

**PETROLEUM RESIDUA SOLUBILITY PARAMETER / POLARITY  
MAP: STABILITY STUDIES OF RESIDUA PYROLYSIS**

**Final Report**

**By**

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## EXECUTIVE SUMMARY

A new molecular weight / polarity map based on the Scatchard-Hildebrand solubility equation has been developed for petroleum residua. A series of extractions are performed with solvents of increasing solubility parameter, and the fractions are analyzed by vapor pressure osmometry for number average molecular weight and by analytical-scale size exclusion chromatography for molecular weight spread. Work was performed for a heavy oil material subjected to three increasing severities of thermal treatment prior to and through the onset of coke formation. The results are diagnostic of the layers of solvations by resin-type molecules around a central asphaltene core.

Two additional stability diagnostic methods were also used. These were the Heithaus titration “P-index” and Gaestel “G” index, which have been applied to paving asphalts for decades. The Heithaus titration involves the titration of three toluene solutions of a residuum at three concentrations with a poor solvent, such as isooctane, to the point of asphaltene flocculation. In the present work, the significance of the data are developed in terms of the Hildebrand solubility parameter. The Heithaus results are combined with data from the new molecular weight / polarity map. The solubility parameters for the toluene-soluble asphaltene components are measured, and the solubility parameters of the maltenes can be calculated. As thermal treatment progresses, the solubility parameters of asphaltene materials increase and the molecular weights decrease. A new coking index is proposed based on Heithaus titration data. Preliminary results suggest that an alternative, simpler coking index may be developed by measuring the weight percent of cyclohexane solubles in heptane asphaltenes. Coking onset appears to coincide with the depletion of these resin-type asphaltene solubilizing components of residua.

## OBJECTIVES

The objective of the present study was to develop a mapping tool that will enhance understanding of the changes that occur in residua during upgrading and support the industry-sponsored work in which Western Research Institute is engaged. WRI performs proprietary industry-sponsored residua and heavy oil upgrading process development and optimization research. The new mapping tool can be used for evaluating heavy oils and residua in both upstream and downstream operations.

## INTRODUCTION

### Solubility Parameter Considerations

The dissolution of a material in a solvent, or the mixing of two liquids to form a single-phase solution, will occur if the free energy of the process is zero or negative as described by

$$\Delta G = \Delta H - T\Delta S$$

where  $\Delta G$  is the free energy,  $\Delta H$  is the heat of mixing,  $T$  is the temperature, and  $\Delta S$  is the change in entropy. Typically in a dissolution process, the entropy term is relatively large, and the heat of mixing determines if the mixing will occur (Burrell 1955). Hildebrand described this heat of mixing as

$$\Delta H = V ((\Delta E_1/V_1)^{1/2} - (\Delta E_2/V_2)^{1/2})^2 \Phi_1 \Phi_2$$

where  $\Delta H$  is the heat of mixing,  $V$  is total volume,  $\Delta E_x$  is the molar energy of vaporization of component  $x$ ,  $V_x$  is the molar volume of component  $x$ , and  $\Phi_x$  is the volume fraction of component  $x$  in the solution (Hildebrand et al. 1970). The term  $(\Delta E/V)^{1/2}$  is called the solubility parameter  $\delta$  and is typically given in units of  $(\text{cal/cc})^{1/2}$ , called the Hildebrand. Numerical values for the solubility parameter of a solvent can be calculated as

$$\delta = (\Delta E/V)^{1/2}$$

from the molar energy of vaporization to the ideal gas state,  $\Delta E$  and the molar volume  $V$ . Other means of estimating solubility parameters have been described (Hildebrand et al. 1970). For large molecules or polymeric systems, group contributions can be used to calculate if the density of the material is known or can be estimated (Small 1953).

The heat of mixing two materials is dependent on the difference between their solubility parameters squared,  $(\delta_1 - \delta_2)^2$ . If the solubility parameters are identical, the heat of mixing is zero and the dissolution/mixing process is driven by the entropy term  $T\Delta S$  alone, and mixing will occur. If the solubility parameters are not identical, the term  $(\delta_1 - \delta_2)^2$  will have a net positive value, which will cause the energy term  $\Delta H$  to oppose the entropy term. If the entropy term is less than the energy term, mixing or dissolution will not occur.

## **Solubility Parameters and Petroleum Residua**

The use of the solubility parameter is complicated by the presence of dipole and hydrogen bonding interactions. For solvents and materials with strong polarity and hydrogen bonding components, dissolution is not predictable by the single component, or dispersion solubility parameter, described above. Two-component and three-component solubility parameter systems have been described (Barton 1974, Wiehe 1996). For such systems, solubility is maximized when all the components for the solvent and material being dissolved are similar in polarity. Two- or three-dimensional maps were used to describe so-called solubility zones, areas, or spheres for such systems. Mixtures of solvents with different solubility parameter components can be used to generate a mixture with custom-formulated solubility parameter components. Thus, it is possible to formulate a mixture of two or more solvents that will dissolve a material that is not soluble in one or more of the solvents alone (Burrell 1955). For petroleum residua and fractions isolated therefrom, solubility characteristics can best be described by the single-component dispersion solubility parameter. Multi-component solubility parameters are not necessary (Wiehe 1996).

Petroleum residua are complex mixtures that are usually separated into well-defined fractions prior to characterization. Separation schemes typically include steps such as precipitation of asphaltenes by a hydrocarbon solvent such as n-heptane and subsequent separation of the deasphalted material (maltenes) by adsorption, ion exchange, size exclusion chromatography, or combinations thereof (Schabron et al. 1993). The isolation of asphaltenes is a solvent separation procedure based on the solubility difference between the precipitating solvent and the precipitated material. The solubility (or lack thereof) of asphaltenes is dependent on both molecular weight and polarity considerations (Long 1979, Speight 1994).

