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Combined Gel Permeation Chromatography—NMR Techniques in the Characterization of Petroleum Residuals*

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Summary

It has been shown that proton nuclear magnetic resonance spectra of fractions obtained by gel permeation chromatography techniques can yield significant information in the characterization of petroleum residuals. Application of empirical relationships developed for the analysis of NMR spectra is shown to be useful when applied to gel permeation chromatography fractions. Whole residues and a deasphaltened fraction have been separated and studied. Unit weights and aromaticities have been obtained by NMR and compared with molecular weights from vapor pressure osmometry measurements. In addition, supplemental information from infrared and mass spectrometry on GPC fractions has been used to characterize a "neutral" portion of the residue.

Adsorption effects have caused an apparent shift in aliphatic and aromatic components as observed by NMR spectra suggesting that information relating to the mechanism of GPC separations, particularly in regard to factors other than molecular size which influence elution rates, might be obtained from petroleum residual characterizations.

INTRODUCTION

The composition of petroleum residuals has been of interest for a number of years, and several analytical methods have been applied to the problem. Over the past 10 years, various spectroscopic techniques have been used in residual characterization as they have become available or have been improved. Of particular importance has been the

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application of proton nuclear magnetic (NMR) resonance spectroscopy to these problems. In 1958 Williams (*1*) used proton NMR in the characterization of saturate, aromatic, and olefinic petroleum fractions. Although the spectra used in this early work were of poor quality and low resolution, the empirical relationships derived were valid and have proven to be extremely useful in NMR petroleum characterization studies. Similar empirical relationships based on the observable proton resonances were reported by Brown and Ladner (*2*) for vacuum carbonization products of coal. Both of these studies were performed on low frequency (30–40 MHz) and relatively low resolution instruments.

The first application of 60 MHz, high resolution NMR techniques to petroleum characterizations was reported by Yen and Erdman (*3*) in 1962 in characterization studies of several asphaltene samples from various sources. A typical high resolution NMR spectrum of a petroleum residual is given in Fig. 1, showing the resonances of interest. Empirical relationships have been developed based on the integrated areas of the proton resonances which are then used to calculate structural parameters.

All of the above studies were concerned with unfractionated petroleum or coal residuals. In 1967, Ramsey, McDonald, and Petersen (*4*) first reported NMR structural studies on various asphalts and asphalts fractionated by elution techniques. Ferris, Black, and Clelland (*5*) studied a series of 22 asphaltene fractions separated according to solubility. NMR analysis of the series revealed a systematic increase in parameters such as aromaticity and aromatic ring size. Parameters measured by other techniques correlated well with the NMR data.

Altgelt (*6*), in 1965, was the first to report the fractionation of asphaltenes by gel permeation chromatography (GPC) techniques. It was clearly shown that GPC was to become an invaluable tool in residual characterization. It was further revealed that a definite molecular weight separation was achieved, and in addition, preliminary spectroscopic studies by infrared (IR) suggested that systematic changes in structural characteristics could be monitored. Dickie and Yen (*7*) later reported the GPC separation of a Baxterville crude petroleum which offered additional evidence for a fractionation by molecular weight (size). More recently, Altgelt (*8*) studied molecular association in asphaltenes through vapor pressure osmometry (VPO) studies on GPC fractions, pointing out that such fractionation was essential in that it strongly reduced the effects of heterogeneity on

