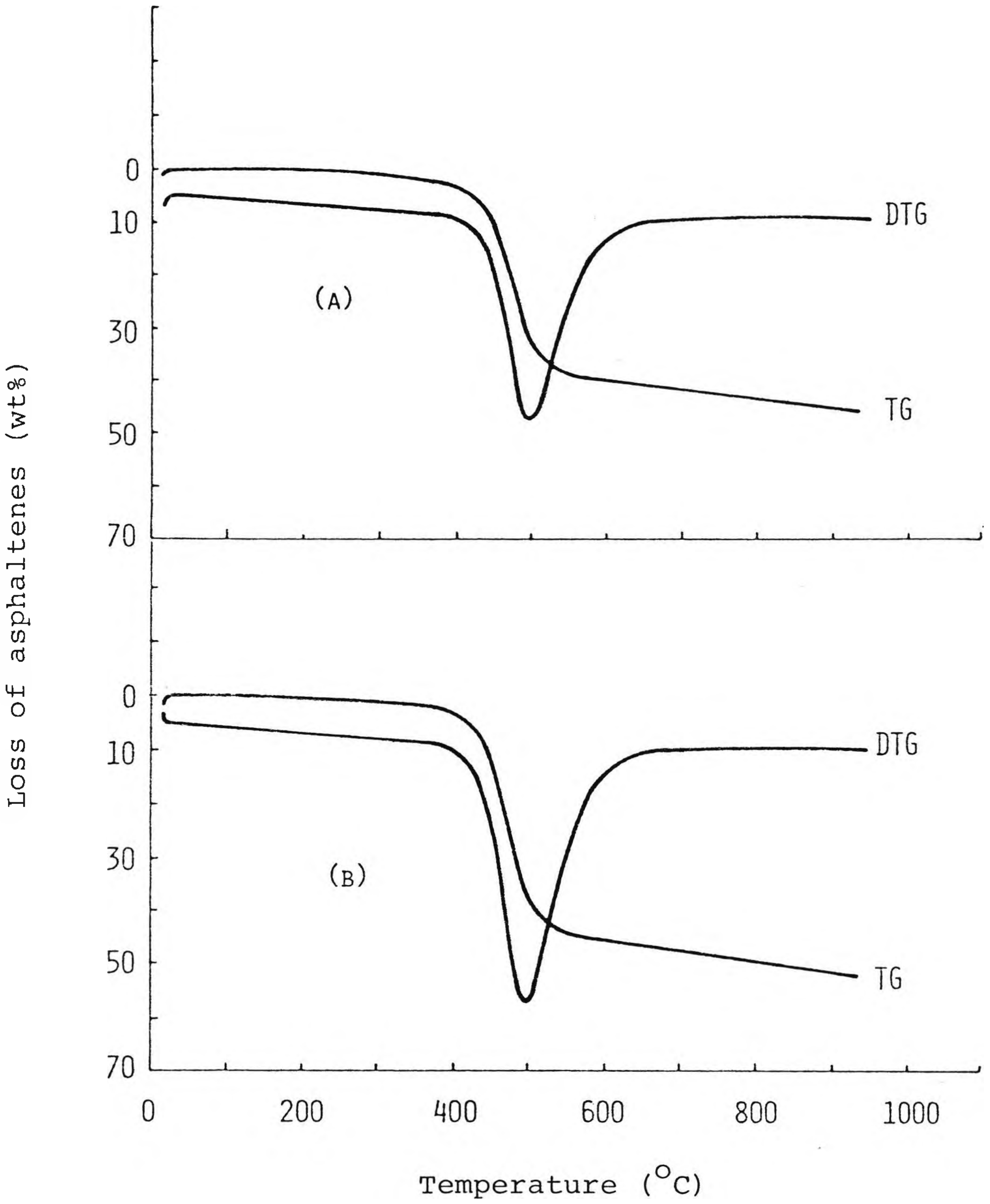

Fig 4.6 : Thermal gravimetric (TG) and differential thermal gravimetric (DTG) analysis of (A) AL5 asphaltenes and (B) AH5 asphaltenes.

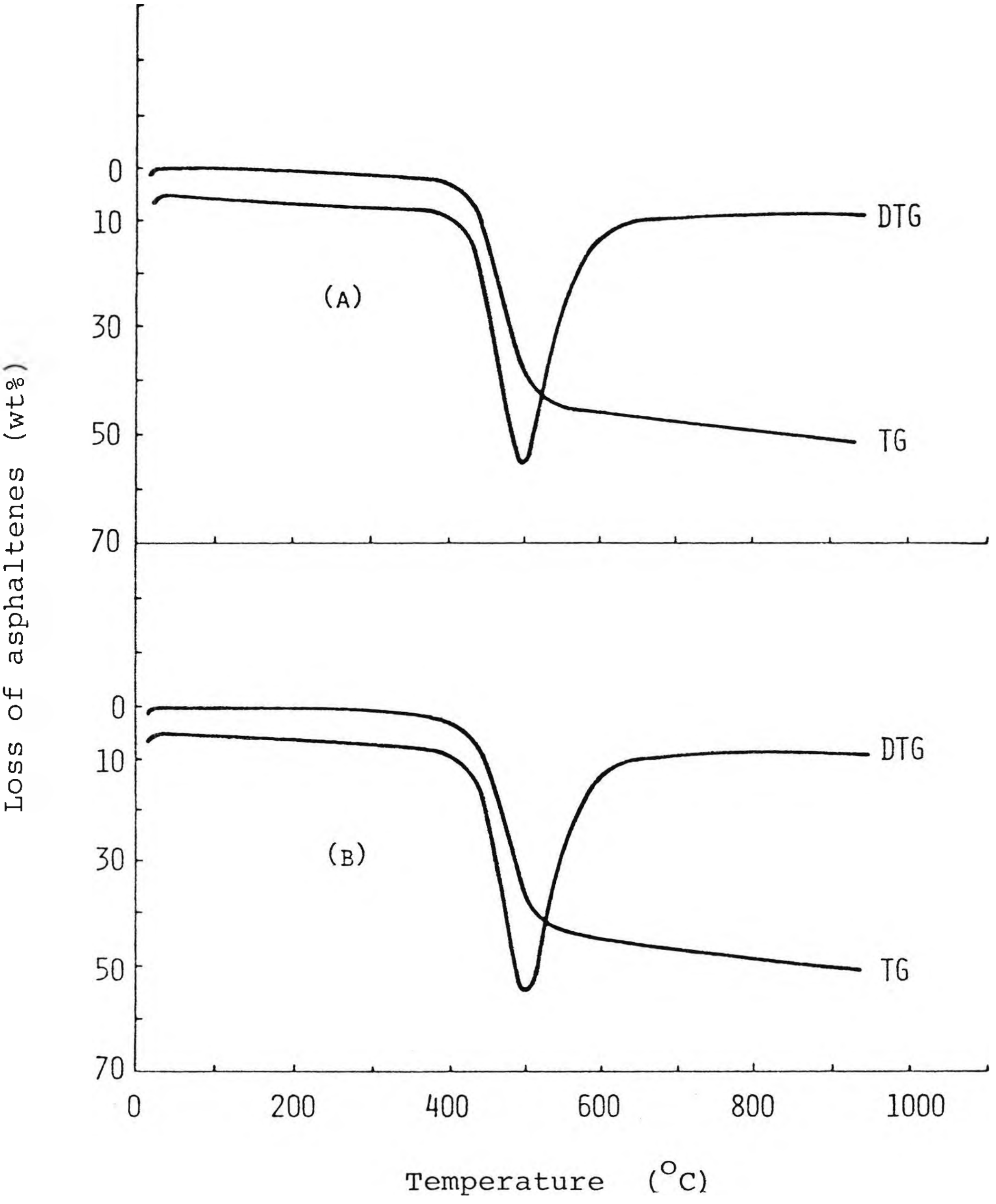

Fig 4.7 : Thermal gravimetric (TG) and differential thermal gravimetric (DTG) analysis of (A) AH7 asphaltenes and (B) AH10 asphaltenes.

Eventually, the rate became quite small. This was probably caused by the increasing proportion of coke and the decreasing proportion of reactive hydrocarbons in the residue.

Comparison of weight loss during thermal gravimetric analysis for the four asphaltenes at different temperatures (Table 4.10) shows that the weight loss was highest (2.4 wt %) for AL5 asphaltenes at 350°C, whereas for the AH asphaltenes it was relatively low and showed a tendency to decrease from AH5 to AH10 asphaltenes . At 520°C, the weight loss was lowest for AL5 asphaltenes whereas for the AH asphaltenes it decreased from 41.7 wt % for AH5 asphaltenes to 40.7 wt % for AH10 asphaltenes. At 920°C, the weight loss was again lowest for AL5 asphaltenes (45.5 wt %) and decreased from 51.7 wt % for AH5 asphaltenes to 50.9 wt % for AH10 asphaltenes. The TGA results indicate that the conversion of asphaltenes into volatile matter (gases and maltenes) is greater for the AH asphaltenes as compared with the AL asphaltenes .

4.7 Pyrolysis of Asphaltenes

The AL5, AH5, AH7 and AH10 asphaltenes were also subjected to pyrolysis at 350°C and 520°C and the evolved gases were analyzed by gas chromatography to obtain data over this temperature range to infer information on structural differences for asphaltenes precipitated from Saudi Arabian crude oils by the use of different alkane solvents.

	LOSS (wt %)*			
	ASPHALTENE			
TEMPERATURE (°C)	AL5	AH5	AH7	AH10
350	2.4	1.8	1.5	1.2
520	35.7	41.7	41.0	40.7
920	45.5	51.7	51.2	50.9

* cumulative

Table 4.10 : Comparison of weight loss of different asphaltenes during thermal gravimetric analysis at different temperatures

4.7.1 Product Distribution from Asphaltene Pyrolysis

The yields of non-condensible gases, condensible gases and oils (maltenes), unreacted asphaltenes and coke obtained on pyrolysis of the four asphaltene samples at 350°C and 520°C are presented in Table 4.11. The results indicate that the amounts of gases released at 350°C were around 2.0 wt % except for AH10 asphaltenes , which gave 0.8 wt % at 350°C and 15-20 wt % at 520°C. Similarly, the yield of maltenes increased from a maximum of 2.6 wt % at 350°C to a maximum of 24.6wt % at 520°C. As expected, the amounts of unreacted asphaltene were greatly reduced as the pyrolysis temperature was increased from 350°C to 520°C. The ultimate gas yields remained nearly equal to maltene yields at 350°C for all the asphaltenes except for AH10 asphaltenes . At 520°C, the yield of maltenes increased from 21.8 wt % for AH5 to 24.6 wt % for AH10 asphaltenes , whereas the yield of gases showed a decreasing trend from AH5 to AH10 asphaltenes. A high proportion of unreacted asphaltenes at 350°C (> 85 wt %) indicated that the pyrolysis was far from completion and the remaining material was not a true coke but a mildly devolatilized asphaltene. The generation of benzene-insoluble material (coke) at 350°C indicates that unsaturated systems that are present in the asphaltenes undergo condensation and dehydrogenation at the low temperature. This effect is greater in the higher alkane precipitated, higher molecular weight asphaltenes . At 520°C, more severe thermal decomposition and condensation have occurred. This is indicated by 98-100 wt % conversion of asphaltenes into the products. The yield of coke ranged from 58 to about 63 wt %. The highest

	COMPOSITION (WT %)							
TEMPERATURE (°C)	350				520			
PRODUCT FRACTION	AL5	AH5	AH7	AH10	AL5	AH5	AH7	AH10
Gases*	2.2	2.2	1.4	0.8	15.6	20.2	17.9	16.3
Maltenes	2.6	2.2	1.8	1.7	20.9	21.8	23.5	24.6
Asphaltenes	85.5	86.4	85.5	85.1	0.7	1.5	0.3	nil
Coke	9.7	9.2	11.3	12.4	62.8	56.5	58.3	59.1

*determined by difference

Table 4.11 : Product distribution from asphaltene pyrolysis at different temperatures.

yield of coke was recorded for the AL5 asphaltenes .

4.7.2 Composition of Pyrolysis Gases

The composition of gases evolved at 350°C and 520°C from the four asphaltenes are presented in Tables 4.12 and 4.13. Figures 4.8 and 4.9 present typical chromatograms for the gases evolved at 350°C and 520°C , respectively. The distributions of gases evolved at the two temperatures are markedly different. The C_1-C_4 normal paraffins constitute the major portion (> 50 vol %) of the gases evolved from AH asphaltenes at 350°C and the oxygen-containing gases, viz CO & CO_2, represent about 31-38 vol %. In the case of AL5 asphaltenes , the proportion of oxygen-containing gases (CO + CO_2) is greater than 60 vol %, whereas the proportion of C_1-C_4 paraffins is about 32 vol %. The gases formed from asphaltene pyrolysis at low temperatures are known to be produced from condensed aromatic derivatives (Lewis and Edstrom, 1963) and various oxygen functional groups (Madison and Roberts, 1958; Moschopedis and Speight, 1976a). Similar trends were reported during the pyrolysis of tar sand asphaltenes (Ritchie et al., 1979), bitumen asphaltenes (Moschopedis et al., 1978) and oil sand and bitumen (Strausz et al., 1977).

It has been suggested (Soodhoo and Philips, 1988) that the production of heteroelement gases (H_2S,CO and CO_2) is appreciable at low temperature pyrolysis such as 350°C and that these gases are the primary products of low temperature hydropyrolysis of thioether and carboxylic acid linkages. Thus, release of large amounts of CO and

	COMPOSITION (Vol % / m mol per 100 gm)			
	ASPHALTENE			
COMPONENT	AL5	AH5	AH7	AH10
Hydrogen	nil	9.4/6.1	nil	nil
Methane	12.0/8.3	36.0/23.1	17.0/8.5	2.1/1.0
CO	16.4/11.3	14.6/9.5	5.8/3.0	0.9/0.5
CO_2	46.3/32.0	16.5/10.7	31.2/16.0	37.8/18.0
Ethylene	1.9/1.3	2.9/1.9	4.8/2.4	5.4/2.4
Ethane	1.6/1.1	8.6/5.5	10.7/6.0	14.6/6.5
Acetylene	nil	0.1/0.1	0.2/0.1	0.4/0.2
Propane	7.7/5.3	3.9/2.5	5.8/3.1	8.0/3.6
Propene	3.5/2.4	2.1/1.2	4.5/2.3	5.8/2.6
Butane	10.6/7.3	5.9/3.9	20.0/10.1	25.9/10.6

Table 4.12 : Composition of gases evolved during pyrolysis of asphaltenes at 350°C.

	COMPOSITION (Vol % / m mol per 100 gm)			
	ASPHALTENE			
COMPONENT	AL5	AH5	AH7	AH10
Hydrogen	20.4/31.8	12.2/21.2	20.2/35.0	36.7/59.8
Methane	46.8/63.2	44.5/67.5	44.2/64.0	42.6/59.5
CO	2.7/4.3	3.2/5.5	1.8/3.1	1.7/2.8
CO_2	2.1/3.3	2.0/3.5	2.4/4.0	3.0/5.0
Ethylene	5.8/9.1	8.4/14.6	7.3/12.2	3.2/5.3
Ethane	11.2/17.4	12.0/20.9	9.7/16.3	6.9/11.2
Acetylene	nil	< 0.1/-	< 0.1/-	nil
Propane	6.4/9.9	9.2/16.1	7.8/13.1	3.1/5.1
Propene	1.5/2.3	2.2/3.9	1.9/3.1	1.1/1.8
Butane	3.1/4.9	6.3/10.8	4.7/7.2	1.7/2.7

Table 4.13 : Composition of gases evolved during pyrolysis of asphaltenes at 520°C.