The solubility parameters of a series of solvents and solvent mixtures used to elute chromatographic fractions from a heavy oil have been estimated assuming a relationship between solvent elution strength on alumina and the solubility parameter of a solvent or solvent mixture (Long and Speight 1989, Snyder 1971). These data were later used to relate solubility parameter to hydrogen content of heavy oil fractions before and after thermal treatment (Wiehe 1996). The solubility parameter of a particular residuum fraction probably constitutes a range that is reflective



of the variety of chemical components of the fraction. Solvent extractions can be performed on residua to obtain a solubility parameter spectrum (Long and Speight 1989). This yields a polarity distribution and can be used as a diagnostic tool during upgrading.

Selected solvents that do not have significant polarity or hydrogen bonding components are listed in Table 1, along with their solubility parameters. The solubility parameter of a mixture of solvents is the sum of the solubility parameter of each component times the volume fraction of that component in the mixture.

**Table 1. Solubility Parameters of Solvents with Predominantly Dispersive Components<sup>a</sup>**

---

<u>Solvent</u>	<u>Solubility Parameter, (cal/cc)<sup>1/2</sup></u>
perfluoro-n-hexane	5.9
isooctane	6.9
n-pentane	7.0
n-hexane	7.3
n-heptane	7.4
cyclohexane	8.2
toluene	8.9
benzene	9.2
carbon disulfide	10.0
diiodomethane	11.8

---

a. Hildebrand et al. 1970

Toluene is known to be a good solvent for whole petroleum residua. This is probably because the solubility parameters of whole residua components lie within about  $\pm 2$  (cal/cc)<sup>1/2</sup> of 8.9, or within 6.9 - 10.9 (cal/cc)<sup>1/2</sup>. Once thermal treatment of residua has begun, however, toluene fails to solvate the more polar components, which are formed as coking ensues.

Relatively large solubility parameters require the use of polar interactive or hydrogen bonding solvents such as the alcohols (methanol  $\delta = 14.6$ , ethanol  $\delta = 12.5$ , etc.). Solubility parameters below those of the perfluorinated hydrocarbons can be attained by using silicone oils or supercritical fluids such as supercritical carbon dioxide.

## Asphaltene Solubility

The solubility parameter difference that results in a phase separation of two materials, such as asphaltenes, in a solvent can be estimated using the Scatchard-Hildebrand equation, which involves several assumptions that take into account both the heat of mixing and entropy terms:

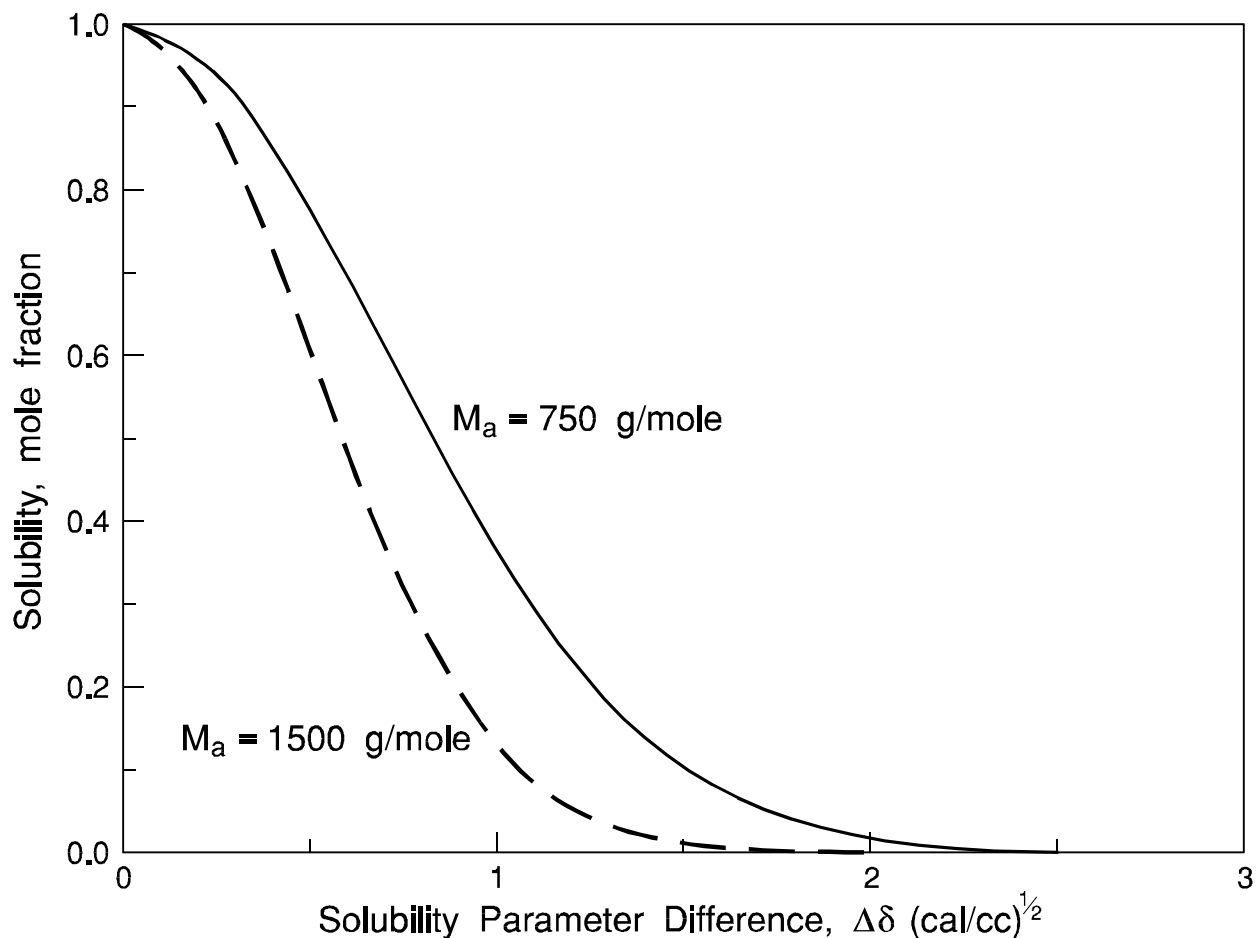
$$\ln a_a = \ln x_a + M_a/RT\rho_a \cdot [N_s^2(\delta_s - \delta_a)^2] \quad (\text{Barton 1974})$$