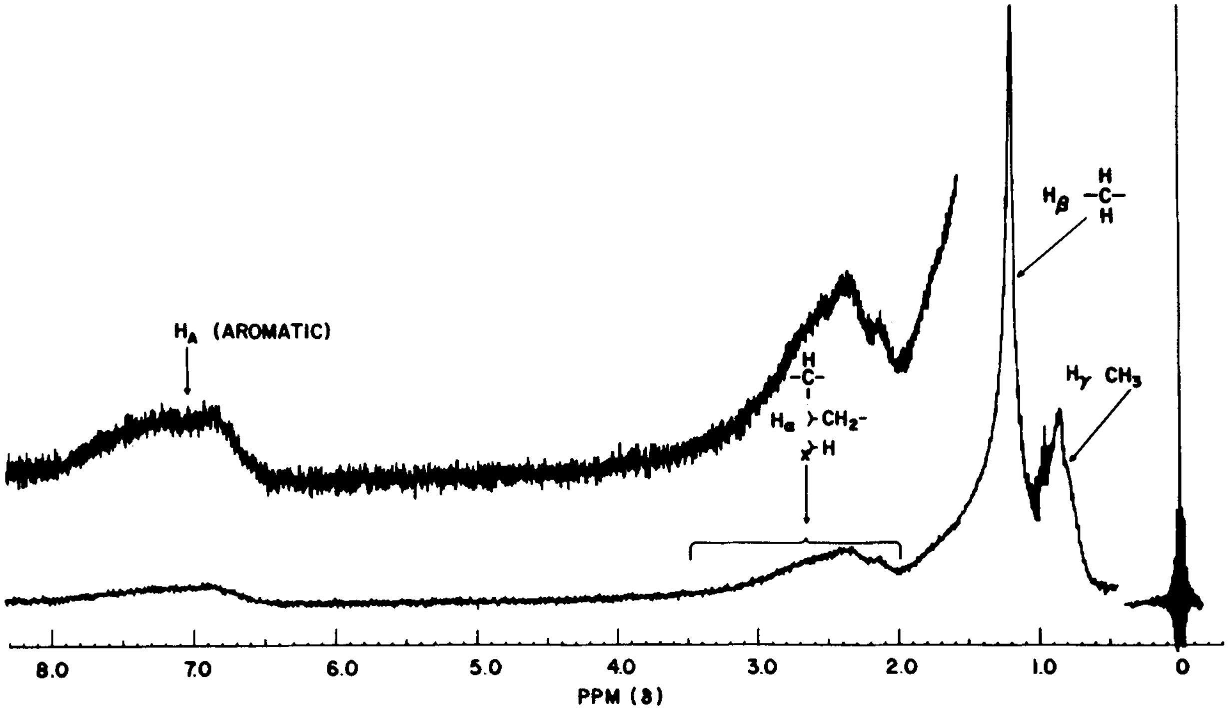

FIG. 1. Proton NMR spectra of Kuwait residual.

the average molecular weight values obtained and it also allowed higher molecular weight samples to be studied.

The application of NMR to the analysis of a series of GPC fractions of petroleum residuals should provide an opportunity to utilize the methods and empirical relationships developed over the past 10 years. Indeed, we have observed systematic changes in aromaticity, f_a, and unit weight (*7*) with GPC fractions. In addition, through NMR analysis, we concur with recent reports (*9*, *10*) that factors in addition to molecular size influence the fractionation process. A recent publication by Coleman, Hirsch, and Dooley (*9*) reported significant molecular separation by GPC as elucidated by mass spectral data. NMR spectra revealed that two of their fractions showed a large difference in basic compound types. We have pursued similar studies on a series of GPC fractions of Kuwait residuals and have shown NMR to be a potentially valuable tool in this application.

EXPERIMENTAL

Samples of Kuwait residual dissolved in benzene were fractionated on a gel permeation unit packed with Styragel of 500 and 1000 Å pore size. This system has been previously described by Albaugh et al. (*12*).

All NMR spectra were obtained on a Varian HA-60 spectrometer system. Samples were dissolved as received from the GPC (solvent removed) in CS_2. Tetramethylsilane was used as the internal reference. Spectra were obtained over a sweep width of 500 Hz at a rate of 2 Hz/sec.

Molecular weights by vapor pressure osmometry were obtained on a Mechrolab VPO unit in benzene.