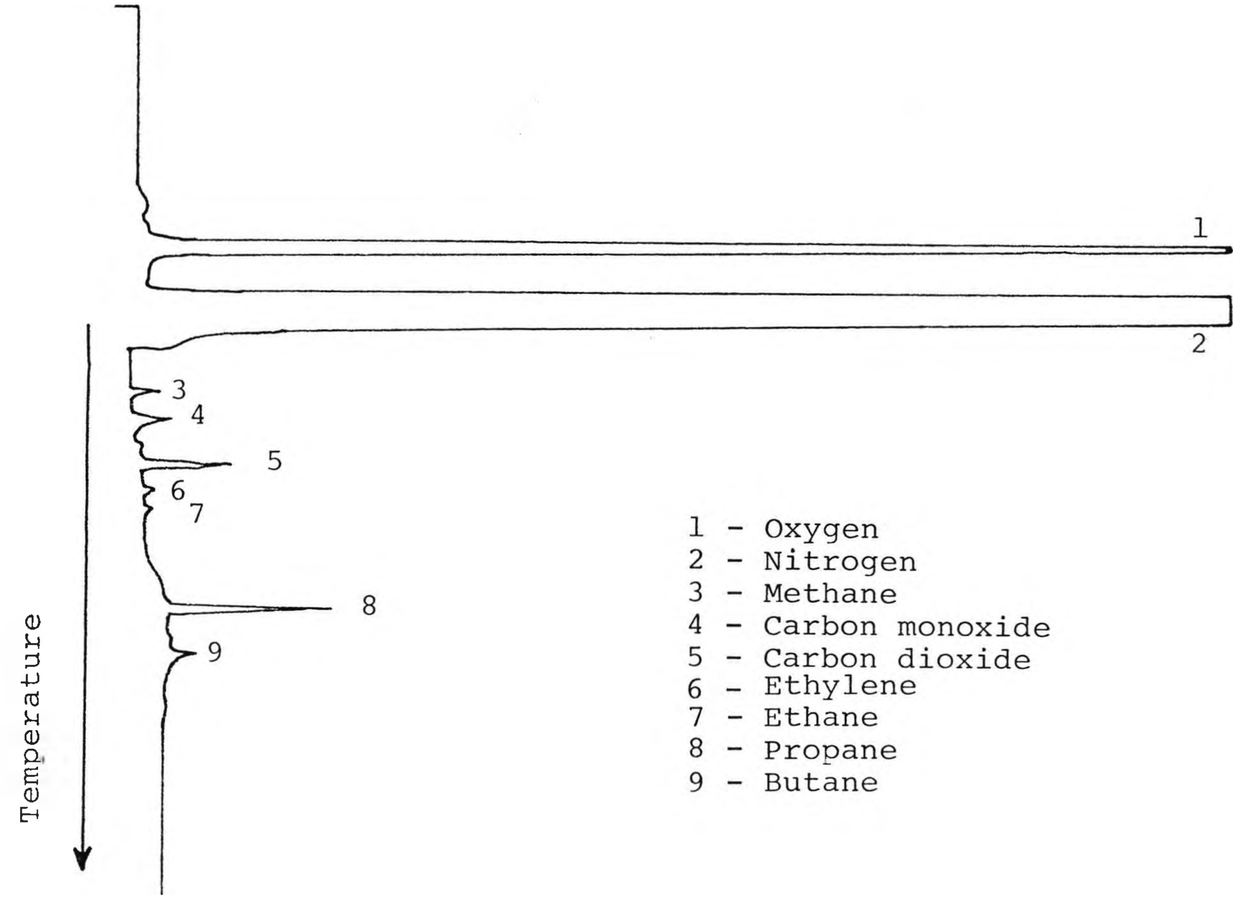

Fig 4.8 : Typical chromatogram of gases from asphaltene pyrolysis at 350°C.

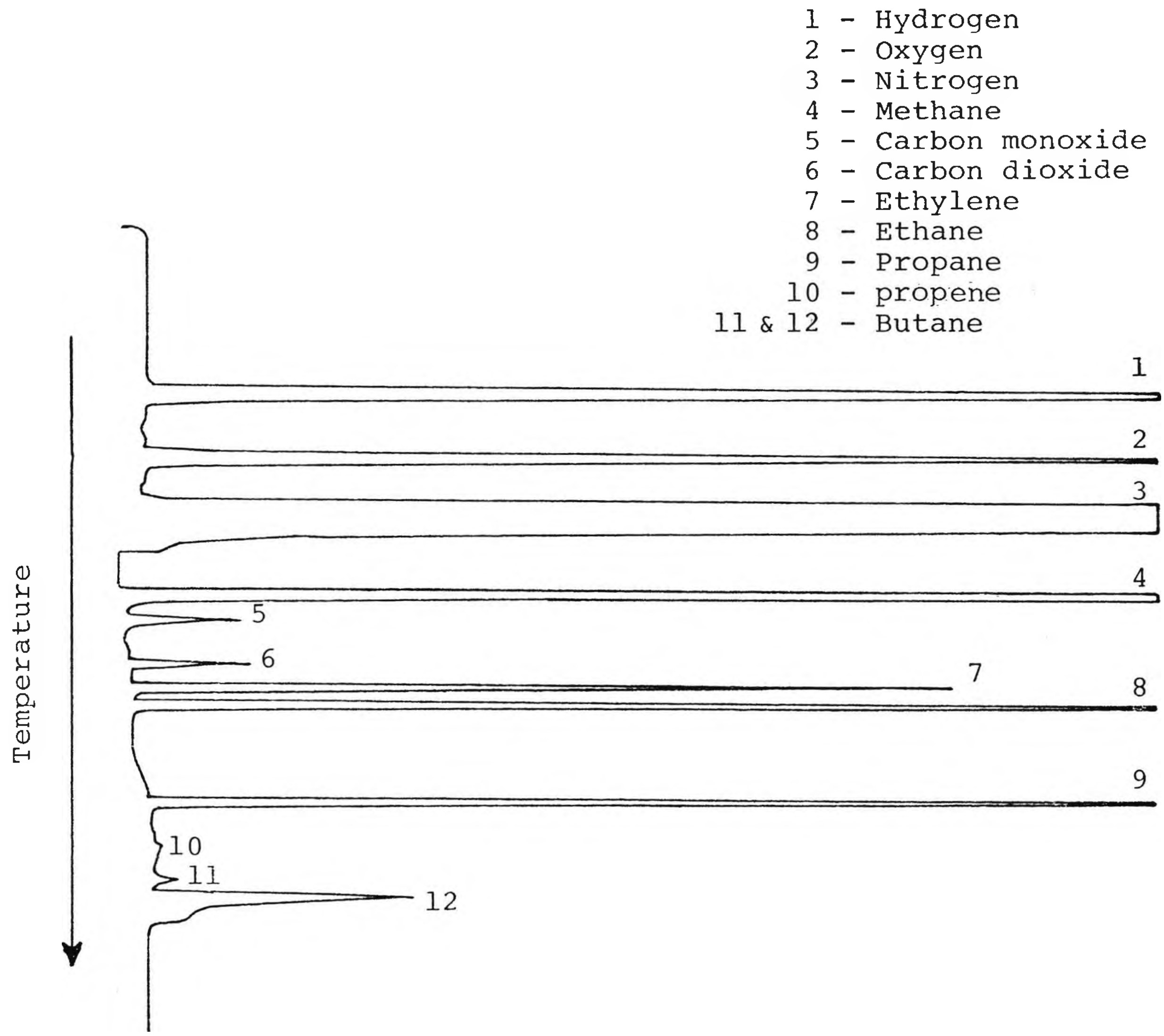

Fig 4.9 : Typical chromatogram of gases from asphaltene pyrolysis at 520^{o}C.

CO_2 from AL5 asphaltenes indicates that these asphaltenes contain greater amounts of oxygen functionalities as compared with the AH asphaltenes . Among the three AH asphaltenes , the quantity of CO released has decreased from 14.6 vol % for AH5 asphaltenes to 0.9 vol % for AH10 asphaltenes , whereas CO_2 has increased significantly from 16.5 vol % for AH5 asphaltenes to 37.8 vol % for AH10 asphaltenes (Table 4.12). This suggests that ether linkages, which are one of the sources of the production of CO (Soodhoo and Philips, 1988) are decreasing and the carboxylic groups which produce CO_2 are increasing with an increase in the carbon number of the precipitating solvent.

At 350°C, the amount of methane evolved was found to decrease from 36 vol % for AH5 asphaltenes to 17 vol % for AH7 asphaltenes and 2.1 vol % for AH10 asphaltenes . The evolution of the higher alkane hydrocarbons (C_2 and above) showed a tendency to increase for pentane to decane precipitated asphaltenes . Figure 4.10 illustrates the variation of different gases evolved from different asphaltenes at 350°C. The quantity of olefins (C_2H_4 + C_3H_6) was found to vary between 5 and 11 vol % (Table 4.12). The highest amount of olefins for AH10 asphaltenes (11.2 vol %) is attributed to more severe thermal degradation of relatively higher molecular weight AH10 asphaltenes as compared with the other three asphaltenes .

Comparison of gas yields at 520°C (Table 4.13) shows that methane and hydrogen constitute the major portion of the gases evolved from all four asphaltenes . The quantity of methane is

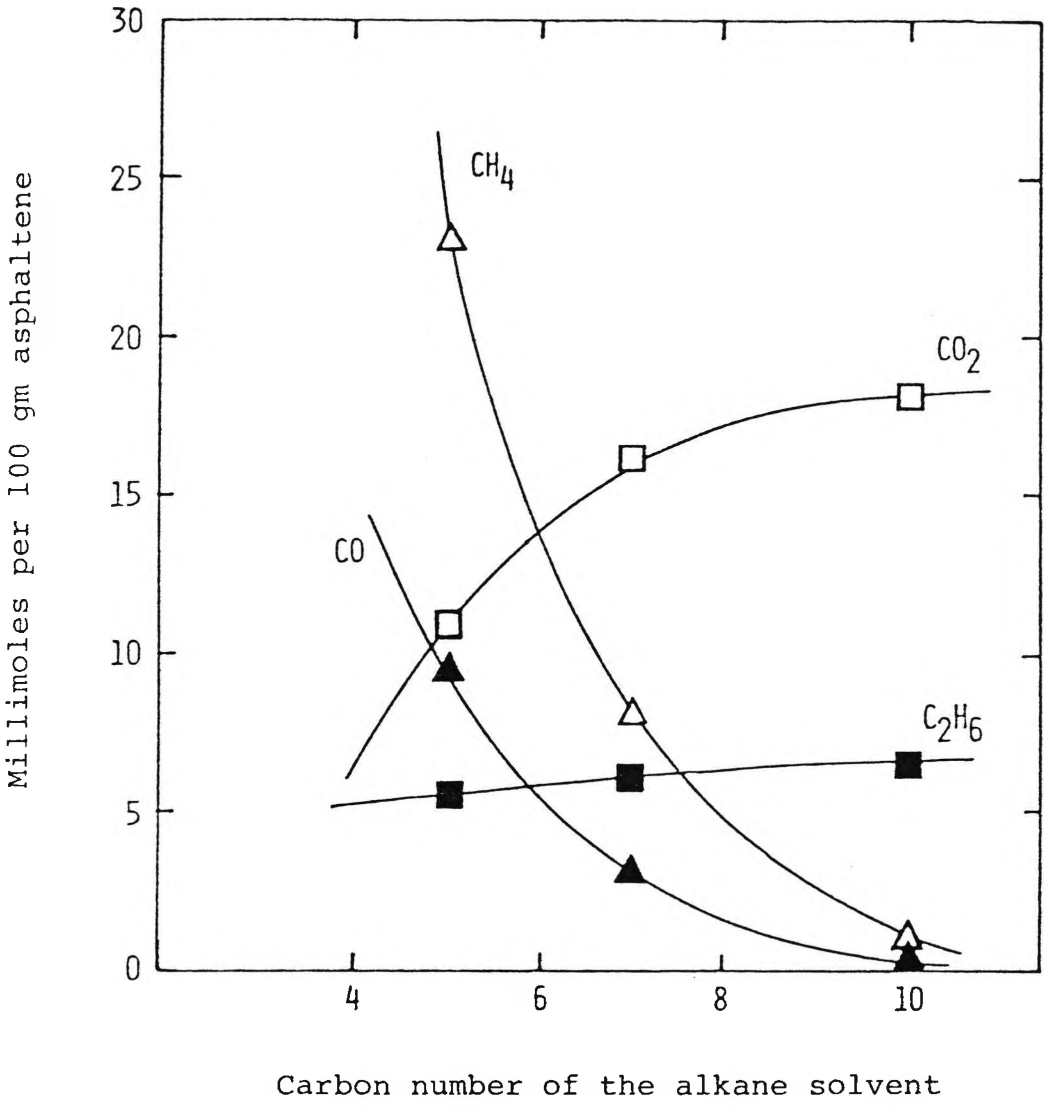

Fig 4.10 : Variation of gases from asphaltene pyrolysis at 350°C for different alkane precipitated asphaltenes.

nearly equal for all samples, but the evolution of hydrogen has increased significantly from 12.2 vol % for AH5 asphaltenes to 36.7 vol % for AH10 asphaltenes . The evolution of oxygen-containing gases at 520°C was sharply reduced for all four samples. For example, for the AL5 asphaltenes , the combined CO & CO_2 at 350°C was found to be 62.7 vol % whereas at 520°C these gases were only 4.8 vol %. The amount of CO was found to decrease and that of CO_2 increased from AH5 to AH10 asphaltenes during pyrolysis at 520°C. A similar trend was noted for the evolution of such gases during pyrolysis at 350°C. The yields of C_1-C_3 alkane hydrocarbons were generally higher for all the asphaltene samples at 520°C as compared with those obtained at 350°C and showed a decreasing trend for asphaltenes precipitated with higher alkane solvents. The release of higher amounts of hydrogen at 520°C from AH10 asphaltenes as compared with the other AH asphaltenes indicates that these asphaltenes undergo severe dehydrogenation at temperatures greater than 350°C. Figure 4.11 illustrates the variation of different gases evolved from different asphaltenes during pyrolysis at 520°C.

Comparison of the amounts of normal alkanes (C_1-C_4) evolved at 350°C and 520°C (Tables 4.12 and 4.13) shows that the amount of methane is significantly increased at 520°C whereas the amount of C_4 alkanes is reduced. This increased production of methane could be due to secondary reactions of maltenes and/or coke, in addition to primary routes from asphaltenes (Savage et al., 1985). Such reactions involve fission of C-C bonds (Soodhoo and Philips, 1988).

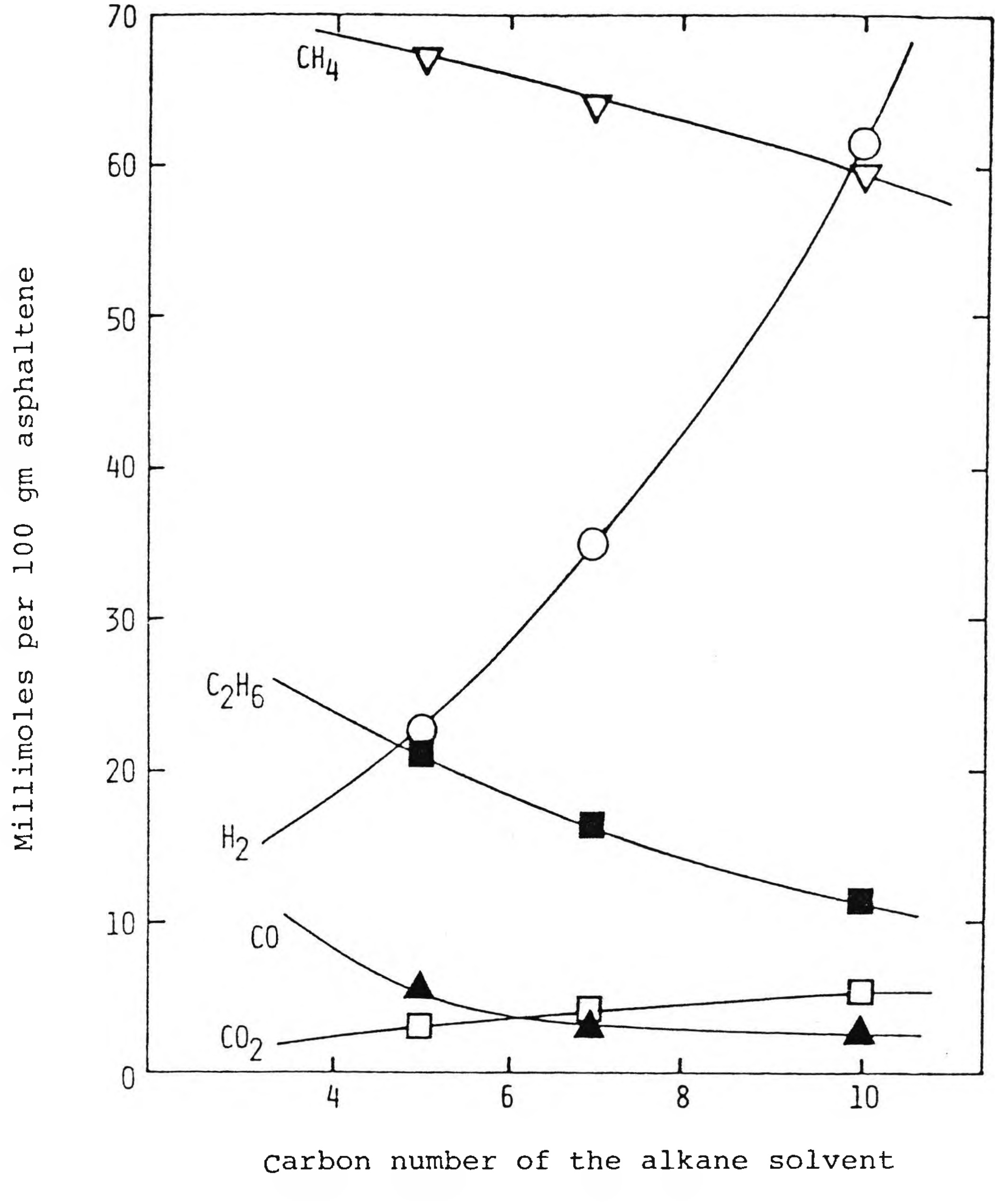

Fig 4.11 : Variation of gases from asphaltene pyrolysis at 520°C for different alkane precipitated asphaltenes.

Gas chromatographic analysis of maltene fractions collected during pyrolysis at 520°C indicated the presence of more than 150 components. Normal paraffin series up to C_{36} and a number of cycloalkanes were tentatively identified in maltenes from all four asphaltene samples.