where  $a_a$  is the activity of the solute  $a$ ,  $x_a$  is the mole fraction solubility of  $a$ ,  $M_a$  is the molecular weight of  $a$ ,  $\rho_a$  is the density of  $a$ ,  $N_s$  is the volume fraction of solvent, and  $(\delta_s - \delta_a)$  is the difference between the solubility parameters of the solute  $a$  and the solvent  $s$ . Assuming that the activity of the asphaltenes  $a_a$  is 1 (solid asphaltenes in equilibrium with dissolved asphaltenes) and the volume fraction of an excess of solvent is essentially 1, the equation can be rearranged into a form that can be used to gain insight into the solubility of asphaltenes:

$$\ln x_a = -M_a/RT\rho_a \cdot [(\delta_s - \delta_a)^2] \quad (\text{Andersen and Speight 1998})$$

Assuming a density for asphaltenes of 1.3 g/cc (Andersen and Speight 1998, Parkash et al. 1979) and molecular weights of 750 and 1,500 g/mole for two hypothetical asphaltene molecules, the solubility as a function of the differences between solubility parameters of the asphaltene molecules and a range of solvent solubility parameters was calculated. The result, shown in Figure 1, illustrates that the solubility of an individual asphaltene molecule decreases as the difference between solubility parameters increases. Also, a lower molecular weight molecule is more soluble than the higher molecular weight molecule for a particular difference in solubility parameter. From the above equations, it is apparent that the solubility depends both on molecular weight and polarity of the particular asphaltene molecule or associated specie. In an asphaltene mixture, there exists a polarity and molecular weight continuum (Schabron and Speight 1998).

Additional information can be gleaned by calculating the solubility parameter difference at several molecular weights ranging from 100 - 10,000 g/mole at which the solubility of asphaltenic or other material is a mole fraction of 0.001 (0.1 %, or 1,000 ppm). Figure 2 shows the results of this calculation and defines a phase diagram that is a function of molecular weight and solubility parameter difference. This figure shows that both polarity and molecular weight of asphaltenes in a solvent define the solubility boundaries. This type of workup tends to explain conceptually how asphaltenes are precipitated from the mixture in crude oils, which can be considered a type of continuum of molecular weights and polarities. Figure 2 also shows in a generalized manner that as the molecular weight of a particular solute decreases, there is an increased tolerance of polarity difference between solute and solvent under miscible conditions.