RESULTS AND DISCUSSION

The effectiveness of GPC separations is usually described by distribution plots of material recovered as well as elemental distributions. Typical GPC distribution plots obtained for a whole Kuwait residual and a deasphaltened Kuwait residual are shown in Fig. 2. Note that an obvious decrease in the amount of material (as indicated by Δ refractive index) eluted in the earlier fractions has occurred with the removal of the asphaltenes. In general, the distribution of hetero elements (e.g., sulfur) and the carbon-to-hydrogen atomic ratio of the fraction series takes the form of a "V"-shaped plot (Fig. 3). Similar

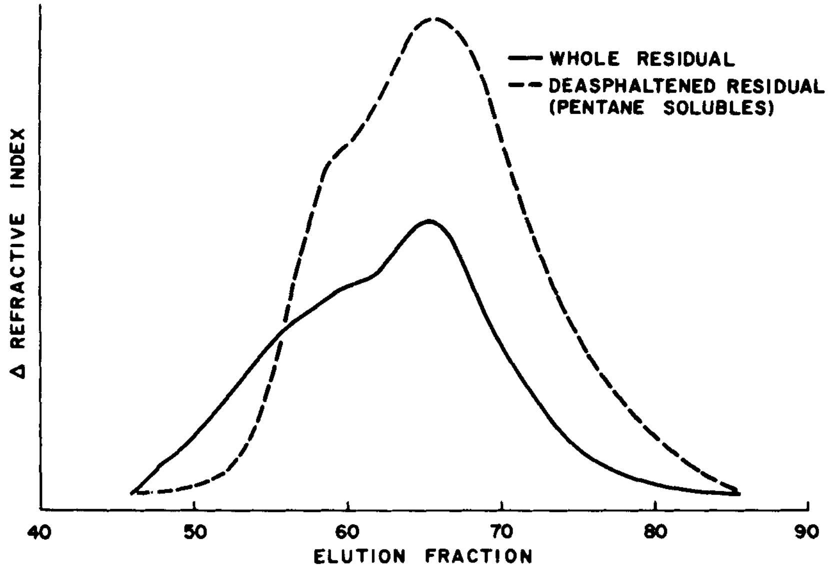

FIG. 2. Kuwait residual.

distributions have been observed for most of the residual fractions studied to date.

Two descriptive parameters developed from NMR data reveal unusual distributions as a function of elution volume. Using the empirical relationships developed for NMR data most recently reported by Ramsey et al. (*4*) and others (*1–3*), one can calculate the aromaticity, f_a, which expresses in percentage the number of aromatic carbon atoms in the material and a second parameter, the unit weight, described by Dickie and Yen (*7*) as the basic "building block" of asphaltic material and as being the weight of a "unit sheet" of pericondensed aromatic rings with aliphatic side chains of varying lengths.

To obtain the unit weight, one must first calculate a "hypothetical unsubstituted unit ring" (*4*) present in the residual material by using the NMR integrated areas. Additional calculations using the aromaticity value, f_a, described above will yield a total unit weight. Since NMR is capable of observing only the "average" structure present in a given GPC fraction, we have suggested (*11*) that the weight thus calculated represents the weight of the unit sheet as proposed by Dickie and Yen.

The distribution or change in these NMR descriptive parameters as a function of GPC fraction should supply meaningful information in