4.7.3 Elemental Composition of Pyrolysis Products

Elemental analysis and atomic ratios for asphaltenes and their pyrolysis products (maltenes and coke) at 520°C are shown in Table 4.14. The percentage losses of elements as gases and maltenes during the pyrolysis of asphaltenes at 520°C are presented in Table 4.15. The AH asphaltenes lost 40-42 wt % of carbon whereas the losses of hydrogen and oxygen were higher (≈ 69 - 74 wt %). For the AL asphaltenes the losses of carbon and hydrogen were 35.3 wt % and 68.8 wt % respectively. The most striking feature for the heteroelements is that the loss of nitrogen for the AH asphaltenes was very low (≈ 1.2 - 6.1 wt %) and the loss of nitrogen for AL5 asphaltenes was not detectable. There is some evidence (Speight, 1970) that nitrogen is selectively retained in coke during pyrolysis.

The loss of sulphur ranged from 28.5 wt % for AH5 asphaltenes to 9.8 wt % for AH10 asphaltenes . It has been shown that considerable amounts of sulphur are retained in coke after thermal degradation. The pyrolysis of sulphur-containing polymers has been shown (Scott and Steedman, 1972) to result in the retention of 42 wt % of the sulphur in the coke at 800°C. Among the three AH asphaltenes studied the losses of nitrogen and oxygen were highest for AH10

		ELEMENT (WT %)					ATOMIC RATIO			
	FRACTION	C	H	N	S	O*	H/C	N/C	S/C	O/C
AL5	Asphaltenes	82.37	7.85	0.79	6.50	2.50	1.1436	0.0082	0.0295	0.0228
	Maltenes	82.70	9.40	0.10	5.10	2.80	n.d.**	n.d.	n.d.	n.d.
	Coke	84.81	3.91	1.26	8.63	1.39	0.5532	0.0127	0.0382	0.0123
AH5	Asphaltenes	82.38	7.65	0.85	7.41	1.71	1.1143	0.0088	0.0337	0.0156
	Maltenes	79.60	8.50	0.10	5.80	6.10	n.d.	n.d.	n.d.	n.d.
	Coke	84.12	3.68	1.48	9.39	1.33	0.5250	0.0151	0.0419	0.0119
AH7	Asphaltenes	82.15	7.40	0.96	7.61	1.88	1.0809	0.0100	0.0347	0.0172
	Maltenes	79.40	8.60	0.10	5.80	6.20	n.d.	n.d.	n.d.	n.d.
	Coke	83.31	3.31	1.63	10.42	1.33	0.4768	0.0168	0.0469	0.0120
AH10	Asphaltenes	81.39	7.30	1.31	7.79	2.21	1.0763	0.0138	0.0359	0.0204
	Maltenes	81.60	9.40	0.10	6.00	3.00	n.d.	n.d.	n.d.	n.d.
	Coke	82.32	2.74	2.09	11.89	0.98	0.3994	0.0218	0.0542	0.0089

*Determined by difference
**n.d., not determined

Table 4.14 : Elemental analysis and atomic ratios of pyrolysis products from asphaltenes at 520°C.

	ELEMENT LOSS (WT %)*				
ASPHALTENE	C	H	N	S	0
AL5	35.3	68.8	nil	16.9	65.2
AH5	42.3	72.8	1.2	28.5	57.5
AH7	40.9	73.9	1.0	20.2	58.5
AH10	40.8	69.7	6.1	9.8	73.8

* based on the amount of the element in asphaltene and the amount of the same element found in coke.

Table 4.15 : Loss of elements as gases and maltenes during the pyrolysis of asphaltenes at 520°C.

asphaltenes and the loss of sulphur was highest for AH5 asphaltenes .

4.8 Nonaqueous Potentiometric Titrations

4.8.1 Basic Functionalities

4.8.1.1 Model Basic Compounds

A series of model basic compounds were titrated in a solvent mixture containing chlorobenzene and acetic anhydride. The list of these compounds is given in Table 4.16. The compounds that titrated partially or did not titrate at all under the experimental conditions are listed accordingly. End points and half neutralization potentials (HNP), which are the potentials corresponding to the midpoint of a potentiometric titration curve, are also recorded. The pK_a (H_2O) values for the model basic compounds ranged from less than zero to 10.0. The compounds were classified into the following three groups, based on their pK_a values (Dutta and Holland, 1984).

(i) Very weak bases : Compounds with pK_a values less than zero fall into this category, which includes amides, pyrroles, indoles and carbazoles. Acetamide and acetanilide titrated quantitatively. Pyrroles and indoles titrated partially while carbazoles did not titrate. This could be due to the reaction of these compounds with acetic anhydride (Anderson and Exner, 1977).

(ii) Weak bases : Compounds with pK_a values between zero and 2 are included in this category, which includes phenazine (pK_a : 1.2)

COMPOUND	pK_a (H_2O)	% TITRATED	HNP(mV)
(a) Very weak bases			
2-methylindole	-0.1	94	620
Acetamide	-0.5	98	590
2,3-dimethylindole	-1.1	80	-
Indole	-2.4	75	570
Acetanilide	-2.9	99	690
Pyrrole	-3.8	65	-
Carbazole	-	(*)	-
N-methylpyrrole	-2.9	(**)	-
(b) Weak bases			
Phenazine	1.2	99	610
Caffeine	0.5	98	590
(c) Strong bases			
N,N-diphenylguanidine	10.0	(*)	-
Imidazole	7.0	98	360
Acridine	5.6	100	450
Pyridine	5.3	100	305
Quinoline	4.9	97	550
Phenanthridine	4.5	99	310

(*) did not titrate
(**) partially titrated

Table 4.16 : Potentiometric titration of model basic compounds.

and caffeine (pK_a : 0.6). Both of these compounds titrated quantitatively.

(iii) Strong bases: Compounds with pK_a values greater than 2 are classified as strong bases. The compounds titrated under this class were imidazole, acridine, pyridine, quinoline, phenanthridine and N,N-diphenylguanidine. All of these compounds titrated quantitatively, except for N,N-diphenylguanidine, which did not titrate.

The resolving capability was investigated for the solvent mixture containing chlorobenzene and acetic anhydride by titrating mixtures of known quantities of titratable compounds shown in Table 4.16 with perchloric acid. Several mixtures containing one compound from each of the three classes were examined. A mixture containing acridine, phenazine and acetanilide was found to be effectively differentiated under the titration conditions. A typical titration curve for a mixture containing these three compounds is shown in Figure 4.12.

4.8.1.2 Asphaltene Samples

Pure asphaltene samples, AH5, AH6, AH7, AH8, AH9 and AH10 were also titrated with perchloric acid under identical titration conditions. The titration curves for these samples showed two end points corresponding to HNP values of about 350 mV and 600 mV. The first end point corresponds to strong bases (HNP : 350 mV) and the second end point is due to weak bases (HNP : 600 mV). Figure 4.13 shows the titration curve obtained for a pure asphaltene sample. The pure asphaltene titrations indicated the presence of strong basic compounds of the pyridine type ranging from 0.06 mM/g for AH5

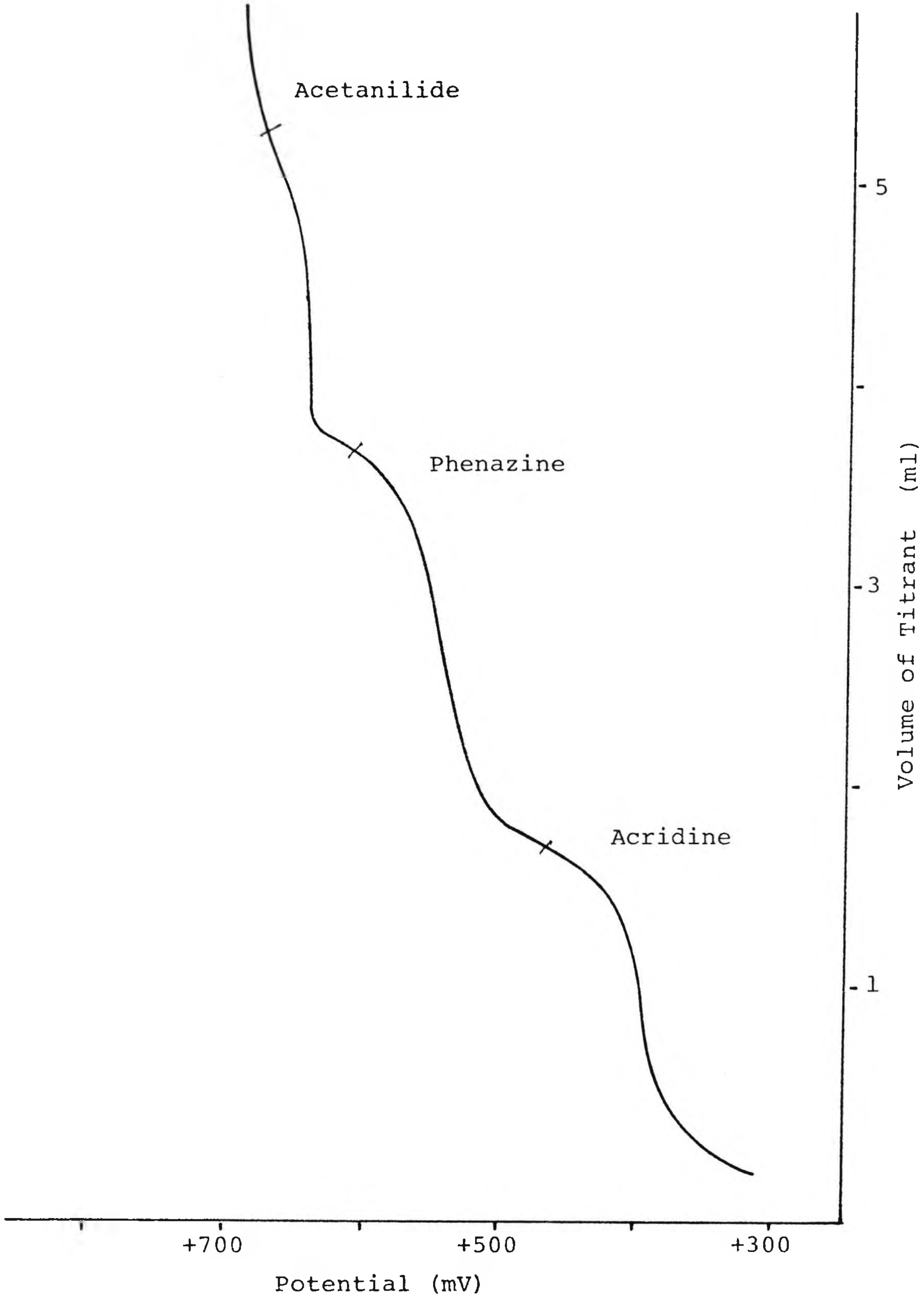

Fig 4.12 : Nonaqueous potentiometric titration curve for a mixture containing three bases: acridine, phenazine and acetanilide in chlorobenzene and acetic anhydride.

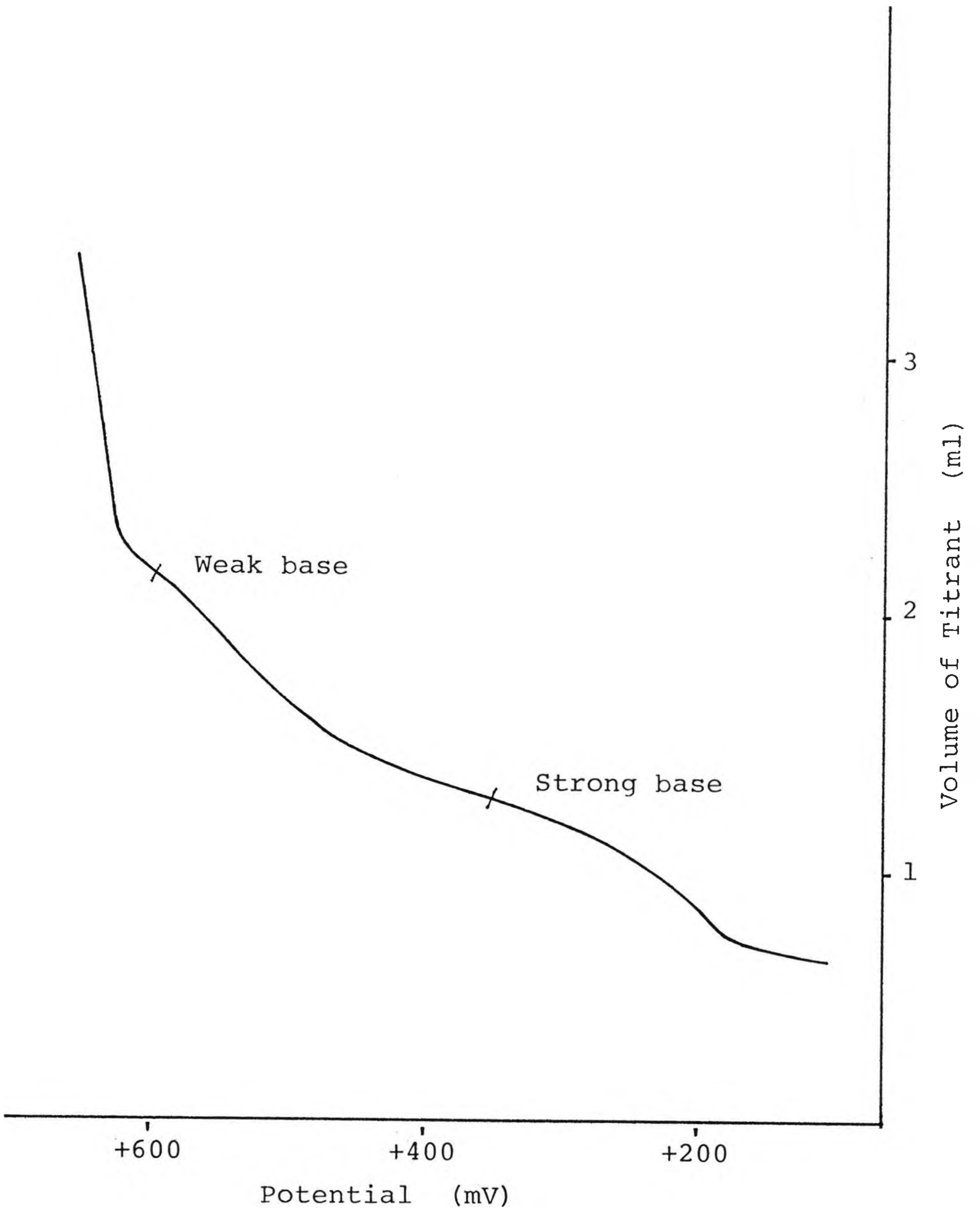

Fig 4.13 : Nonaqueous potentiometric titration curve for pure asphaltene in chlorobenzene and acetic anhydride.

asphaltenes to 0.11 mM/g for AH10 asphaltenes (Table 4.17). Darlage et al. (1978) have reported the presence of about 50% of the total nitrogen in coal-derived asphaltenes being in the form of pyridine or aniline type structures, which correspond to pK_a values between 4.5 and 6.7. The weak bases at $pK_a \approx 0\text{-}2$ are due to phenazine or caffeine groups and range from 0.16 mM/g to 0.19 mM/g of asphaltene.

The asphaltene samples spiked with known amounts of very weak base (acetanilide), weak base (phenazine) and strong base (acridine) were also titrated with perchloric acid to determine the amounts of bases in the asphaltenes that titrate along with each of these model basic compounds. This procedure defines both the strength and the amount of bases in the samples titrated. A typical titration curve obtained for asphaltene spiked with known amounts of bases is shown in Figure 4.14. The amounts of the different classes of bases titrated in the presence of model basic compounds for different asphaltenes are shown in Table 4.18. The differences in the amounts of strong and weak bases obtained by the titration of pure asphaltenes (Table 4.17) and for the spiked asphaltenes (Table 4.18) are insignificant.

Spiking experiments have shown that the AH crude asphaltenes contain very weak bases, which are due to amide and indole type functionalities, corresponding to pK_a values less than zero. The amounts of very weak bases vary from 0.25 mM/g for AH5 asphaltenes to 0.30 mM/g for AH10 asphaltenes . Total titratable bases

	BASES TITRATED AS	
ASPHALTENE	WEAK BASE (mM/g)	STRONG BASE (mM/g)
AH5	0.16	0.06
AH6	0.16	0.07
AH7	0.17	0.08
AH8	0.18	0.08
AH9	0.18	0.10
AH10	0.19	0.11

Table 4.17 : Potentiometric titration of pure asphaltenes.