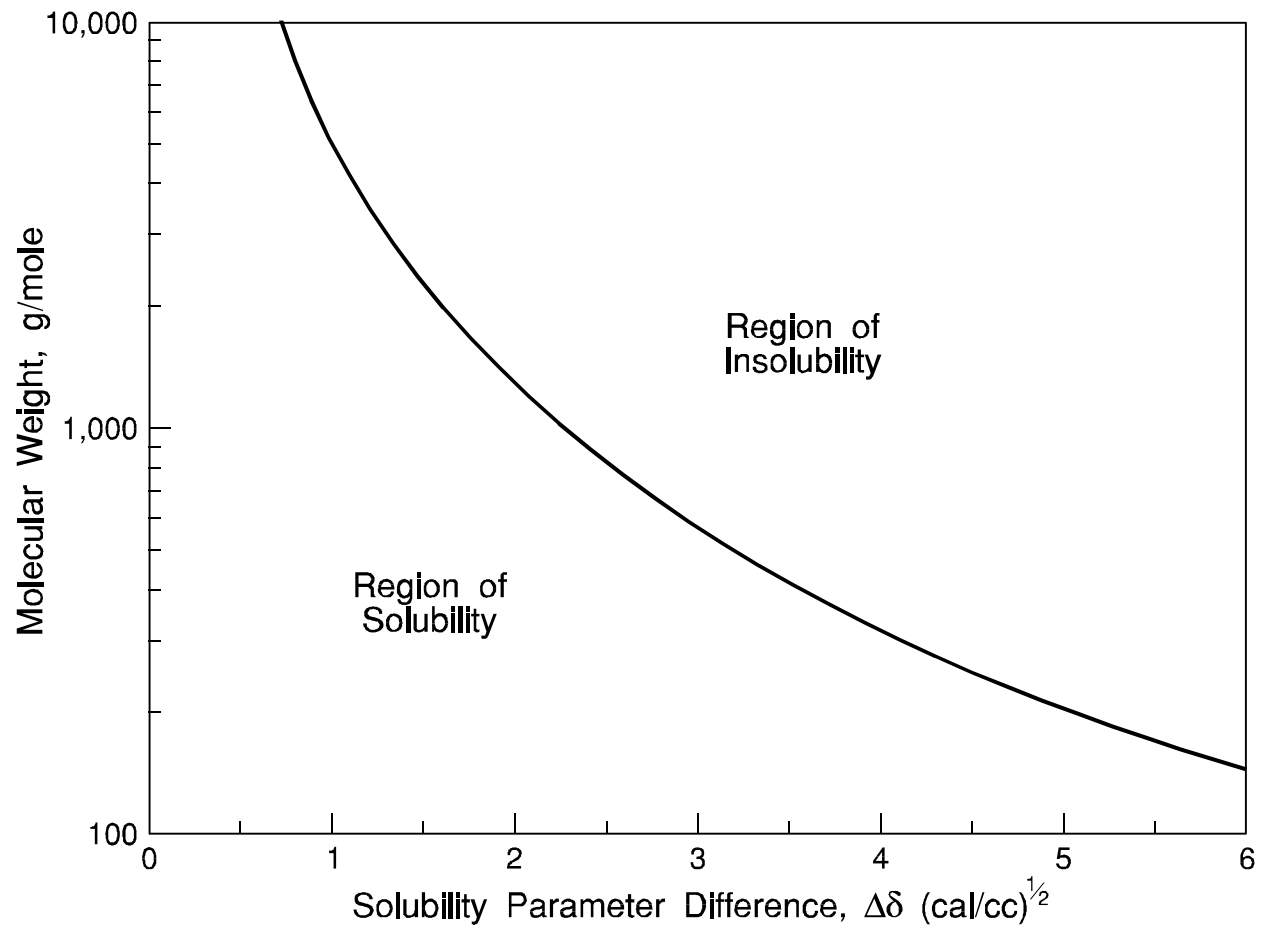


**Figure 1. Solubility of Two Hypothetical Asphaltene Molecules**

The absolute difference in solubility parameters that will result in a two-phase system or precipitation for a particular system is not straightforward. Based on the above discussions and the results illustrated in Figure 2, some generalizations can be made. For a polymer to dissolve in a solvent, the solubility parameter of the solvent should be within about  $1.1 (\text{cal/cc})^{1/2}$  of the solubility parameter of the polymer (Small 1953). For a non-polymeric solid material, such as naphthalene, to dissolve in a solvent, the difference in solubility parameters should be less than about  $2 (\text{cal/cc})^{1/2}$  (Scatchard 1931). And finally, for two liquids to be miscible, the difference in their solubility parameters should be less than about  $7 (\text{cal/cc})^{1/2}$  (Burrell 1955).

### **The Heithaus Titration**

The automated Heithaus titration is performed only with the toluene-soluble components of residua. Three toluene solutions at different concentrations of residuum are titrated with a weak



**Figure 2. Solubility / Polarity Phase Diagram**

solvent such as isooctane. The weight of residuum or asphalt ( $W_a$ ), the volume of toluene ( $V_s$ ), and volume of isooctane titrant ( $V_t$ ) are recorded at the flocculation point where asphaltenes just begin to precipitate for each solution. The flocculation ratio and dilution concentration are calculated as follows (Heithaus 1962):

$$FR = \text{Flocculation Ratio} = V_s / (V_s + V_t)$$

$$C = \text{Dilution Concentration} = W_a / (V_s + V_t)$$

A plot of FR vs. C is made and the intercepts are determined ( $FR_{\max}$  and  $C_{\min}$ ). The Heithaus parameters are defined as follows (Heithaus 1962):

$p_a = 1 - FR_{\max}$	Peptizability of Asphaltenes
$p_o = FR_{\max} \times (1/C_{\min} + 1)$	Solvent Power of Maltenes
$P = p_o / (1 - p_a) = 1/C_{\min} + 1$	Overall Compatibility of Residuum

Larger values of  $p_a$  indicate peptizable asphaltenes, and larger values of  $P$  indicate an overall compatible system. A larger  $p_o$  value is subject to a mixed interpretation.

### **Stability Evaluations**

Three stripper bottoms samples were evaluated to gauge their stability relative to impending coke formation. Data were evaluated in terms of the effect of thermal treatment on the oils prior to and during coke formation. Work was also performed to determine how close these materials were to coke formation and to recommend a relatively simple and inexpensive approach to measuring the nearness to coke formation during pilot and demonstration runs.