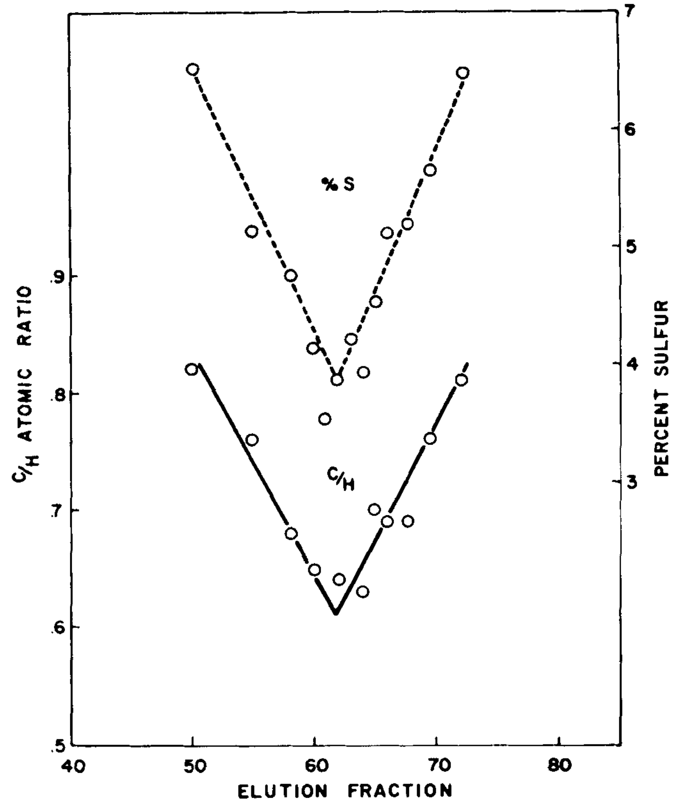

FIG. 3. Kuwait residual. Elemental data vs. GPC elution fractions.

the characterization of the residual material. For example, the distribution of aromaticity, f_a, takes the form of a "V" distribution similar to that observed for sulfur content in the whole residue, suggesting a relation between sulfur and aromaticity.

Of even greater interest, however, is the distribution of unit weights calculated from the NMR data (Fig. 4). These weights agree with VPO measurements in the molecular weight region below ~1000. Above ~1000 the VPO weights increase rapidly as a function of GPC fraction while the NMR unit weights are seen to increase somewhat erratically to a maximum of ~1200 at elution count #50. This behavior of the NMR unit weight distribution plot has been interpreted (*11*) as resulting from the combination of two effects. First, the fact that NMR unit weights are the weights of the *average* unit sheets, or

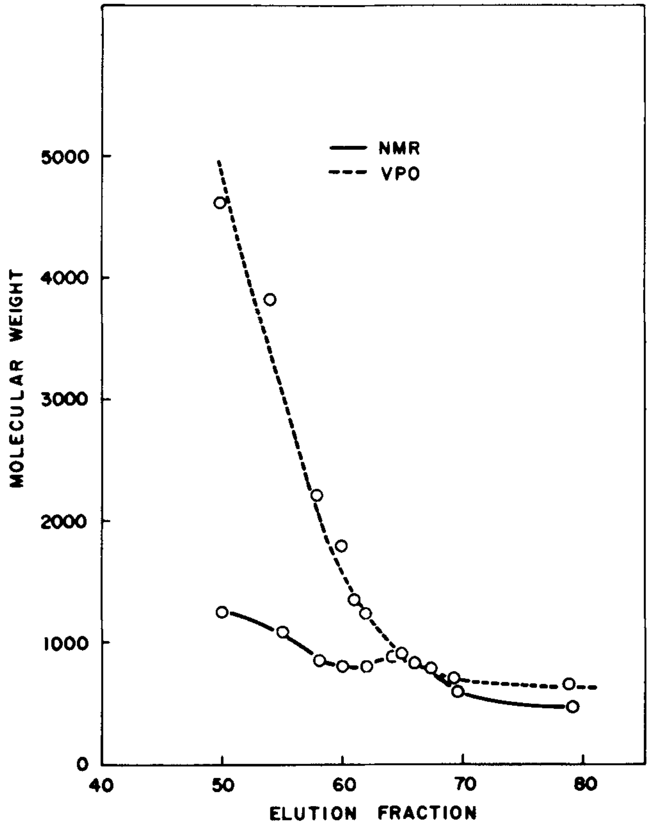

FIG. 4. Molecular weight of Kuwait residual vs. elution fraction from GPC.

the *average* monomer weight of any associated (or coordinated) species in the material (while the higher VPO weights, >1000, represent the weight of coordinated species), and second that the GPC is separating not only by molecular size, but, in addition, adsorption effects have caused a separation by molecular type (e.g., asphaltenes, oils, etc.). Several recent GPC studies concur in this latter observation (*9*, *10*). For example, the material above elution count ~64 has been shown to have a relatively high concentration of aromatic material while the material at earlier elution counts is apparently a mixture of overlapping paraffinics, naphthenics, and aromatics. The change in concentration (and molecular size) of these various molecular types with