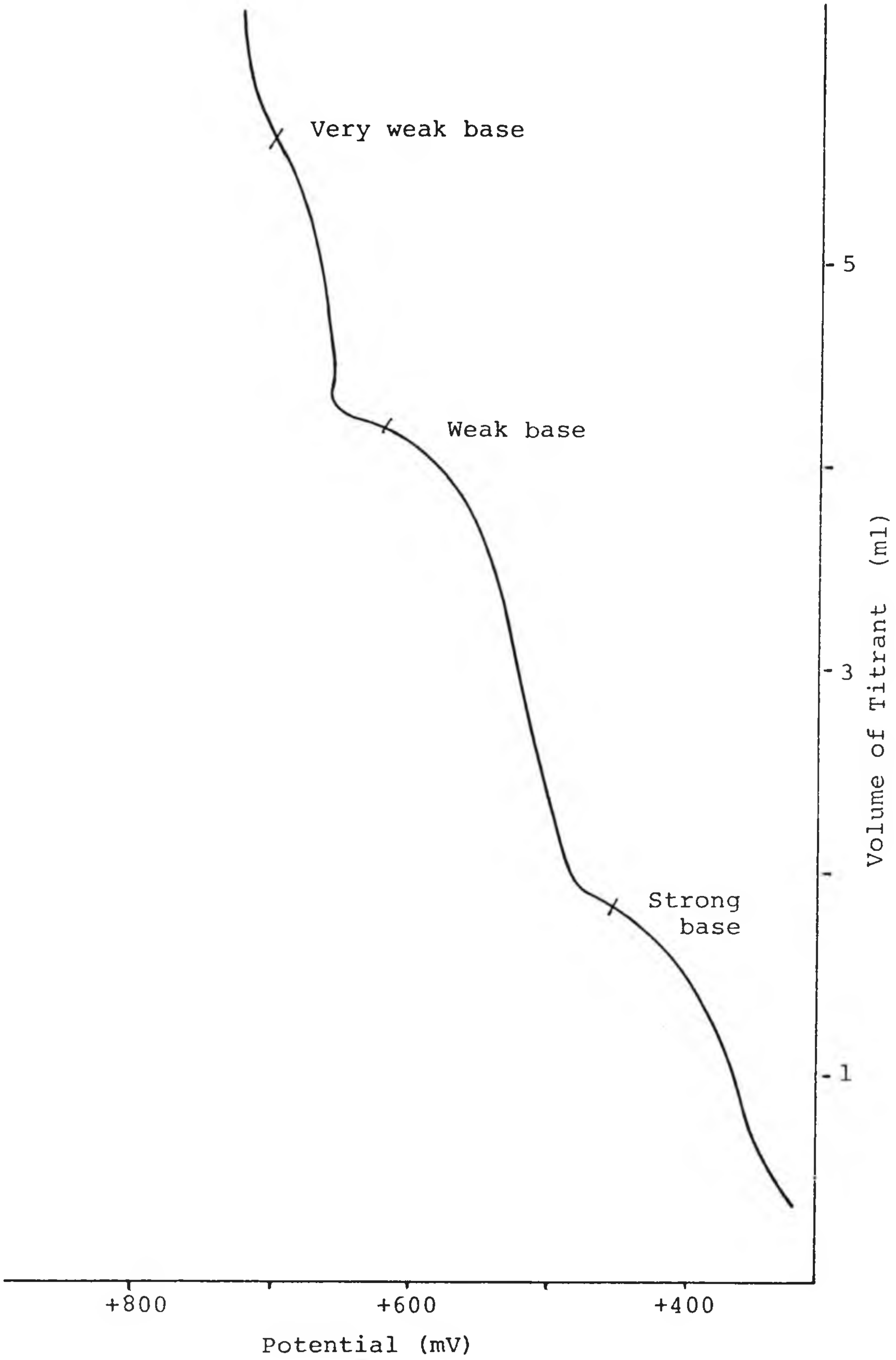

Fig 4.14 : Nonaqueous potentiometric titration curve for asphaltene spiked with known amounts of acridine, phenazine and acetanilide in chlorobenzene and acetic anhydride.

ASPHALTENE	BASES (mM/g of asphaltene) TITRATED IN THE PRESENCE OF		
	ACETANILIDE	PHENAZINE	ACRIDINE
AH5	0.25	0.17	0.07
AH6	0.27	0.17	0.07
AH7	0.27	0.17	0.08
AH8	0.28	0.19	0.09
AH9	0.30	0.18	0.10
AH10	0.30	0.19	0.11

Table 4.18 : Potentiometric titration of asphaltenes spiked with known model basic compounds.

were found to be 0.49 mM/g for AH5 asphaltenes and 0.60 mM/g for AH10 asphaltenes .

4.9 Fourier Transform Infrared Spectroscopy of Asphaltenes

Fourier transform infrared (FT-IR) spectroscopy provides important information concerning the functional groups and their structural features in asphaltene molecules. Figures 4.15 and 4.16 show the FT-IR spectra of AL5, AH5, AH7 and AH10 asphaltenes in the frequency range 4000-2000 cm^{-1} and 2000-600 cm^{-1}, respectively. The assignment of the observed vibrational bands was based on published data for petroleum- and coal-derived asphaltenes (Yen et al., 1984; Moschopedis and Speight, 1976a; Malhotra and Crelling, 1987). The region of 3500-3100 cm^{-1} is characteristic of hydrogen bonded groups. The spectra of the four asphaltenes (Figure 4.15) do not show sharp and well resolved peaks in this region. A very weak band around 3440 cm^{-1} was attributed to hydroxyl (-OH) groups and N-H vibrations. The absence of a sharp peak at 3610 cm^{-1} indicated the absence of free OH groups from all four asphaltenes . A very weak notch at around 3480 cm^{-1} in the spectra of AH7 and AH10 asphaltenes corresponds to the N-H stretching vibration of pyrrolic groups. The AL5 and AH5 asphaltenes , which are low in nitrogen content, showed comparatively very weak absorption in this region. This indicated that AH7 and AH10 asphaltenes contain higher amounts of pyrrolic groups.

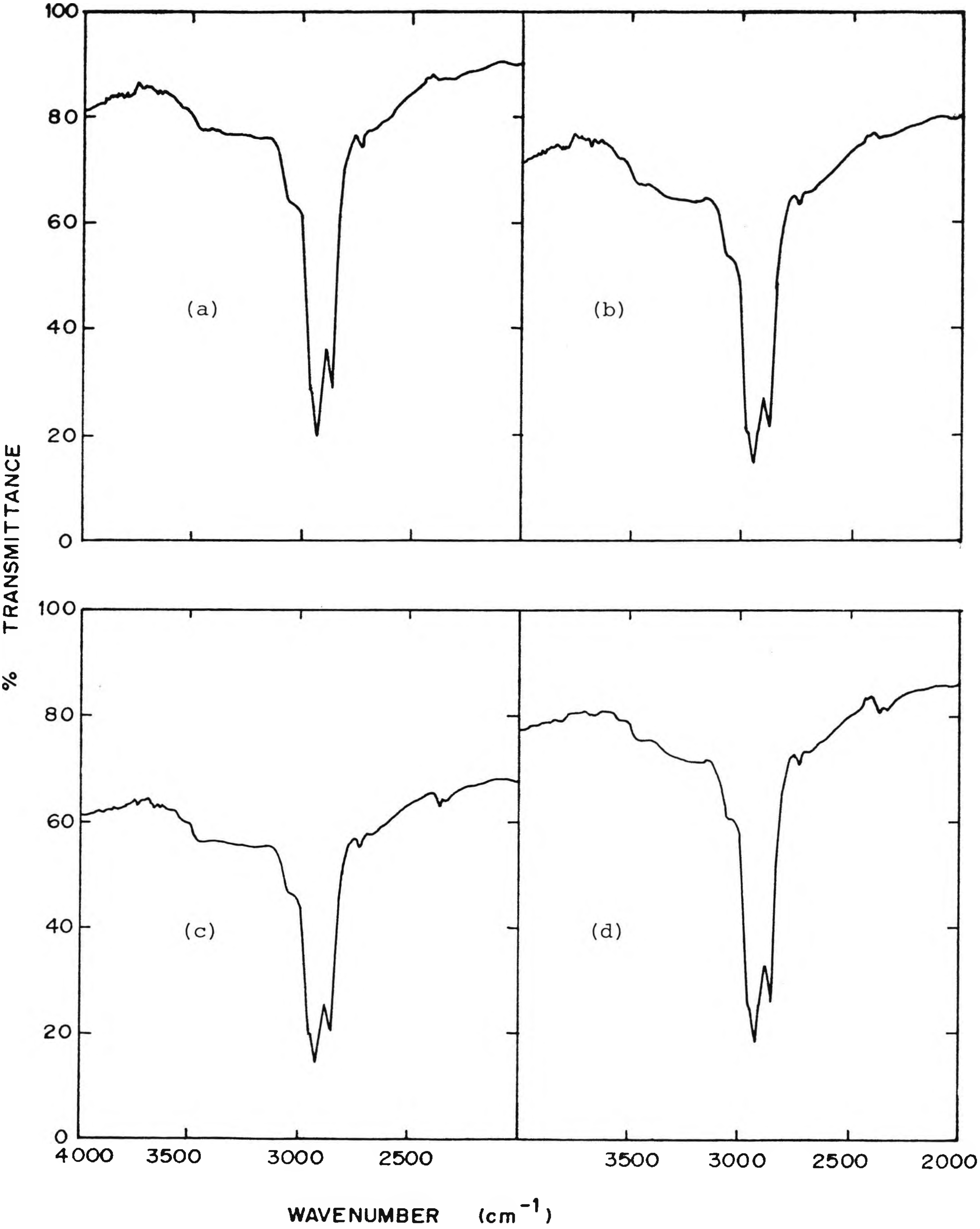

Figure 4.15 : FT-IR spectra of (a) AL5 ; (b) AH5 ; (c) AH7 and (d) AH10 asphaltenes in the frequency range 4000-2000 cm^{-1}.

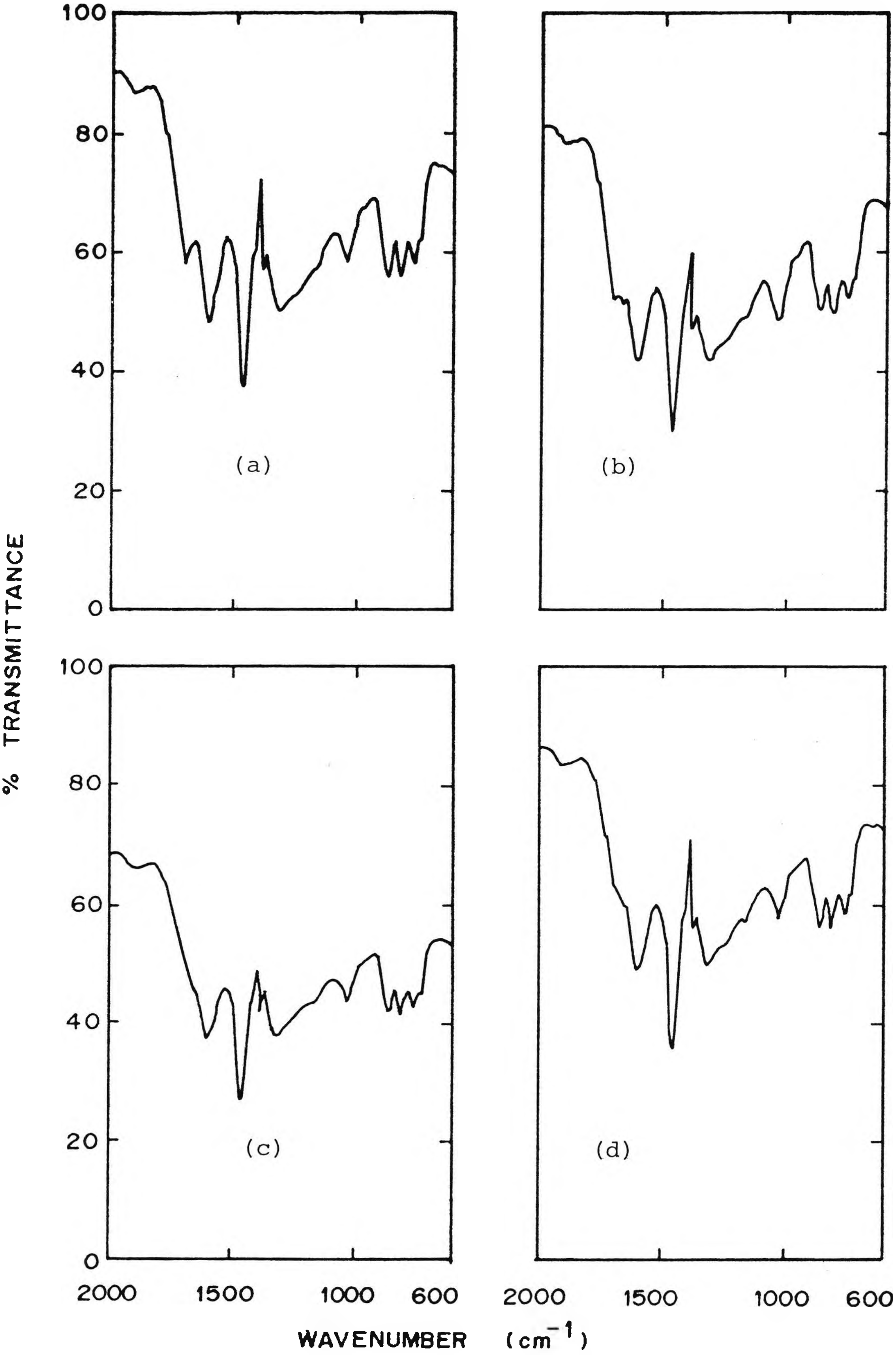

Figure 4.16 : FT-IR spectra of (a) AL5 ; (b) AH5 ; (c) AH7 and (d) AH10 asphaltenes in the frequency range 2000-600 cm^{-1}.

The spectra of all four asphaltenes showed a group of bands between 3050 cm^{-1} and 2800 cm^{-1}, particularly two distinct absorption peaks at 2855 cm^{-1} and 2920 cm^{-1} and a shoulder at 2970 cm^{-1}. These bands result from the C-H asymmetric and symmetric stretching modes of vibration, respectively. A very small peak at 2717 cm^{-1} in all of the spectra was ascribed to dimers of carboxylic acid present.

Weak, broad bands in the region of 2000 - 1800 cm^{-1} (Figure 4.16), were attributed to overtone absorption bands. Overtone bands are characteristic of highly aromatic polycondensed compounds containing long-chain substituents. A small peak at 1700 cm^{-1} in the spectrum of AL5 asphaltenes was due to the C=0 stretch of aldehyde and ketone groups. This peak appeared as a shoulder in the spectrum of AH5 asphaltenes and almost disappeared from the spectra of AH7 and AH10 asphaltenes . This suggests that the AL5 asphaltenes have the highest amount of oxygen-containing functions such as aldehyde and ketone.

All of the IR spectra showed an intense, fairly sharp peak in the 1590-1600 cm^{-1} region, which is characteristic of the stretching vibration of the carbon-carbon bonds in aromatic systems. It is believed that some oxygen-containing groups also contribute to the intensity of the 1600 and 1610 cm^{-1} bands. A small peak at 1380 cm^{-1} was observed in the spectra of all four asphaltenes . According to Yen and Erdman (1962), this absorption band is due to C-H symmetrical bending vibrations of methyl groups.

A weak absorption band in the region 1032-1034 cm^{-1}, which results from the aliphatic C-O stretching vibration, indicated the presence of ether linkages in all four asphaltenes . Absorption bands in the low frequency region at 865, 812 and 756 cm^{-1} and a small shoulder at 747 cm^{-1} are mainly due to HCC (hydrogen-carbon-carbon) rocking vibrations (Brown et al., 1977).