## **EXPERIMENTAL DETAILS**

### **Stripper Bottoms Materials**

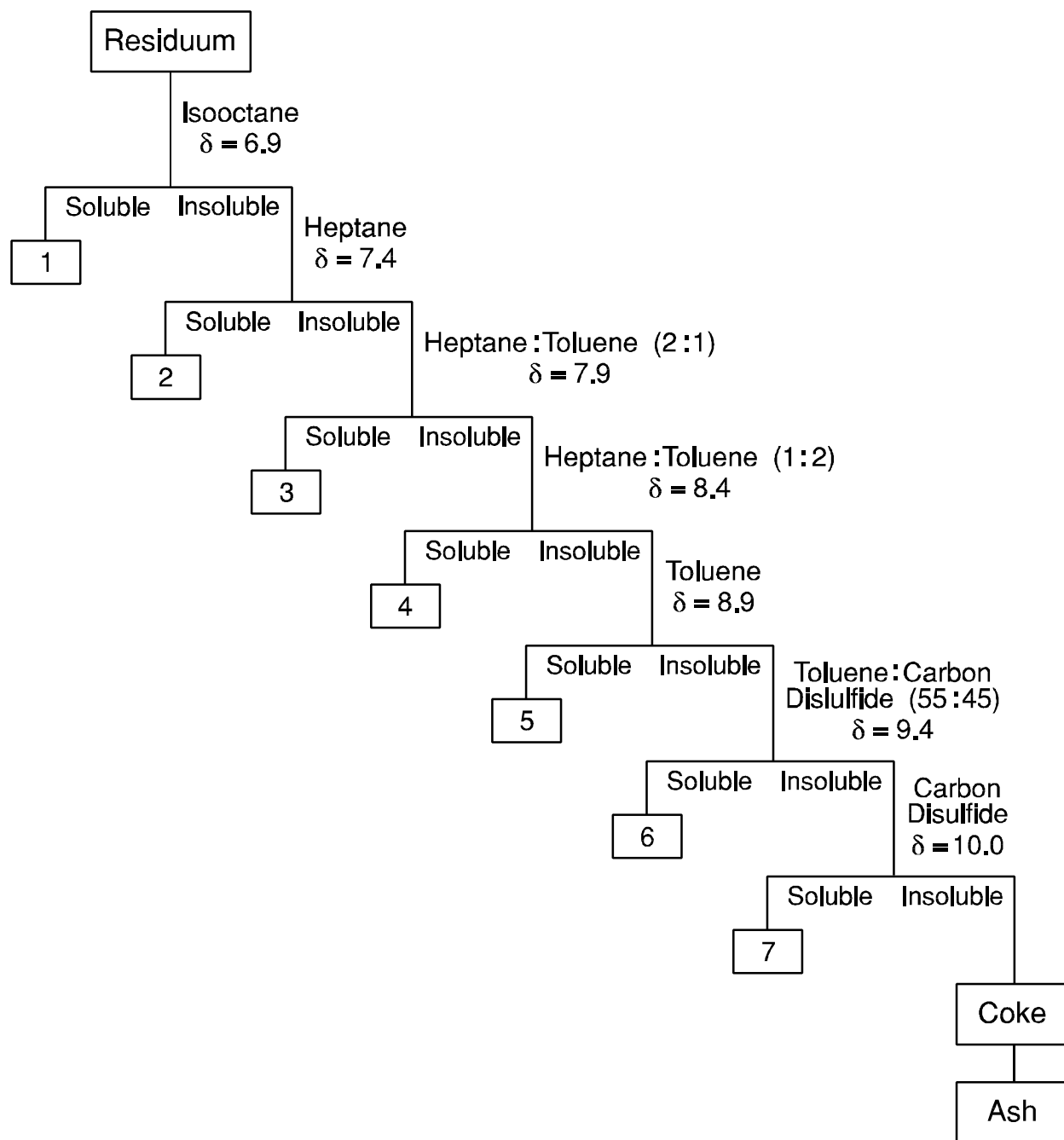
The heavy oil materials studied were three samples of bench-scale stripper bottom oils from a laboratory-scale pilot study at Western Research Institute. The conditions at which the samples were generated are listed below.

- A. Stripper Bottoms – 273 °C (525 °F)
- B. Stripper Bottoms – 343 °C (650 °F)
- C. Stripper Bottoms – 371 °C (700 °F)

These three materials represent a series of increasing severity of thermal treatment at atmospheric pressure for the same feed material. As such, they are ideal materials for demonstrating how the new molecular weight / polarity map, the Heithaus titration, and Gaestel index apply to thermally treated petroleum residua. In the sequence of increasingly severe treatment, the A bottoms were fed into the B unit, whose bottoms were fed into the C unit. These particular materials were allowed to remain in the strippers as they cooled down, so they may not be representative of the materials that would be sampled during an actual pilot run. Both Materials A and B were fully soluble in toluene, while Material C contained 13.5 wt. % toluene insolubles, which yielded 17.9 wt. % ash.

### **Sequential Solvent Extraction**

All solvents used in this study were reagent grade or better from commercially available sources. The solvent extraction sequence for the molecular weight/polarity map is shown in Figure 3.



**Figure 3. Solvent Extraction Sequence and Solubility Parameters of Solvents (cal/cc)<sup>1/2</sup>**

Isooctane asphaltenes were obtained by heating the whole residuum with a 40:1 (v:w) portion of isooctane to about 70 °C for 1 hour with stirring. The mixture was stirred at room temperature overnight, then allowed to set for at least 0.5 hour prior to vacuum filtering through a medium frit (10-15 µm) sintered glass filter. To remove solvent from the insolubles, air was passed through the filter for 5 min, they were placed in a vacuum oven at 120 °C and 23 in. Hg vacuum for 1 hour, were

cooled, then weighed. A 40:1 ratio (v:w) of n-heptane was mixed with the insolubles and stirred overnight. The insolubles were filtered using vacuum filtration through a medium glass filter. These steps were repeated with the series of solvents shown in Figure 3. At the end of the series, the carbon disulfide insolubles (coke) were ashed in a muffle furnace at 400 °C overnight to obtain wt. % ash.

### **Vapor Pressure Osmometry**

Number average molecular weights were determined with a Knauer vapor pressure osmometry (VPO) instrument using toluene at 60 °C (ASTM D-2503-92). Determinations were made with 1-4 wt.% sample solutions. Benzil was used for calibration.