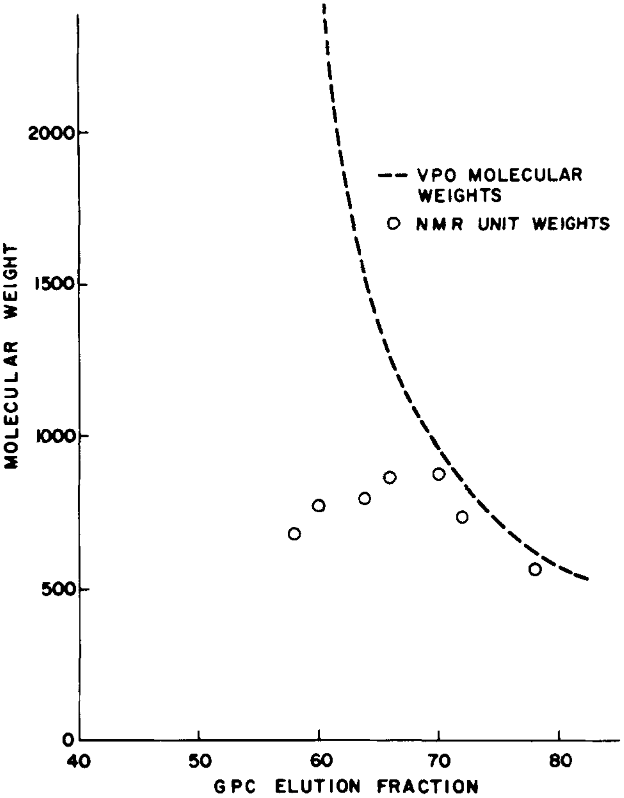

FIG. 5. Kuwait residual "neutral" fraction. Molecular weight vs. elution fraction.

elution volume contributes to the behavior of the plot at early elution volumes. The plot suggests, however, that a maximum unit weight of 1000–1200 is present below elution count ~#62.

This interpretation has been supported by a more rigorous analysis of a "neutral" fraction of the Kuwait residual obtained by fractionation of the pentane soluble portion. Figure 5 shows the behavior of the NMR "unit weights" and VPO weights as a function of GPC fraction. Note that the behavior is very similar to that observed for the whole residue with excellent agreement below molecular weight ~900. Aromaticities (Fig. 6) calculated by NMR show a "V"-shaped distribution similar to the distribution of heteroatoms and aromaticities observed for the whole residue. These data suggest an interpretation

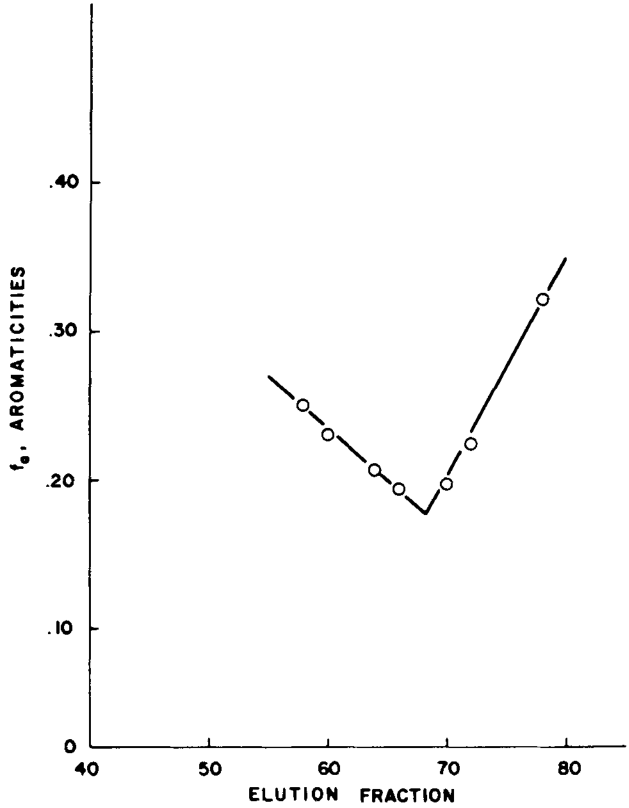

FIG. 6. Kuwait residual "neutral" fraction. Aromaticities, f_a, vs. GPC elution fraction.