4.10 Nuclear Magnetic Resonance Spectroscopy of Asphaltenes

4.10.1 Proton NMR Spectroscopy of Asphaltenes

The proton NMR spectra of AL5, AH5, AH7 and AH10 asphaltenes recorded at 200 MHz are shown in Figures 4.17 to 4.20. The spectra do not show sharply defined peaks characteristic of pure compounds, but they consist mainly of featureless envelopes resulting from a large range of chemical shifts and complicated spin-spin couplings. The basis of quantitative analysis of such spectra is dependent upon the resonances which are characteristic of different functional groups being sufficiently separated from each other and upon the fact that under certain conditions different concentrations of different nuclei contribute to the resonances. The different types of protons producing resonances in the proton NMR spectra of asphaltenes which are defined (relative to tetramethylsilane) by the chemical shift ranges : aliphatic protons (H_{al}), δ : 0.5 - 4.0 ppm and aromatic protons (H_{ar}), δ : 6.0 - 9.0 ppm are shown in Table 4.19. The aliphatic region has been further sub-divided into H_α, H_β, and

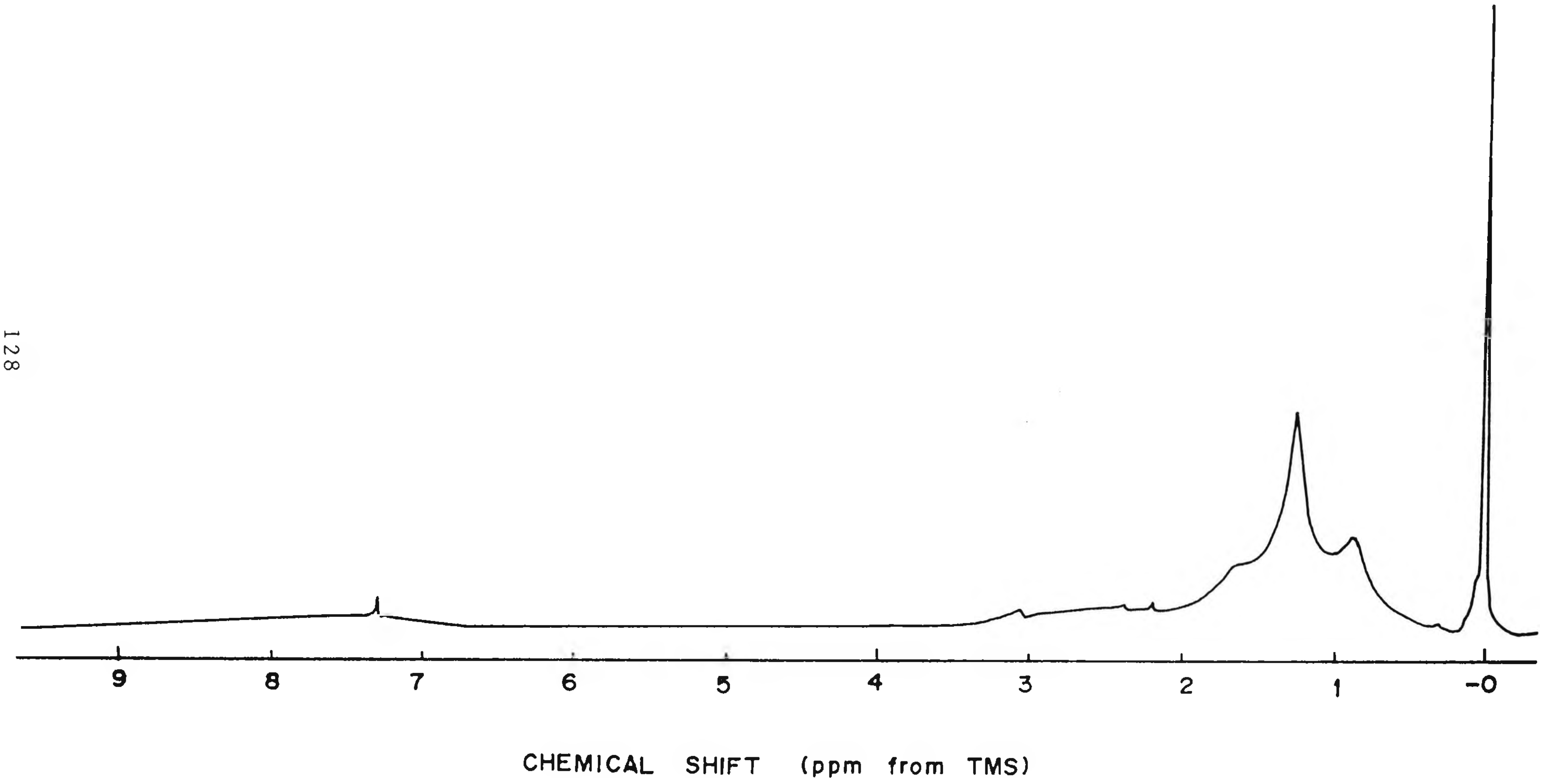

Figure 4.17 : Proton NMR spectrum of AL5 asphaltene

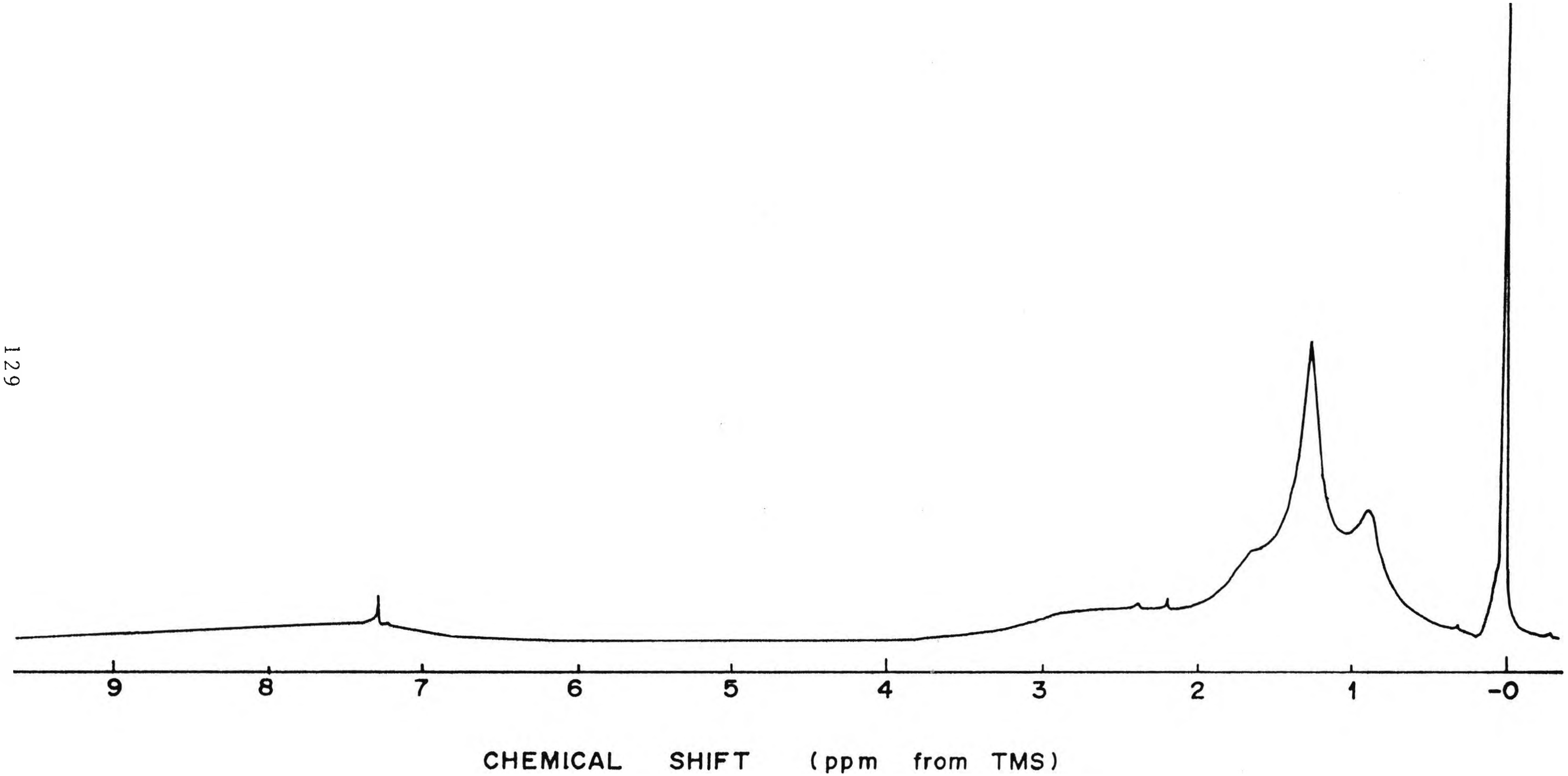

Figure 4.18 : Proton NMR spectrum of AH5 asphaltene

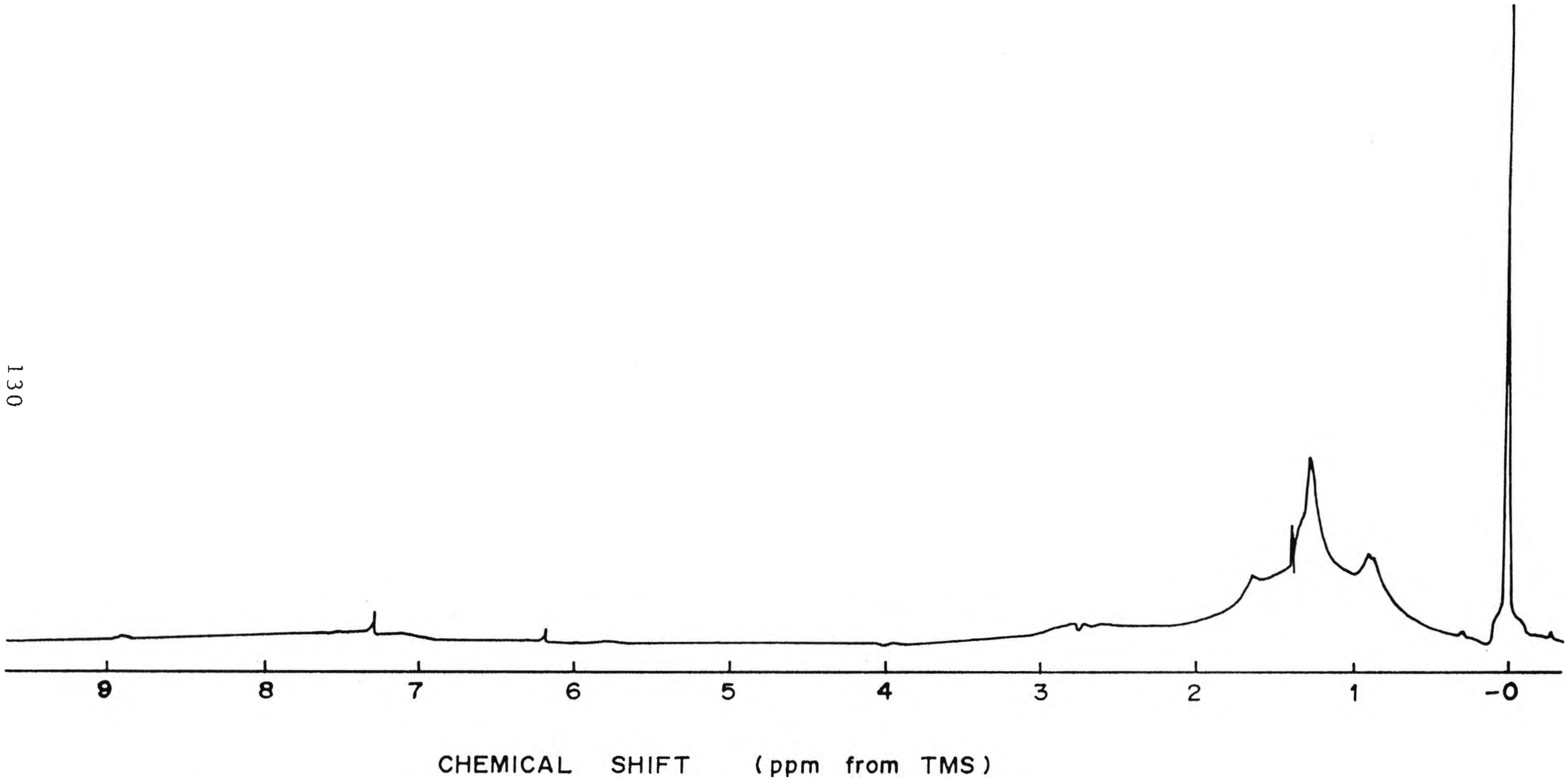

Figure 4.19 : Proton NMR spectrum of AH7 asphaltene

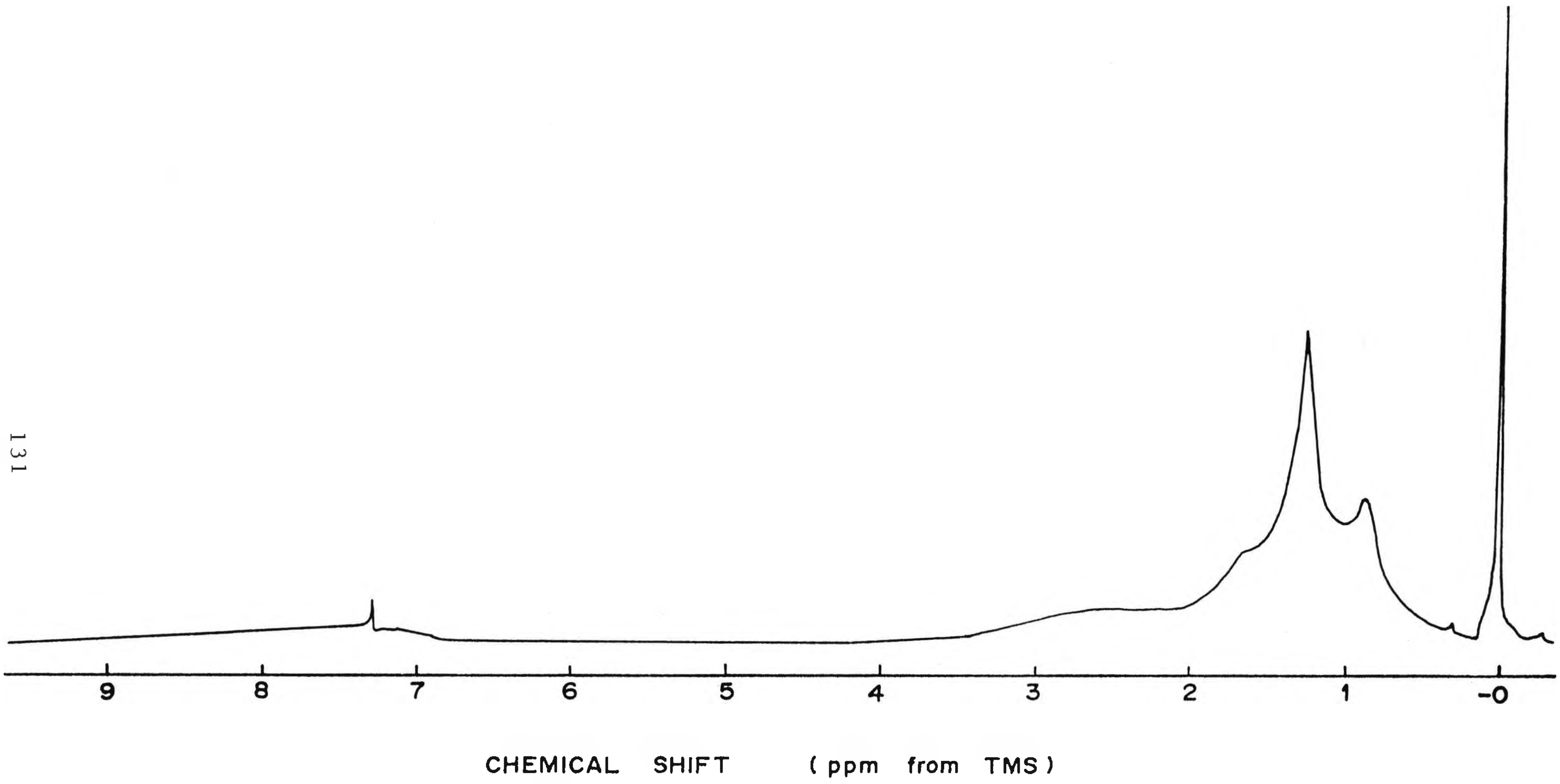

Figure 4.20 : Proton NMR spectrum of AH10 asphaltene

SYMBOL	PARAMETER	CHEMICAL SHIFT PPM FROM TMS
H_{ar}	Fraction of aromatic hydrogen	6.0-9.0 ppm
H_{al}	Fraction of aliphatic hydrogen	0.5-4.0 ppm
H_α	Fraction of aliphatic hydrogen α to an aromatic ring	2.0-4.0 ppm
H_β	Fraction of aliphatic hydrogen β to an aromatic ring	1.0-2.0 ppm
H_γ	Fraction of aliphatic hydrogen γ to an aromatic ring	0.5-1.0 ppm
C_{al}	Fraction of aliphatic carbon	0.0-70.0 ppm
C_{ar}	Fraction of aromatic carbon	110-160 ppm
C%	Percent carbon	-
H%	Percent hydrogen	-
E_{1380}	Absorbance at 1380 cm^{-1} in IR spectra	-
E_{2920}	Absorbance at 2920 cm^{-1} in IR spectra	-
x	Hydrogen-carbon atomic ratio of alkyl substituents	- -
MWt	Molecular weight (VPO, toluene at 60°C)	- -

Table 4.19 : Symbols for and definitions of input parameters for the calculation of average molecular parameters for asphaltenes .

H_γ protons according to published reports (Retcofsky and Friedel, 1970; Takegami et al., 1980; Chamberlain, 1974). H_α (δ : 2.0-4.0 ppm) are the protons attached to a saturated carbon in the α position with respect to an aromatic ring; H_β (δ : 1.0-2.0 ppm) are the protons of paraffinic methylenes and methines, naphthenes, methylene groups β or further from an aromatic ring and methyls β to an aromatic ring and H_γ (δ : 0.5-1.0 ppm) are the protons of paraffinic methyls or methyls in the γ position or further removed from an aromatic ring. The H_α contribution is a sum of the individual contributions from methyl groups and hydrogens from α-carbons of alkyl groups. The olefinic protons were ignored, since none of the samples produced significant resonances in the olefinic region (δ: 4.0 - 6.0 ppm).