### **High-Performance Size Exclusion Chromatography**

High-performance size exclusion chromatography was performed with a 300 x 7.8 mm Phenomenex Linear-2 size exclusion column maintained at 40 °C. Elution was with toluene at 1 mL/min. Portions of 150  $\mu$ L of 0.1 wt. % standards and 0.2 wt. % samples in toluene were injected using a Waters 717 autosampler. Calibration was performed using a series of polystyrene standards from Waters Associates. The chromatograms were interpreted using ChromPerfect size exclusion chromatography software, version 3.5. Polystyrene calibration was used to monitor the performance of the system.

### **Heithaus Titration**

Automated Heithaus titrations were performed in toluene solutions using isooctane as titrant. The instrument and procedure used are described in detail elsewhere (Pauli 1996).

### **Gaestel Index**

Heptane asphaltenes were isolated by heating the whole residuum with a 40:1 (v:w) portion of heptane at about 70 °C for 1 hour with stirring. The mixture was stirred at room temperature overnight, then allowed to set for at least 0.5 hour prior to vacuum filtering through a medium frit sintered glass filter. To remove solvent from the insolubles, air was passed through the filter for 5 min, they were placed in a vacuum oven at 120 °C and 23 in. Hg vacuum for 1 hour, were cooled, then weighed. Solvent was removed from a portion of the maltenes. An aluminum oxide separation was performed using Alcoa F-20 alumina calcined overnight at 400 °C (ASTM D-4124-91). The separations were performed in a 19 mm x 400 mm glass column using 70 g of alumina and 700 mg sample from a 10 % solution in heptane. Elution was performed with heptane, and the first 50 mL (saturates) was collected. Solvent was removed and the wt. % saturates were determined gravimetrically.

## RESULTS AND DISCUSSION

### The New Molecular Weight / Polarity Map

A new molecular weight / polarity map was developed for petroleum residua components. The map is based on the simplified version of the Scatchard-Hildebrand equation described in the Introduction. The phase diagram map was developed by calculating the regions of asphaltene solubility in a variety of solvents ranging from isooctane, with a solubility parameter of  $6.9 \text{ (cal/cc)}^{1/2}$ , to carbon disulfide, with a solubility parameter of  $10.0 \text{ (cal/cc)}^{1/2}$  (Figure 3). The map is based on solubility-parameter-tuned solvent mixtures providing even spacing between contour lines of  $0.5 \text{ (cal/cc)}^{1/2}$  except for the last series between toluene:CS<sub>2</sub> (55:45)(v:v) and CS<sub>2</sub>, where the spacing is  $0.6 \text{ (cal/cc)}^{1/2}$ . The calculations assume a series of individual molecules with apparent molecular weights ranging from 100 - 50,000 g/mole and a density of 1.3 g/cc (Andersen and Speight 1998, Parkash et al. 1979). The border between the soluble and insoluble regions is defined arbitrarily as the solubility of a mole fraction of 0.001 (0.1 %, or 1,000 ppm). This border is actually a point on a solubility gradient, where solubility increases towards the left-hand portion of a curve and decreases to the right (see Figure 1).

The location of a particular material on the map was determined by three measurements. (1) First, a solubility or solvent spectrum of the material was obtained to determine between what lines on the map the material lies. This was accomplished by performing a series of solubility measurements in a series of solvents of increasing or decreasing solubility parameters and determining their weight percentages. Excess solvent to solute (40:1 v:w) ratios were used to minimize any potential effect of the solute on the overall solubility parameter of the system. (2) Then a number average molecular weight of the molecules and/or associated species mixture was determined on the isolated fractions using vapor pressure osmometry in toluene at 60 ° C, followed by (3) analytical-scale size exclusion chromatography.

A particular molecule or associated specie in an actual residuum or asphaltene mixture occupies a single point on the map. A mixture of molecules and associated species in a continuum of polarity and apparent molecular weight values (either of individual molecules or associated species) can be visualized as occupying a particular area on the map. For a particular solvent, the solubility of a solute increases with decreasing polarity, decreasing apparent molecular weight, or a combination of the two. As the material undergoes thermal alteration, solvent perturbation, or aging, the changes in the molecules or associated species cause the points representing these materials to move to a different region of the map. Thus, such a map can be used as a means of evaluating heavy oils or residua and diagnosing processing conditions and the state of thermal degradation. It can also be used as a tool in efforts to diagnose and possibly intervene in the incipient precipitation of polar materials during petroleum production.