similar to that proposed for the whole residue outlined above. However, NMR and IR data clearly show that the early GPC cuts contain no aromatic material while the late GPC fractions (i.e., #80, etc.) are highly aromatic (Fig. 7). This apparent contradiction may be resolved by an examination of the empirical equation reported in the literature for the calculation of aromaticities (Fig. 8) and reiterates the value of GPC in these studies. A serious dependence on the presence of naphthenic material in the sample is evidenced in the equation. If the concentration of condensed ring saturates is significant, then the calculation will give positive aromaticity values in the absence of aromatic material. This is due to the fact that the calculation is dependent on the assumption that the average number of aliphatic

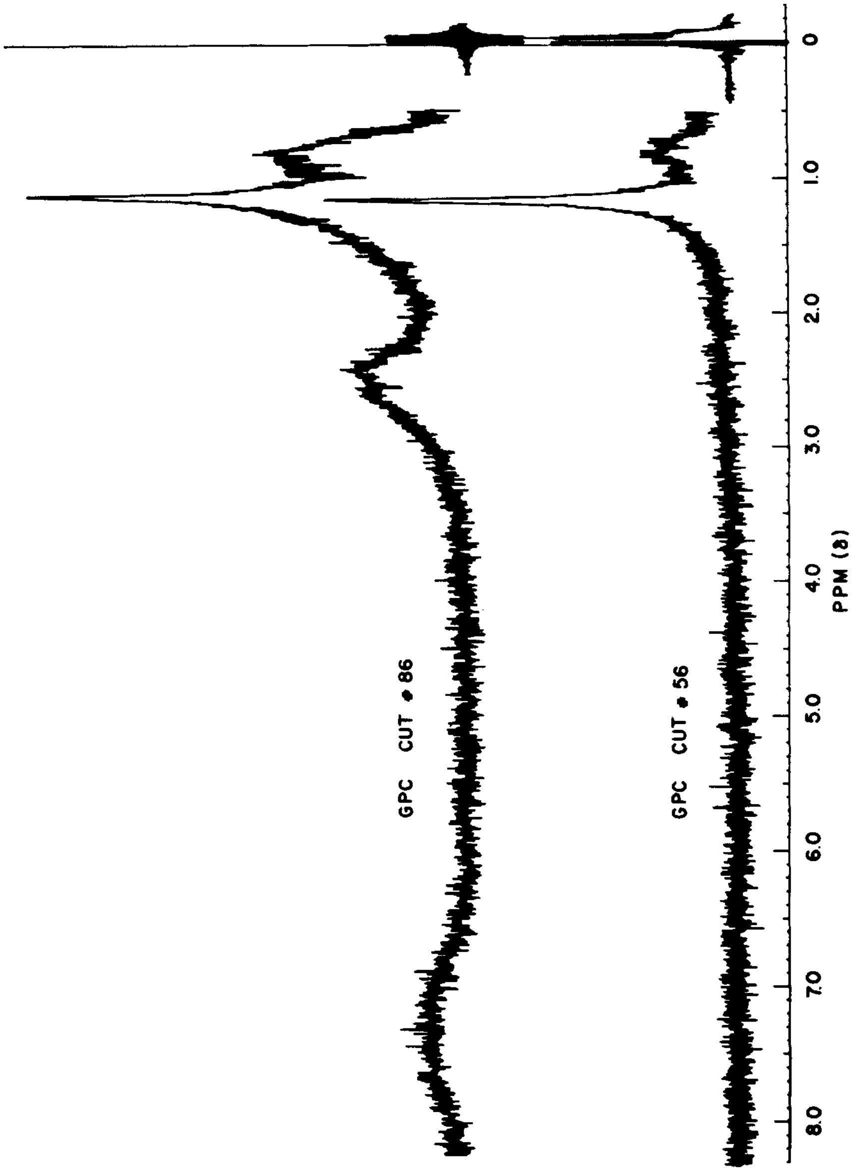

FIG. 7. Kuwait residual "neutral" fraction.