The integrated total aliphatic hydrogen (H_{al}) and aromatic hydrogen (H_{ar}) intensities were normalized over the complete spectrum (δ: 0.5-9.0 ppm). The precision of the measurement of the aromatic hydrogen intensities (H_{ar}) was determined for three repeated runs on the AH7 asphaltenes. The standard deviation was found to be ± 0.01 i.e. 1%. The fractions of hydrogen as H_{al}, H_{ar}, H_α, H_β and H_γ determined for AL5, AH5, AH7 and AH10 asphaltenes are reported in Table 4.20. The AL5 asphaltenes showed the highest fraction of aromatic hydrogen (0.235). Among the three AH asphaltenes , a gradual decrease in the fraction of aromatic hydrogen was noted from the lowest alkane precipitated asphaltenes to the highest alkane precipitated asphaltenes . This indicates that the aromatic structures in

PARAMETER	ASPHALTENE AL5	AH5	AH7	AH10
H_{ar}	0.235	0.194	0.172	0.150
H_{al}	0.765	0.806	0.828	0.850
H_{α}	0.173	0.184	0.189	0.191
H_{β}	0.442	0.466	0.474	0.488
H_{γ}	0.150	0.156	0.165	0.171
C_{al}	0.395	0.424	0.425	0.45
C_{ar}	0.605	0.576	0.575	0.55
C%	82.37	82.38	82.15	81.39
H%	7.85	7.65	7.40	7.30
MWt	6250	7150	8950	13500
E_{1380}	0.2426	0.3279	0.3788	0.2526
E_{2920}	0.71	0.8327	0.8416	0.7423
x	2.24	2.27	2.29	2.24

Table 4.20 : Experimental input data for the calculation of average molecular parameters for asphaltenes.

the higher alkane precipitated asphaltenes are comparatively more condensed and highly substituted. The fraction of aliphatic hydrogen (H_{al}), which is the lowest for the AL5 asphaltenes , increases from 0.806 for AH5 asphaltenes to 0.85 for the AH10 asphaltenes . Similarly, H_α, H_β and H_γ are also higher for the higher alkane precipitated asphaltenes . Among the three types of aliphatic hydrogen (H_α, H_β and H_γ), the H_β constitutes the major portion of the aliphatic hydrogens for all four asphaltenes . The higher values of H_β for the higher alkane precipitated asphaltenes indicate an increase in the chain length of the paraffin and the presence of alkyl groups attached to an aromatic group in the higher alkane precipitated asphaltenes .

4.10.2 ^{13}C NMR Spectroscopy of Asphaltenes

A typical ^{13}C NMR spectrum of asphaltene isolated from Arab Heavy 370°C+ residue, recorded at 50.3 MHz, is shown in Figure 4.21. The ^{13}C NMR spectra of asphaltenes were divided into an aliphatic region (δ : 0.0 - 70 ppm) and an aromatic region (δ : 110 - 160 ppm), according to Moekawa et al. (1979) and Snape et al. (1979). Each of these regions can be further sub-divided into various types of aliphatic carbon and aromatic carbon. The aliphatic region of the spectra showed some small peaks at 14.1, 22.9, 29.7 and 32.2 ppm, which are characteristic of α,β,γ and δ or further removed carbons respectively in a long paraffinic chain (Takegami et al., 1980). A relatively sharp peak at 29.7 ppm indicated the presence of a large amount of methylene groups in a long straight chain, e.g.

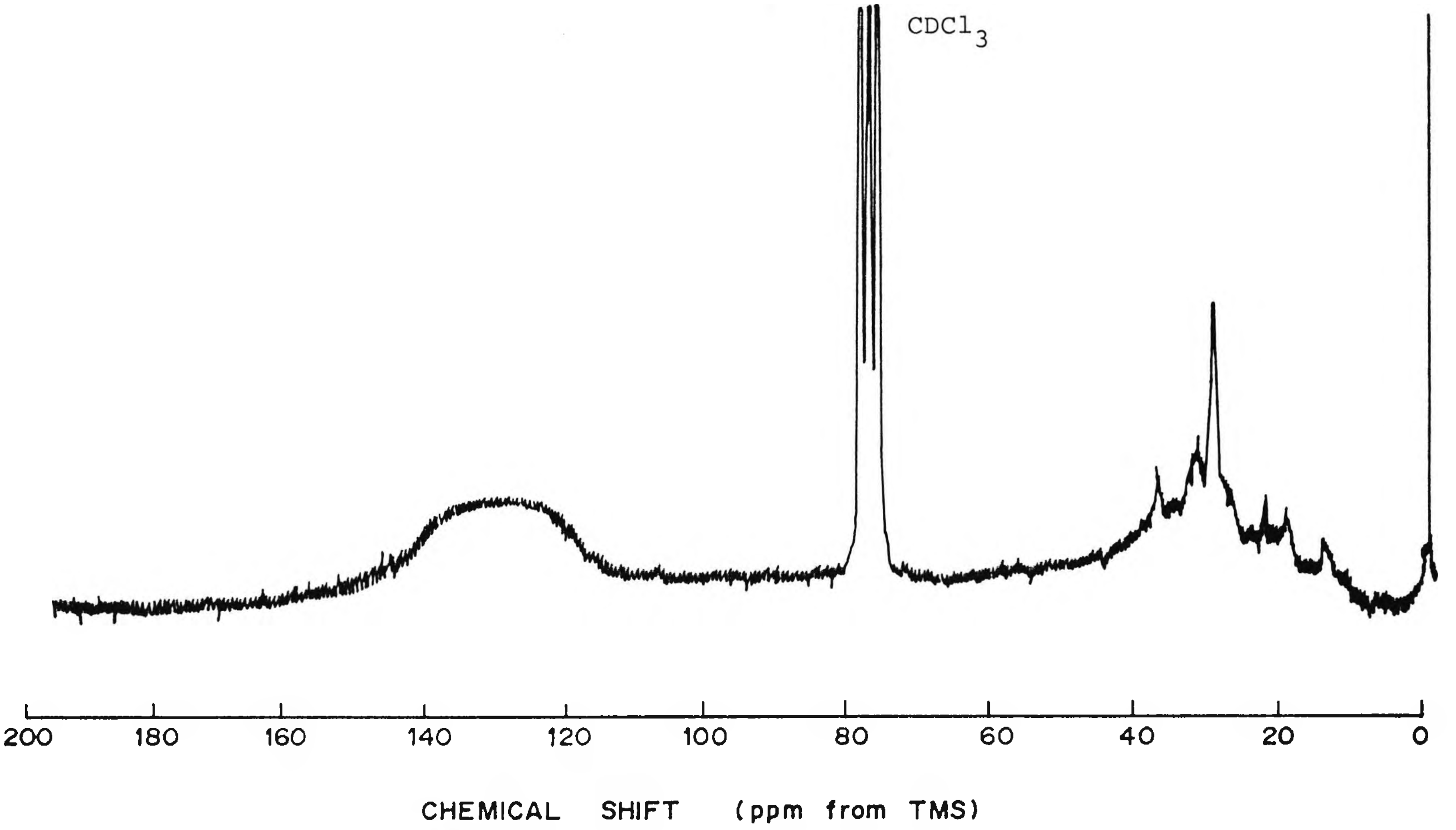

Figure 4.21 : A typical ^{13}C NMR spectrum of asphaltene isolated from Arab Heavy 370°C+ residue.

$CH_3-CH_2-CH_2-(\underline{C}H_2)_n-CH_2-CH_2$. The aromatic regions of all the ^{13}C NMR spectra were characterized by a broad featureless peak (δ : 110-160 ppm), indicating overlapping due to various types of aromatic carbon. The aromatic region can be further sub-divided into several parts (Takegami et al., 1980; Gillet et al., 1981 and Yokoyama et al., 1979), including carbon attached to hydrogen (110-130 ppm), carbon attached to methyl groups (129-137.5 ppm) and carbon attached to alkyl groups, other than methyl (137.5-160 ppm). As the characteristic peaks in the aliphatic region of the ^{13}C NMR spectra of asphaltenes were broadened, it was difficult to integrate different peaks for different types of aliphatic carbon. Similarly, the aromatic region has not been integrated for different types of aromatic carbon. However, the whole spectra were integrated for total aliphatic carbon (C_{al}) and total aromatic carbon (C_{ar}). The fractions of carbon appearing as aliphatic and aromatic carbon for AL5, AH5, AH7 and AH10 asphaltenes are given in Table 4.20. The AL5 asphaltene contains the lowest fraction of aliphatic carbon (0.395), whereas for AH5, AH7 and AH10 asphaltenes , C_{al} was found to be 0.424, 0.425 and 0.45, respectively. Consequently, the AL5 asphaltene contains the highest fraction of aromatic carbon (0.605).

4.10.3 Calculation of Average Molecular Parameters for Asphaltenes

Experimental data obtained for asphaltenes from elemental analysis, molecular weight determination, infrared spectroscopy and proton and ^{13}C NMR spectroscopy have been used to compute the average molecular parameters for asphaltenes . The following two combinations of analytical techniques were used:

(i) Infrared spectroscopy, proton NMR spectroscopy, elemental analysis and molecular weight determination (IR/proton NMR method)

(ii) Proton and ^{13}C NMR spectroscopy, elemental analysis and molecular weight determination (proton NMR/ ^{13}C NMR method).

The input data required for the calculation of average molecular parameters for asphaltenes are given in Table 4.20. The heteroatoms such as oxygen, nitrogen and sulphur were not considered in the calculations in order to simplify the average structure.

The equations used to calculate the average molecular parameters by the IR/proton NMR method are presented in Table 4.21. The value of x, which is the hydrogen-carbon atomic ratio of methyl and methylene (MMHC) groups on substituted aliphatic side chains, was calculated by the following method, as proposed by Haley (1972):

$$\text{MMHC} = \frac{\dfrac{W_{CH_3}}{5} + \dfrac{W_{CH_2}}{7}}{\dfrac{W_{CH_3}}{15} + \dfrac{W_{CH_2}}{14}}$$

where:

W_{CH_3} = amount of methyl

SYMBOL	AVERAGE PARAMETER	EQUATION
C_t	Total carbons per average molecule	$C\%.MWt/12$
x	Hydrogen-carbon atomic ratio of alkyl substituents	Calculated from IR spectra
f_a	Aromaticity index	$\frac{C/H-(H_\alpha+H_\beta+H_\gamma)/x}{C/H}$
SI	Substitution index	$\frac{H_\alpha/x}{H_\alpha/x + H_{ar}}$
C_a	Aromatic carbons per average molecule	$f_a.C_t$
C_p	Peripheral carbons in aromatic nucleus per average molecule	$(\frac{H_\alpha}{x} + H_{ar}).H\%.MWt.$
C_p/C_a	Condensation index	$\frac{H_\alpha/x + H_{ar}}{C/H-(H_\alpha+H_\beta+H_\gamma)/x}$
RA	Aromatic rings per average molecule	$\frac{C_a - C_p}{2} + 1$
RT	Total rings per average molecule	$\frac{C_t\ (2-H/C - f_a)}{2} + 1$
RN	Naphthenic rings per average molecule	RT - RA
n	Alkyl substituents on aromatic nucleus per average molecule	$\frac{H_\alpha}{x}\ .\ H\%.MWt.$
ℓ	Average carbons per alkyl side chain	$\frac{H_\alpha + H_\beta + H_\gamma}{H_\alpha}$

Table 4.21 : Equations used for the calculation of average molecular parameters for asphaltenes from IR and proton NMR spectroscopy.

W_{CH_2} = amount of methylene

constants = atomic weights.

The values of x (MMHC) were computed from the relative intensity values of methyl (1380 cm^{-1}) and methylene (2920 cm^{-1}) absorptions in the FT-IR spectra of asphaltenes , using a base-line technique. The equations used to calculate the aromaticity index (f_a), the substitution index (SI) and the condensation index (C_p/C_a) are those given by Brown and Ladner (1960). The equation used to calculate the total number of rings (RT) is that given by Takeya et al. (1964). The average molecular parameters computed for AL5, AH5, AH7 and AH10 asphaltenes by the IR/proton NMR method are given in Table 4.22. The data indicate that AL5 asphaltenes consist of the lowest number of carbon atoms, whereas for the AH asphaltenes , the value of C_t increases from 491 for AH5 to 943 for the AH10 asphaltenes . The aromaticity index (f_a) for all four asphaltenes is of the same order. The substitution index (SI) increases from 0.29 for AH5 asphaltenes to 0.36 for AH10 asphaltenes . The numbers of total rings (RT) and aromatic rings (RA) are found to increase with an increase in the carbon number of the precipitating alkane solvent. However, the values of RT for AH5, AH7 and AH10 asphaltenes are less than the corresponding values of RA, and consequently the values for the number of naphthenic rings (RN = RT - RA) obtained for AH5, AH7 and AH10 asphaltenes are unrealistic. The number of alkyl substituents on the aromatic nucleus per average molecule (n) and the average number of carbons per alkyl side chain (ℓ) have also

AVERAGE MOLECULAR PARAMETER	ASPHALTENE			
	AL5	AH5	AH7	AH10
C_t	429	491	613	943
x	2.24	2.27	2.29	2.24
f_a	0.60	0.61	0.61	0.59
SI	0.23	0.29	0.32	0.36
C_a	257	299	374	556
C_p	153	150	169	239
C_p/C_a	0.60	0.50	0.43	0.43
RA	53	75	103	159
RT	56	69	95	158
RN	3	-	-	-
n	37.9	44.3	54.7	86.5
ℓ	4.42	4.38	4.38	4.45

Table 4.22 : Average molecular parameters for asphaltenes calculated from IR and proton NMR spectra.

shown a tendency to increase from the lower alkane precipitated asphaltenes (AH5) to the higher alkane precipitated asphaltenes (AH10).

The equations used to calculate the average molecular parameters by the proton NMR / ^{13}C NMR method are presented in Table 4.23. The equations are those given by Knight (1967), Seshadri (1982) and Dickinson (1980). The average molecular parameters computed for AL5, AH5, AH7 and AH10 asphaltenes are given in Table 4.24. The results indicate that the carbon-hydrogen ratios of total alkyl groups (f_c) range from 5.42 for AL5 to 6.28 for AH10 asphaltenes . The value of x obtained for AH10 asphaltenes (2.03) is very close to the Brown-Ladner assumption, x = 2 (Brown and Ladner, 1960). The percentage of aromatic carbon (CA%), the percentage of unsubstituted aromatic carbon (CUS%), and the percentage of non-bridge aromatic carbon (CNB%) have decreased with an increase in the carbon number of the precipitating solvent. The percentage of substituted aromatic carbon (CS%) is the lowest (7.35) in AL5 asphaltenes and the highest (8.23) in the higher alkane precipitated, higher molecular weight AH10 asphaltenes. The numbers of aromatic rings (RA) and naphthenic rings (RN) are highest in the AH10 asphaltenes. The numbers of aliphatic hydrogen and aliphatic carbon are also significantly higher in the AH10 asphaltenes.

The average molecular parameters calculated by the two methods are compared in Table 4.25. The data indicate that the average molecular parameters for AL5 asphaltenes calculated by the IR/proton NMR method are equal or very close to the corresponding parameters

SYMBOL	AVERAGE PARAMETER	EQUATION
ℓ	Average carbons per alkyl side chain	$\frac{H_\alpha + H_\beta + H_\gamma}{H_\alpha}$
f_c	Carbon-hydrogen weight ratio of total alkyl groups	$\frac{C\%.C_{al}}{H\%.H_{al}}$
x	Hydrogen-carbon atomic ratio of alkyl groups	$12/f_c$
CA%	Percentage aromatic carbon	$C\%.C_{ar}$
CS%	Percentage substituted aromatic carbon	$C\%.C_{al}/\ell$
CUS%	Percentage unsubstituted aromatic carbon	$12\ H_{ar}.H\%$
CNB	Percentage non-bridge aromatic carbon	CS% + CUS%
C_a	Aromatic carbons per average molecule	CA%.MWt/12
C_p	Aromatic non-bridge carbons per average molecule	CNB%.MWt/12
RA	Aromatic rings per average molecule	$\frac{C_a - C_p}{2} + 1$
AS%	Percentage substitution of aromatic rings	CS%/CNB%
n	Alkyl substituents per average molecule	$AS\%\ .\ C_p$
RN	Naphthenic rings per average molecule	$n(\ell+\frac{1}{2}-6\ell/f_c)$
C_{al}	Aliphatic carbons per average molecule	$\ell.n.$
H_{al}	Aliphatic hydrogens per average molecule	$\ell.n.x.$

Table 4.23 : Equations used for the calculation of average molecular parameters for asphaltenes from proton and ^{13}C NMR spectroscopy.

AVERAGE MOLECULAR PARAMETER	ASPHALTENE			
	AL5	AH5	AH7	AH10
ℓ	4.42	4.38	4.38	4.45
f_c	5.42	5.66	5.7	6.28
x	2.21	2.12	2.10	2.03
CA%	49.8	47.5	47.2	44.8
CS%	7.35	7.97	7.97	8.23
CUS%	22.1	17.8	15.3	13.1
CNB%	29.4	25.8	23.3	21.3
C_a	258	282	352	504
C_p	153	154	174	240
C_p/C_a	0.59	0.54	0.49	0.48
RA	53.5	65	90	133
AS%	0.25	0.31	0.34	0.39
n	38.3	47.7	59.2	93.6
RN	1.1	11.4	16.0	65.5
C_{al}	169	209	259	416
H_{al}	374	443	544	845

Table 4.24 : Average molecular parameters for asphaltenes calculated from proton and ^{13}C NMR spectra.