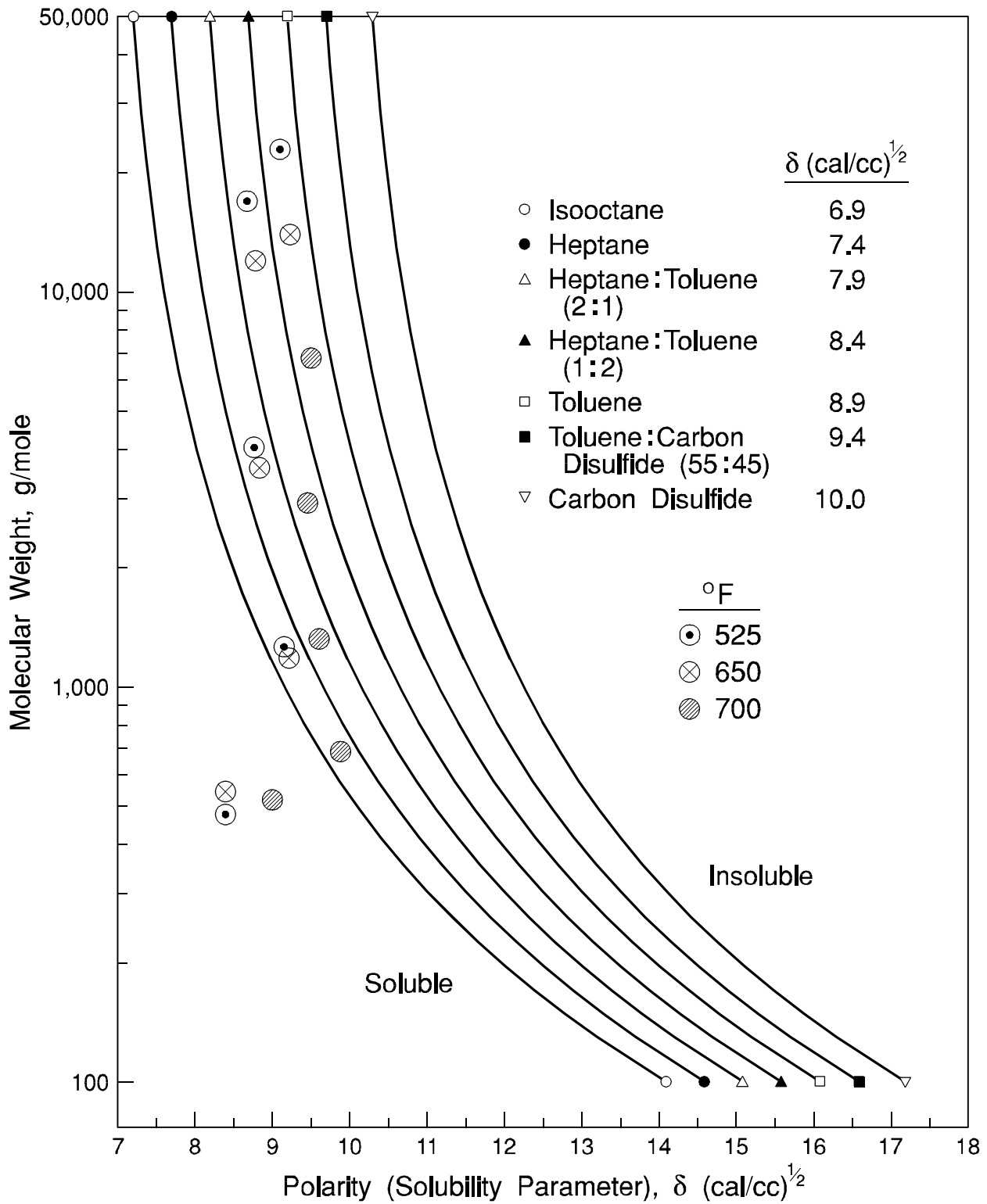
## Pyrolysis Series Map

The new map was demonstrated initially with a heavy oil material subjected to three severities of thermal treatment (Figure 4), and the effects of thermal treatment on the oils prior to and during coke formation were evaluated. The new molecular weight / polarity map allows us to “peel” the layers of association in this colloidal system (progressively less polar material surrounding a more polar core). The data for the three stripper bottoms materials are presented in Table 2. The gravimetric data show the progression towards more polar species as the severity of thermal treatment increases. Material C is generating both coke and coke precursors (Fractions 6 and 7).

**Table 2. Solubility Map Data for Three Stripper Bottoms**

<u>Sample</u>	<u>Measurement</u>	Fraction (See Figure 3.)								
		<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>	<u>coke</u>	<u>ash</u>
A	Weight Percent	85.9	0.8	6.3	5.1	0.7	1.1	0.1	<0.1	<0.1
	VPO Mn g/mole	474	1260	4040	17000	23000	–	–	–	–
	$\delta$ (cal/cc) <sup>1/2</sup>	8.4	9.2	8.8	8.8	9.2	–	–	–	–
B	Weight Percent	83.4	0.9	6.7	5.5	1.0	2.2	0.1	0.2	<0.1
	VPO Mn g/mole	542	1180	3580	12000	14000	–	–	–	–
	$\delta$ (cal/cc) <sup>1/2</sup>	8.4	9.2	8.8	8.8	9.2	–	–	–	–
C	Weight Percent	64.0	2.0	5.3	5.8	2.9	4.5	1.5	11.5	2.5
	VPO Mn g/mole	516	684	1320	2920	6800	–	–	–	–
	$\delta$ (cal/cc) <sup>1/2</sup>	9.0	9.9	9.6	9.5	9.5	–	–	–	–

The data also show that the number average molecular weights of the isooctane-soluble maltenes are about the same for all three oils. The molecular weight of each of the more polar fractions decreases significantly with thermal treatment. The main difference between the various polar fractions for a particular material seems to be molecular weight. The solubility parameters are similar for a particular series of polar materials with large differences in apparent molecular weight. This leads to the speculation that a residuum colloidal system self-adjusts to lower the overall energy of the system by matching as closely as possible the polarity of the associated complexes to the solvent matrix (isooctane maltenes). This appears to occur by automatic adjustment of the apparent molecular weights of the complexes.



**Figure 4. Molecular Weight / Polarity Map for Three Stripper Bottoms**

For the pyrolysis series, the higher molecular weights are probably due to associated species, which the thermal treatment is breaking apart. This results in an overall less stable colloidal-type system with increasing severity of thermal treatment, as was observed with the Heithaus titration data discussed below. Also, significant cracking has taken place in Material C, which further reduces the apparent molecular weight of the corresponding fractions soluble in the various solvents compared to Materials A and B. The solubility parameters (polarities) of the fractions from C are larger than the corresponding fractions from A and B. The data clearly show some significant differences between Material C, and the less severely treated Materials A and B.