$$\text{Aromaticity, } f_a = \frac{\dfrac{\mathrm{C}}{\mathrm{H}} - \dfrac{H_\alpha^*}{x} - \dfrac{(H_\beta^* + H_\gamma^*)}{y}}{\dfrac{\mathrm{C}}{\mathrm{H}}}$$

where C/H = atomic ratio of carbon to hydrogen,
H_α^*, H_β^*, H_γ^* = normalized NMR integrated areas,
x = av number of protons/α-carbons
y = av number of protons/β- and γ-carbons.
usual assumption, $x = y = 2$
for naphthenic material present, $x = y < 2$

FIG. 8. Equation for calculation of aromaticity from NMR data (*2*).

protons per aliphatic carbon atom in the system is equal to two ($x = y = 2$). This assumption is necessary to properly interpret the methylene and methine (H_β and H_α) absorptions and is usually valid for large aromatic ring systems with relatively long aliphatic side chains such as asphaltenes and whole residues. However, if the material should contain a high concentration of condensed naphthenic ring systems, as is the case in our "neutral" material, then the assumption is invalid ($x = y < 2$) and introduces errors in the aromaticity calculations and ultimately into the unit weight calculations which are dependent on f_a. It has already been shown that the unit weights determined thus far for all the residue fractions studied agree with vapor pressure osmometry measurements and mass spectral measurements below ~1000 (~elution cut #62) (Table 1). This indicates that the NMR calculations are valid in this region and presumably little or no naphthenic material is present. The reason NMR unit weights for the earlier eluted material tend not to agree with VPO data is, in the case of the "neutral" fraction, a result of the presence of condensed naphthenic rings yielding abnormally high aromaticity values. When introduced into the unit weight calculations, these aromaticity values will yield low unit weights.

Mass spectral analysis of the earlier eluted material of the "neutral" fraction supports our NMR interpretation, showing that the material is composed of a high concentration of small ring condensed and noncondensed saturates. Furthermore, ultimate separation of the saturate material from the aromatic material in the bulk "neutral" fraction indicated that 20% of the original material was saturate.

Even though the possibility of error in the aromaticity calculations due to the presence of naphthenic material exists in the earlier GPC fractions, the NMR average unit sheet weights in this region still

TABLE 1

Kuwait Residual Fractions Molecular and Unit Weights

Fractions	NMR	VPO	Mass spectroscopy
		Whole Residual	
74–84	460	650	400
69–70	590	675	546
66	820	840	>700
		Deasphaltened Residual	
78	325	—	350
74	460	—	—
70	670	765	620
68	760	760	—
66	925	920	—
64	1064	1180	980–1000
		Neutral Fraction	
78	550	660	—
72	740	825	—
70	880	850	—
66	860	800	—
64	800	~1000	—

tend to be grossly below those reported by VPO measurements. The agreement between mass spectral molecular weights, VPO number-average molecular weights, and our calculated NMR unit weights in the later GPC fractions (>elution count #62) suggests the NMR empirical relationship to be valid and useful in characterizing GPC fractions with respect to unit weight. In addition, the anomalies caused by naphthenic material suggest that the technique may offer a method of detection for naphthenic material (e.g., comparison of calculated aromaticities with actual aromatic content by NMR).

CONCLUSIONS

Because of the ability of gel permeation chromatography to separate materials by molecular size as well as possibly other inherent properties, its usefulness in the characterization of petroleum residuals has been recognized. The application of proton NMR to analysis of the separated fractions can yield supplementary information.

We have suggested that the empirical relations developed using NMR integrated areas can yield meaningful trends in fundamental characterizing parameters as a function of gel permeation fraction. Aromaticity and unit weight have been shown to vary with elution volume. Other more esoteric but perhaps useful NMR parameters which have been described in the literature (*1–4*) may also show the same trends. Future studies will explore these possibilities. In addition, it appears that the application of NMR techniques to GPC fractions can yield data not only on the characterization of petroleum residuals but also information related to the mechanism of GPC separations, possibly showing trends in the fractionation of molecular types.

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