AVERAGE MOLECULAR PARAMETER (*)	ASPHALTENE							
	AL5		AH5		AH7		AH10	
	IR & Proton NMR	Proton & ^{13}C NMR	IR & Proton NMR	Proton & ^{13}C NMR	IR & Proton NMR	Proton & ^{13}C NMR	IR & Proton NMR	Proton & ^{13}C NMR
x	2.24	2.21	2.27	2.12	2.29	2.10	2.24	2.03
f_a	0.60	0.60	0.61	0.58	0.61	0.57	0.59	0.55
SI	0.23	0.25	0.29	0.31	0.32	0.34	0.36	0.39
C_a	257	258	299	282	374	352	556	504
C_p	153	153	150	154	169	174	239	240
C_p/C_a	0.60	0.59	0.50	0.54	0.43	0.49	0.43	0.48
RA	53	53	75	65	103	90	159	133
RT	56	54	69	76	95	107	158	198
RN	3	1.1	-	11.4	-	16	-	65.5
n	37.9	38.3	44.3	47.7	54.7	59.2	86.5	93.6
C_{al}	172	169	192	209	239	259	387	416
H_{al}	375	374	440	443	539	544	862	845

(*) For explanation of the symbols, refer to Tables 4.21 and 4.23.

Table 4.25 : Comparison of the main molecular parameters for asphaltenes calculated from IR/proton NMR and proton NMR/^{13}C NMR spectra.

calculated by the proton NMR/ ^{13}C NMR method. However, the parameters obtained for AH5, AH7 and AH10 asphaltenes do not show close agreement for the two spectroscopic methods. Some of the values of the parameters x, f_a, C_a and RA, calculated by the IR/proton NMR method, are higher than the corresponding values derived from the proton NMR/ ^{13}C NMR method, whereas the values of other parameters such as SI, C_p, C_p/C_a, RT, n, C_{al} and H_{al}, calculated by the IR/proton NMR method, are lower than the corresponding values calculated by the proton NMR/ ^{13}C NMR method. The differences in the average molecular parameters calculated by the two spectroscopic methods are higher for the higher alkane precipitated, higher molecular weight AH10 asphaltenes , as compared to the lower alkane precipitated, lower molecular weight AH5 asphaltenes .

The values of the average molecular parameter RN, the number of naphthenic rings including methylene bridges, show the greatest disagreement between the two methods. The values of RN obtained by the IR/proton NMR method were found to be less than zero, whereas by the proton NMR/ ^{13}C NMR method the values of RN were 11.4, 16 and 65.5 for AH5, AH7 and AH10 asphaltenes , respectively. The value of RN obtained by the IR/proton NMR method is the difference between the values of RT and RA (Table 4.21) and hence, either the value of RT or RA seems to be incorrect. Also, the equation used to calculate the parameter RN by the proton NMR/ ^{13}C NMR method (Table 4.23) has been shown to introduce a large error in its value (Cantor, 1978; Dickinson, 1980). Therefore, the value of this particular parameter should be regarded only as an estimate. It has been suggested that proton coupled ^{13}C NMR spectroscopy, which involves no assumptions, is the most precise method for calculating average molecular parameters for petroleum heavy fractions (Takegami et al. 1980; Suzuki et al., 1982).

From the foregoing structural analysis, a knowledge of the gross structural differences between the different asphaltenes has been obtained.

5. SUMMARY AND CONCLUSIONS

The results of this study may be summarised as follows:

(i) The precipitation and isolation of asphaltenes from the crude oil are the first steps toward the structural characterization of this complex fraction of petroleum. In the present study, asphaltenes were precipitated from Saudi Arabian Heavy crude oil by the use of different solvent-to-oil ratios and also by the use of different carbon number alkane solvents to investigate the effect of these important parameters on the yields of asphaltenes . Equal amounts of purified asphaltenes were obtained from Arab Heavy (AH) crude oil by the use of twenty, forty and sixty fold volumes of normal heptane solvent. The precipitation of asphaltenes by the use of different carbon number alkane solvents (nC_5 - nC_{10}) showed that the yields of asphaltenes decrease with an increase in the carbon number of the precipitating alkane solvent. For example, the yield of asphaltenes obtained by the use of normal pentane as solvent was found to be 12.2 wt.%, whereas for normal decane solvent, it was 5.3 wt.%. The lower yields of asphaltenes obtained by the use of higher carbon number alkane solvents are probably due to the fact that these solvents maintain high molecular weight resins and low molecular weight asphaltenes in solution and consequently precipitate smaller amounts of asphaltenes . The asphaltenes precipitated by the use of sixty fold volumes of the solvent also contained coprecipitated resins, which were removed by Soxhlet extraction. The results indicated that the addition of a thirty fold volume of the precipitating solvent and 16h contact time, followed by Soxhlet extraction, are the most suitable parameters to obtain stable and reproducible yields of asphaltenes from the Saudi Arabian crude oils.

(ii) Elemental analysis of the asphaltenes precipitated from AH residue for carbon, hydrogen, nitrogen and sulphur has shown that the amounts of carbon and hydrogen decrease gradually with an increase in the carbon number of the precipitating alkane solvent, whereas the amounts of heteroelements (N, S, O) increase for the higher carbon number alkane precipitated asphaltenes . A corresponding decrease in the atomic H/C ratio and increase in the atomic N/C, S/C and O/C ratios indicates that the asphaltenes precipitated by the higher carbon number alkane solvents have a higher degree of aromaticity and also have greater proportions of heteroelement compounds. The greater proportions of nitrogen and oxygen in the higher alkane precipitated asphaltenes indicate that these asphaltenes contain greater amounts of basic and acidic functionalities. On the basis of the differences in yield and elemental analysis for asphaltenes obtained by the use of different alkane precipitating solvents, it is suggested that these asphaltenes are substantially different from each other.

(iii) The molecular weights of the asphaltenes precipitated from AH residue were determined by the vapour pressure osmometry (VPO) method. The effects of an increase in the solution temperature and an increase in the dielectric constant of the solvent on the VPO molecular weights were also investigated. The molecular weights of the asphaltenes increased with an increase in the carbon number of the precipitating alkane solvent. The higher molecular weight asphaltenes precipitated by the higher carbon number alkane solvents, which also gave lower yields, suggested that these solvents maintain high molecular weight resins and low molecular weight asphaltenes in solution. Lower values of molecular weight at higher solution temperatures, e.g., 9950, 8950 and 7900 at 40, 60 and 80°C, respectively, for normal heptane precipitated asphaltenes , are probably due to stripping or dissociation of some of the unit sheets from the asphaltene molecule.

The molecular weights of asphaltenes decreased considerably when solvents of high dielectric constant were employed. This could also be due to dissociation of asphaltene agglomerations in these solvents. The results showed that the VPO molecular weights of asphaltenes from Saudi Arabian crude oils are dependent not only on the solution temperature at which the determinations are carried out, but also on the dielectric constant of the solvent. The higher alkane precipitated asphaltenes (AH8, AH9 and AH10) had poor solubility in a solvent of high dielectric constant, such as pyridine (ε, 12.3).

(iv) Thermal gravimetric analysis (TGA) of the asphaltenes precipitated from AH residue (AH5, AH7 and AH10) and AL residue (AL5) has shown that these asphaltenes undergo little decomposition up to a temperature of 400°C. The greatest changes in the residue weight occur between 400°C and 520°C. However, the production of gases, maltenes and coke from low temperature pyrolysis at 350°C indicated that the asphaltenes undergo thermal decomposition and condensation under mild pyrolysis conditions. The decomposition of asphaltenes at 520°C resulted in 98-100% conversion of the asphaltenes into gases, maltenes and coke.

The evolution of methane and other low molecular weight alkane gases under mild pyrolysis conditions suggested that the asphaltenes contain thermally labile groups on the periphery of their structures. The higher yields of ethane and other alkane gases produced from the higher alkane precipitated asphaltenes could be due to the presence of larger amounts of such groups on the periphery of these asphaltenes . The larger amounts of olefins produced from the higher alkane precipitated asphaltenes (AH10) were attributed to more severe thermal decomposition of comparatively high molecular weight AH10 asphaltenes as compared with the other three asphaltenes (AL5, AH5 and AH7).

The evolution of significant amounts of carbon monoxide from the pyrolysis of the lower alkane precipitated asphaltenes at 350°C was noted. Ether linkages are reported to be one of the main sources for the production of carbon monoxide from the pyrolysis of asphaltenes (Soodhoo and Philips, 1988). This indicated that the lower alkane precipitated asphaltenes have higher amounts of ether linkages. The evolution of larger amounts of carbon dioxide from the higher alkane precipitated asphaltenes indicated the presence of larger amounts of carboxylic groups in these asphaltenes (Soodhoo and Philips, 1988).

The evolution of carbon monoxide and carbon dioxide during pyrolysis and the loss of oxygen and sulphur as gases and maltenes, as indicated by the estimation of these elements in pyrolysis coke, suggested that oxygen and sulphur are the most thermally labile heteroelements in asphaltene molecules and that measurable amounts of oxygen and sulphur atoms are located on their periphery. The loss of sulphur as gases and maltenes was lowest for the highest alkane precipitated AH10 asphaltenes . Retention of over 90% of the total nitrogen in pyrolysis coke suggested that a major portion of nitrogen functionalities belonged to those parts of the asphaltene structure which tend to form coke. The coke formed by the higher alkane precipitated asphaltenes retained a higher proportion of sulphur and lower proportions of oxygen and nitrogen.

(v) Nonaqueous potentiometric titration was employed for the estimation of basic functionalities in the asphaltenes . A series of model basic compounds were titrated in a solvent mixture containing chlorobenzene and acetic anhydride. Perchloric acid in dioxane was used as the titrant. The model basic compounds were classified into very weak bases, weak bases and strong bases, based on their pK_a (H_2O) values. Pure asphaltene samples were titrated under similar titration conditions. The titration curves for the pure asphaltenes showed two end points corresponding to HNP values of about 350 mV and 600 mV. The first end point was due to strong bases (HNP : 350 mV) and the second end point was due to weak bases (HNP : 600 mV). Asphaltene samples spiked with known amounts of model basic compounds were also titrated. The spiking titrations showed three end points corresponding to strong bases, weak bases and very weak bases (HNP: 700 mV). The nonaqueous potentiometric titrations suggested the presence of very weak, weak and strong basic functionalities in the asphaltenes which were due to indole, phenazine and pyridine groups, respectively. The proportions of these functionalities were higher in the higher alkane precipitated asphaltenes . The amounts of total titratable bases were 0.49 mM/g for AH5 asphaltenes and 0.60 mM/g for the AH10 asphaltenes . The quantities of very weak bases of the indole type were high in these asphaltenes and represented about 50% of the total titratable bases.

(vi) The Fourier transform infrared spectra of all four asphaltenes (AL5, AH5, AH7 and AH10) showed a group of bands between 3050 cm^{-1} and 2800 cm^{-1}. These bands result from the C-H asymmetric and symmetric stretching modes of vibration. Weak broad bands in the region 2000-1800 cm^{-1} indicated the presence of highly aromatic polynuclear systems containing long-chain substituents. The AL5 and AH5 asphaltenes showed a small peak at 1710 cm^{-1} which corresponded to the C=0 stretch of aldehyde and ketone groups. A small notch at about 3480 cm^{-1} in the spectra of AH7 and AH10 asphaltenes was attributed to the N-H stretching vibrations of pyrrolic groups. The spectra of AL5 and AH5 asphaltenes , which were low in nitrogen content, showed comparatively very weak peaks for pyrrolic groups.

The proton NMR spectra of the asphaltenes showed that the AL5 asphaltenes have the highest fraction of aromatic hydrogen. Among the three AH asphaltenes , a gradual decrease in the fraction of aromatic hydrogen was noted from the lowest alkane precipitated asphaltenes to the highest alkane precipitated asphaltenes . This suggested that the aromatic structures in the higher alkane precipitated asphaltenes are comparatively more condensed and highly substituted.

The aliphatic region of the ^{13}C NMR spectra of the four asphaltenes showed small peaks at 14.1, 22.9, 29.7 and 32.2 ppm, which were characteristic of α, β, γ and δ or further removed carbons, respectively, in a long paraffinic chain. The aromatic regions of all the ^{13}C NMR spectra were characterized by a broad featureless peak indicating overlapping due to various types of aromatic carbon. The AL5 asphaltene contained the highest fraction of aromatic carbon (0.605), whereas for AH5, AH7 and AH10 asphaltenes the fractions of aromatic carbon were found to be 0.576, 0.575 and 0.55, respectively.

The average molecular parameters for the asphaltenes were calculated by the use of experimental data for asphaltenes obtained from elemental analysis, molecular weight determination, infrared spectroscopy and proton and ^{13}C NMR spectroscopy. Two combinations of analytical techniques were used: (i) Infrared spectroscopy, proton NMR spectroscopy, elemental analysis and molecular weight determination (IR/proton NMR method) and (ii) Proton and ^{13}C NMR spectroscopy, elemental analysis and molecular weight determination (proton NMR/ ^{13}C NMR method).

The values of x, the carbon-hydrogen atomic ratio of methyl and methylene (MMHC) groups on substituted aliphatic side chains, were calculated from the relative intensity values of methyl ($1380cm^{-1}$) and methylene ($2920cm^{-1}$) absorption bands in the FT-IR spectra of the asphaltenes . The average molecular parameters calculated by the two methods indicated that the parameters for AL5 asphaltenes calculated by the IR/proton NMR method were equal or very close to the corresponding parameters calculated by the proton NMR / ^{13}C NMR method. However, the parameters obtained for AH5, AH7 and AH10 asphaltenes did not show close agreement for the two spectroscopic methods. The differences in the average molecular parameters calculated by the two methods were higher for the higher molecular weight AH10 asphaltenes as compared to the lower molecular weight AH5 asphaltenes .

Gross differences in the structural parameters for different alkane precipitated asphaltenes were noted. These differences in the structures may possibly be responsible for the different behaviour of the asphaltenes on pyrolysis. The asphaltenes precipitated by the higher alkane solvents from AH crude oil had higher numbers of aromatic and peripheral carbon, aliphatic carbon, and aliphatic hydrogen. The substitution index was also higher for the higher alkane precipitated asphaltenes , whereas the aromaticity index, condensation index and the percentages of aromatic carbon, unsubstituted carbon, and nonbridge carbon were lower in the higher alkane precipitated asphaltenes .

A comparison of the average molecular parameters for AH5 and AH10 asphaltenes , calculated by the proton NMR / ^{13}C NMR method showed that the numbers of aromatic carbon (C_a) and peripheral carbon (C_p) for AH5 asphaltenes were 282 and 154, respectively, whereas for AH10 asphaltenes , the corresponding values were 504 and 240. The numbers of aliphatic carbon (C_{al}) and aliphatic hydrogen (H_{al}) for AH5 asphaltenes were 209 and 443, respectively, whereas for AH10 asphaltenes the corresponding values were 416 and 845. The numbers of alkyl substituents per average molecule (n) were 38.3 and 93.6 for AH5 and AH10 asphaltenes . The average numbers of carbon atoms per alkyl side chain (ℓ) were found to be 4.38 and 4.45 for AH5 and AH10 asphaltenes . A comparison of the average molecular parameters calculated for AL5 asphaltenes with those obtained for AH5, AH7 and AH10 asphaltenes showed that the AL5 asphaltene had the lowest numbers of aromatic rings, aliphatic carbon, aromatic carbon, aliphatic hydrogen and alkyl substituents per average molecule. The substitution index was the lowest and condensation index was the highest for the AL5 asphaltenes .

(vii) A more detailed and meaningful structural characterization could be accomplished by fractionating the asphaltenes and then determining the average molecular parameters for the resultant fractions, using proton and ^{13}C NMR spectroscopy and mass spectrometry. Separation could be carried out, for example, by chromatographic separation (HPLC, adsorption, ion exchange or gel permeation) or solvent extraction. The narrower the molecular weight range, the more meaningful is the concept of hypothetical average molecular parameters.

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ASPHALTENES IN SAUDI ARABIAN HEAVY CRUDE OIL SOLUBILITY AND MOLECULAR WEIGHTS IN HYDROCARBON SOLVENTS

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ABSTRACT

The asphaltenes from Saudi Arabian Heavy crude oil residue (370°C+) were precipitated by adding n-alkane solvents (n-C_5 to n-C_{10}) to the crude oil / residue. The asphaltenes thus prepared were examined for their percent yields, VPO molecular weights and ultimate composition. VPO molecular weights were measured in five different solvents of varying dielectric constant (2.2 to 12.3).

The yield and atomic H/C ratio of Arabian Heavy asphaltenes were found to decrease with an increase in the carbon number of precipitating solvent. There was a general increase in the VPO molecular weights of these asphaltenes with increasing carbon number of the n-alkane solvent. The effect of dielectric constant of the solvent on the VPO molecular weight of asphaltenes was found to be very significant. Arabian Heavy asphaltenes showed considerable variation in their observed molecular weight values depending on the nature of solvent. The solvents of high dielectric constant generally decreased the observed molecular weight.

INTRODUCTION

Petroleum asphaltenes are commonly regarded as an undesirable component of the crude oil which creates adverse effects in processibility and upgrading of petroleum heavy ends. They form coke deposits in the heaters and poison the catalysts in the reactors. Asphaltenes are precipitated from petroleum by addition of a nonpolar solvent such as pentane or hexane and are soluble in benzene. The molecular nature of the asphaltene fractions of petroleum has been extensively discussed in the literature (Speight,1972; Yen,1972). It is believed that they are macromolecular compounds, comprising polyaromatic nuclei linked by aliphatic chains or rings of various lengths and bearing heteroatoms such as nitrogen, oxygen or sulfur, scattered throughout the molecule. The aromaticity and heteroatomic contents increase with increasing molecular weight (Speight and Long,1980).

The yield percent of asphaltenes depends on the nature of the crude oil and the precipitating solvent. Lower yields of asphaltenes are reported with increasing carbon number of the precipitating solvent (Corbett and Petrossi,1978; Ali and Ghannam,1981).

The solvent-to-oil ratio is also an important factor that effects the yield percent. Speight (1981) strongly stressed that a minimum of 40 volumes of precipitating solvent is required for complete precipitation of asphaltenes. If a lower volume of precipitating solvent is used, the raw asphaltenes must be purified in the correct manner (Speight,1984). There are, however, reports in which lower proportions of precipitating solvents are used (McKay et al.,1978; Jacobs and Filby,1983). In a separate study Acevedo et al. (1985) employed 20, 40 and 60 volumes of solvent for precipitating asphaltenes. The difference in the yields of purified asphaltenes was insignificant.

The molecular weight of asphaltenes has been the subject of many investigations. Several methods have been used but vapor pressure osmometry (VPO) is the one most commonly employed. It was shown that VPO molecular weight depends not only on the nature of the solvent but also on the solution concentration and the temperature at which the determinations are made (Moschopedis et al.,1976). There is also a tendency for asphaltenes to associate even in dilute solution of nonpolar solvents (Mitchell and Speight,1973). In polar solvents, the VPO molecular weight was observed to decrease with an increase in dielectric constant of the solvent. It has also been shown that intermolecular bonding is involved in asphaltene molecular weight and has a significant effect on the observed molecular weight (Ignasiak et al.,1977).

This paper discusses the separation of asphaltenes from the Saudi Arabian Heavy crude oil residue, using six different normal alkane solvents(n-C_5 to n-C_{10}) at ambient temperatures. The asphaltenes thus precipitated were analyzed for their elemental composition , VPO molecular weights and yield percent, the results are compared. VPO molecular weights were measured in five different solvents of varying dielectric constant(non polar, 2.2 to highly polar, 12.3) to study the effect of solvent's polarity on the molecular weight of the asphaltene from Saudi crude oil. The effect of temperature on the molecular weight of the asphaltene in toluene was also studied and the results are discussed.

EXPERIMENTAL

Residue Preparation

Arab Heavy (AH) 370°C+ residue was prepared by removing the distillates boiling up to 320°C using a Podbielniak column for atmospheric and vacuum distillation using ASTM method D2892-78 (ASTM,1987). The 320°C+ residue was then passed through a wiped film molecular still to remove distillate upto 370°C cut point. The residue 370°C+ and AH crude oil were characterized for yield wt.%, gravity, viscosity, pour point, carbon residue, sulfur, nitrogen, nickel, vanadium and iron contents.

Asphaltene Separation

Asphaltenes from AH crude oil were precipitated by adding 20, 30, 40 and 60 volumes of n-heptane to the crude oil and stirring the mixture for 90 minutes. The mixture was allowed to stand for 16 hours and then centrifuged for 60 minutes at 1500 rpm. The supernatant liquids were decanted, fresh volumes of heptane were added and the mixture recentrifuged. Asphaltenes were collected from the bottom of the centrifuge tubes, washed with solvent heptane and were dried in a vacuum oven at 60°C. These asphaltenes were weighed as impure asphaltenes. These were purified by 24 hour extraction with n-heptane on a Soxhlet extractor followed by drying in a vacuum oven. In one of the experiments, the insoluble asphaltenes were purified by dissolving in toluene and reprecipitating with n-heptane.

Asphaltenes were isolated from 370°C+ residue by digestion of the residue with 30 volumes of n-alkane solvent(n-C_5 to n-C_{10}) followed by centrifugation and Soxhlet extraction by the procedure described above.

Elemental Analysis

Elemental analysis for carbon, hydrogen, nitrogen and sulfur on asphaltenes were done on Carlo Erba elemental analyzer model 1106.

Molecular Weight

Molecular weights of asphaltene samples were determined using Knauer type vapor pressure osmometer equipped with variable temperature thermostat. Benzil solutions in toluene were used to calibrate the instrument at three different temperatures i.e. 40, 60 and 80°C. Chloroform, chlorobenzene and pyridine were also used for calibration at 40°C. Concentration of asphaltene solutions were varied in the range 2-8 wt %. Results obtained at four different concentrations were then extrapolated to infinite dilution to obtain average molecular weight.

Molecular weights of asphaltenes obtained from 370°C+ residue by the six normal alkane solvents were determined in toluene at three different temperatures i.e. 40, 60 and 80°C. These asphaltenes were also examined in chloroform, chlorobenzene and pyridine solvents at 40°C.

RESULTS AND DISCUSSION

The properties of Arab Heavy(AH) crude oil and 370°C+ residue from this crude are given in Table I. Arab Heavy is a medium gravity paraffinic crude oil produced from offshore field, Safaniya, which is located about 125 miles northwest of the exporting terminal Ras Tanura. The 370°C+ residue comprises 55.3 weight percent of crude oil.

TABLE I

Physico-Chemical Characteristics of Arab Heavy Crude Oil and 370°C+ Residue

	Arab Heavy	
	Crude Oil	370°C+ Residue
Gravity, °API	28.0	10.7
Gravity, Specific 60/60°F	0.8871	0.9950
Sulfur, wt %	2.79	4.36
Carbon Residue, wt %	6.75	14.2
Viscosity, SUS	118@37.8°C	122@99°C
Pour Point, °F	-10	+70
Ash Content, ppm	110	430
Nitrogen, wt %	0.16	0.30
Iron, ppm	1.0	17
Nickle, ppm	8.4	32
Vanadium, ppm	28	105
Distillation Yield on Crude wt %	-	55.3
% Cumulative Weight		
@ 100°C	7.0	-
@ 200°C	18.9	-
@ 300°C	33.6	-
@ 370°C	44.7	-

The asphaltenes, impure and purified, were isolated from AH crude oil (one volume) by adding 20, 30, 40 and 60 volumes of n-heptane. The yields (wt.%) are recorded in Table II. There appears to be a marked decrease in the yield of impure asphaltenes with an increase in solvent to oil ratio from 20 to 60 volumes. These results indicate that higher amounts of resins are coprecipitated when lower solvent volumes are used. This is further confirmed by a considerable reduction in the asphaltene yields on Soxhlet extraction of impure material. Similar results are reported for asphaltenes from Athabasca bitumen (Speight,1981).

Table III shows the asphaltenes yield wt. % for 370°C+ residue. Six different n-alkane solvents from C_5 to C_{10} were used at a solvent to residue ratio of 30 volumes to one volume. The data presented in Table III supports previous observations that the asphaltene yields decrease with an increasing carbon number of the precipitating alkane solvent (Corbett and Petrossi,1978; Ali and Ghannam,1981).

Ultimate composition of asphaltenes isolated from AH crude oil and 370°C+ residue using different solvents are remarkably similar (Table IV). Careful inspection of data, however, shows differences in the composition. H/C (atomic) ratios are showing a general decrease with an increase in the carbon number of n-al-

TABLE II

Yield of Asphaltenes from Arab Heavy Crude Oil

Volumes of n-Heptane Added	Asphaltenes Wt %	
	Impure	Purified
20	8.8	5.0
20(*)	8.8	4.9
30	8.2	4.9
40	7.0	4.9
60	5.7	4.9

(*) Dissolved in toluene and reprecipitated before Soxhlet extraction.

TABLE III

Yield of Asphaltenes from Arab Heavy 370°C+ Residue with Different Alkane Solvents

Precipitating Solvent (30 Volumes to 1 Volume of Residue)	Asphaltene Yield Wt %
n-Pentane	12.2
n-Hexane	10.0
n-Heptane	8.5
n-Octane	6.7
n-Nonane	5.7
n-Decane	5.3

TABLE IV

Elemental analysis and atomic ratios of asphaltenes from Arab Heavy crude oil and 370°C + residue

Alkane solvent	Elemental analysis of asphaltenes* weight %					Atomic ratios			
	C	H	N	S	O**	H/C	N/C	S/C	O/C
a) AH 370°C + residue									
n-Pentane	82.38	7.65	0.85	7.41	1.71	1.1143	0.0088	0.0337	0.0156
n-Hexane	82.40	7.61	0.91	7.30	1.78	1.1083	0.0095	0.0332	0.0162
n-Heptane	82.15	7.40	0.96	7.61	1.88	1.0809	0.0100	0.0347	0.0172
n-Octane	82.01	7.35	1.04	7.61	1.99	1.0755	0.0109	0.0348	0.0182
n-Nonane	81.68	7.32	1.19	7.71	2.10	1.0754	0.0125	0.0354	0.0193
n-Decane	81.39	7.30	1.31	7.79	2.21	1.0763	0.0138	0.0359	0.0204
b) AH crude oil									
n-Heptane	81.90	7.35	0.95	7.85	1.95	1.0769	0.0099	0.0359	0.0179

* Precipitated by adding 30 volumes of alkane solvent. ** By difference

TABLE V

V.P.O. Molecular Weight of Asphaltenes from Arab Heavy 370°C+ Residue Determined in Toluene at Different Temperatures.

	V.P.O. Molecular Weight in Toluene (*)		
Precipitant	40°C	60°C	80°C
n-Pentane	7900	7150	6250
n-Hexane	8800	7900	7050
n-Heptane	9950	8950	7900
n-Octane	11200	10300	9800
n-Nonane	13050	12050	11500
n-Decane	14850	13900	13050

(*) Accuracy ±10%

kane solvent, thus indicating a higher degree of aromaticity in higher alkane asphaltenes. Atomic N/C, S/C and O/C ratios of asphaltenes are increasing with the increasing carbon number of the solvent. This increase is in line with the higher proportions of nitrogen, sulfur and oxygen in the samples.

The ultimate composition for n-heptane asphaltenes from AH crude oil is also recorded in Table IV. Both

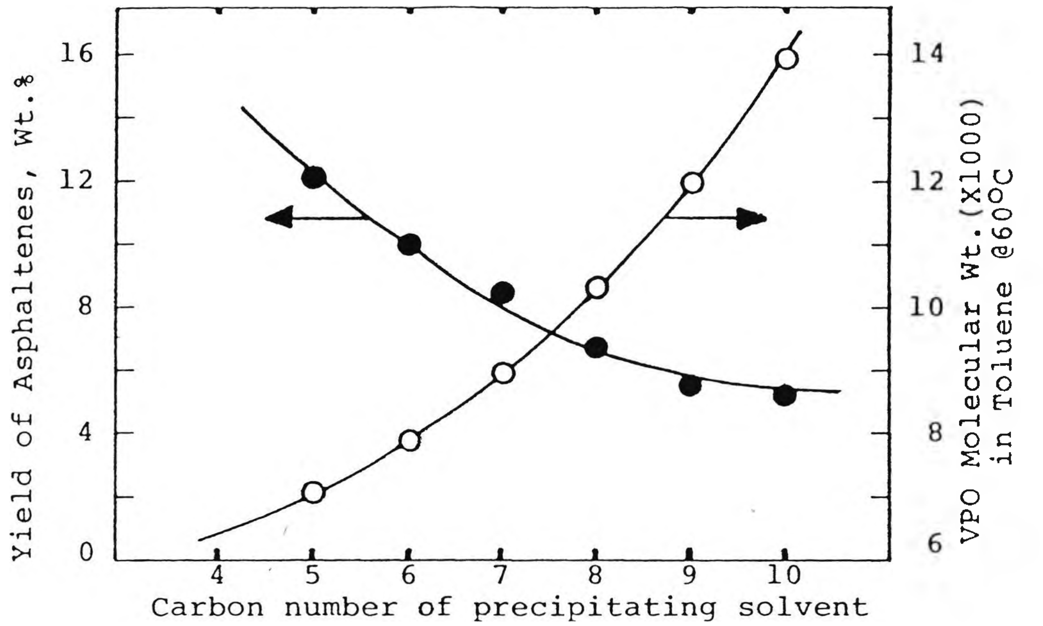

FIG.1 Effect of carbon number of precipitating solvent on yield and VPO molecular weight of asphaltenes

the AH crude oil and 370°C+ residue give the n-heptane asphaltenes of very similar ultimate composition.

VPO molecular weights of the n-C_5 to n-C_{10} asphaltenes isolated from AH 370°C+ residue are given in Table V. The molecular weights were measured in toluene solutions at 40, 60 and 80°C. There is an increase in the molecular weight with the increase in the carbon number of n-alkane solvent. An increase in temperature appears to decrease the molecular weight. The percent yield and molecular weight of asphaltenes are plotted against carbon number of the n-alkane solvent in Figure 1. These results are in agreement with

TABLE VI

V.P.O. Molecular weight of Asphaltenes from Arab Heavy $370^{o}C+$ residue in different solvents

Solvent	Carbon Tetra-chloride	Toluene	Chloroform	Chlorobenzene	Pyridine
Dielectric constant	2.24	2.37	4.81	5.71	12.30
Temperature ^{o}C	60	40	40	40	40
Precipitating solvent					
n-Pentane	7300	7900	3400	3300	2850
n-Hexane	8100	8800	4200	4050	3250
n-Heptane	8700	9950	4550	4250	3450*
n-Octane	10600	11200	5200	5400	##
n-Nonane	11850	13050	6350	6300	##
n-Decane	13100	14850	7400	7250	##

* sparingly soluble ## insoluble

those reported earlier by Speight (1984) for Athabasca asphaltenes, but are in conflict with the findings of Ali and Ghannam (1981) who reported an increase in the molecular weight of asphaltenes from Qaiyarah crude oil as the deasphaltening temperature and the carbon number of the solvent are decreased.

Molecular weights of asphaltenes from AH 370°C+ residue were also measured in solvents of different dielectric constant (Table VI). These asphaltenes are sparingly soluble in the solvents of high dielectric constant (e.g. Pyridine), particularly the asphaltenes precipitated by using higher n-alkane (i.e. n-C_7 and

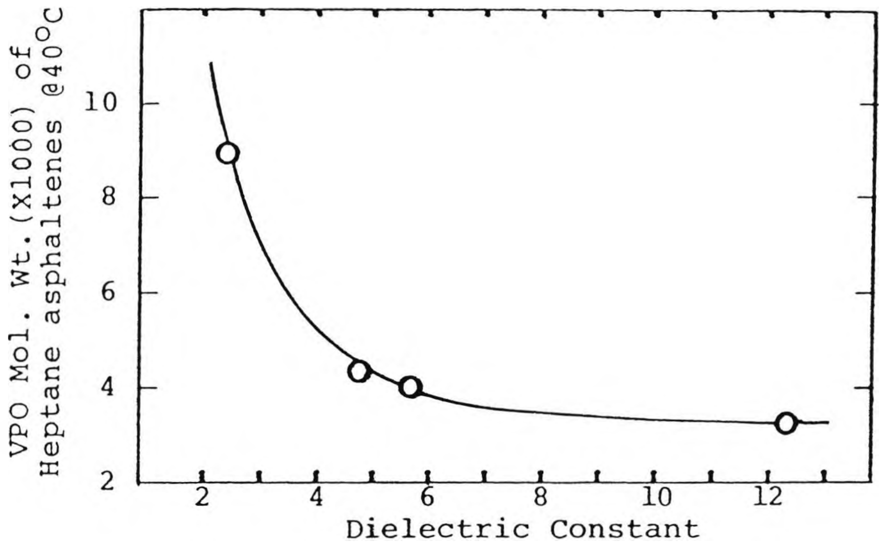

FIG.2 Effect of Dielectric constant on VPO molecular weight of asphaltenes

above). The effect of dielectric constant on VPO molecular weight of asphaltenes is illustrated in Figure 2. The molecular weight of AH asphaltenes show considerable variation and appear to be dependent upon the nature of the solvent. The solvents of high dielectric constant generally decrease the observed molecular weights.

CONCLUSIONS

Addition of 30 volumes of alkane solvent, 16 hour contact time followed by Soxhlet extraction for 24 hours are found to be satisfactory parameters to obtain stable asphaltene yield from Arab Heavy crude oil.

Yield and H/C ratio of Arab Heavy asphaltenes decrease with an increase in the carbon number of precipitating solvent. VPO molecular weight of these asphaltenes increase with increasing carbon number of the n-alkane solvent and decrease when the temperature are lowered at which measurements are made.

Asphaltenes obtained by higher n-alkane solvents (heptane and above) show poor solubility in solvents of high dielectric constant such as pyridine.

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