### Size Exclusion Chromatography

The high-performance analytical scale size exclusion chromatography (SEC) results for the fractions are listed in Table 3. Portions of 150 uL of 0.2 wt. % solutions of the fractions were injected (0.3 mg). The values are reported relative to polystyrene calibration and as such must be used with caution since polystyrene and residua components are different materials.

**Table 3. High-Performance Size Exclusion Chromatography Results**

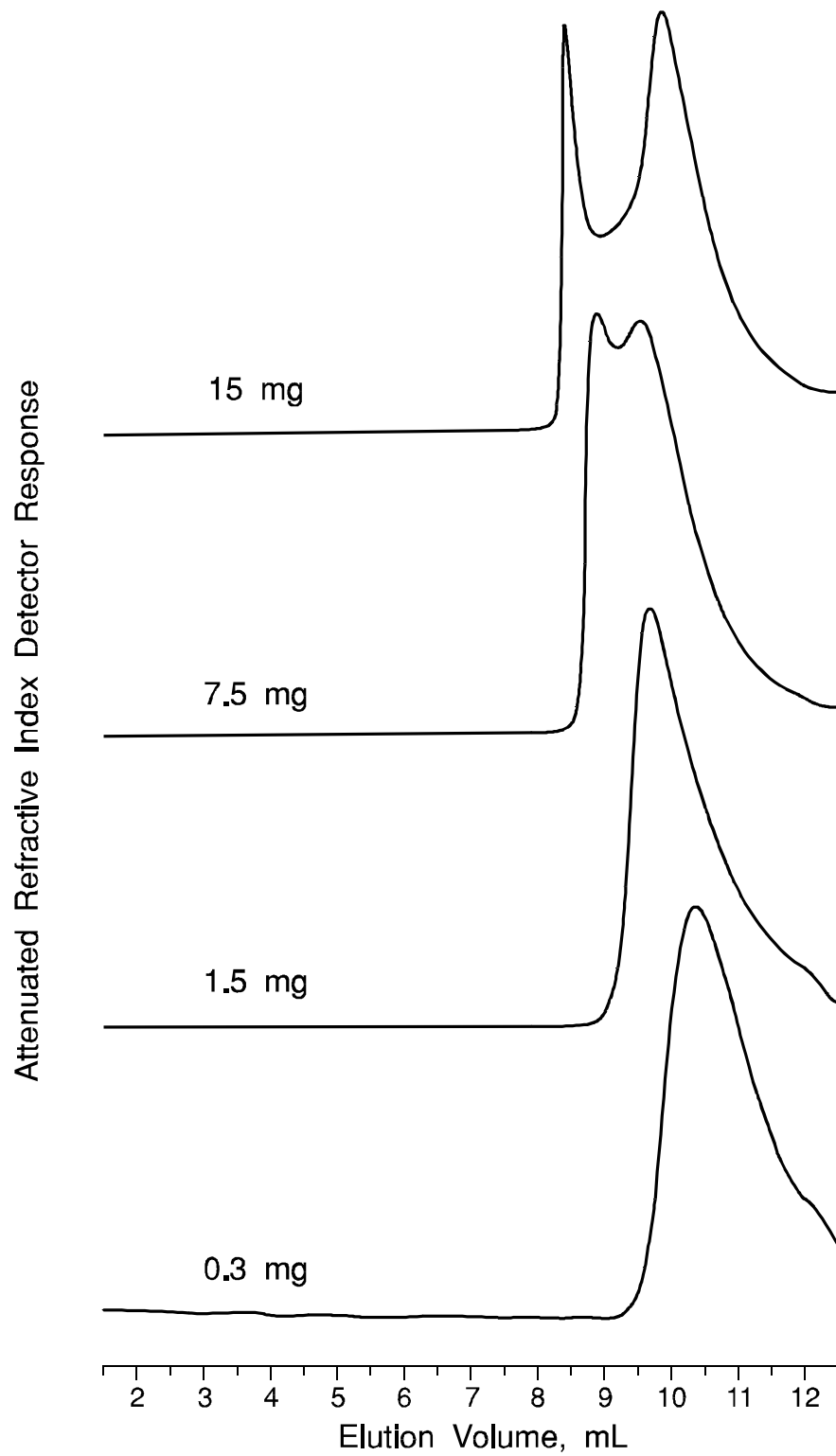
<u>Fraction</u>	<u>Size Exclusion Chromatography</u>			<u>VPO</u>	
	<u>Mw</u>	<u>Mn</u>	<u>Range<sup>a</sup></u>	<u>Mw/Mn</u>	<u>Mn</u>
<u>A (273 °C/525 °F)</u>					
1	928	422	210-2200	2.20	474
2	1490	585	270-3400	2.55	1260
3	2440	772	340-5600	3.16	4040
4	2240	618	260-5400	3.62	17000
5	2120	523	210-5300	4.05	23000
<u>B (343 °C/650 °F)</u>					
1	923	439	220-2100	2.10	542
2	1320	539	250-3000	2.45	1180
3	2110	703	310-5000	3.00	3580
4	2090	611	260-5000	3.42	12000
5	1930	510	210-4800	3.78	14000
<u>C (371 °C/700 °F)</u>					
1	705	395	210-1500	1.78	516
2	788	388	190-1800	2.03	684
3	1140	481	220-2600	2.37	1320
4	1350	516	230-3200	2.61	2920
5	1230	455	200-2900	2.70	6800

a. From elution volumes at 10% to 90% of peak area

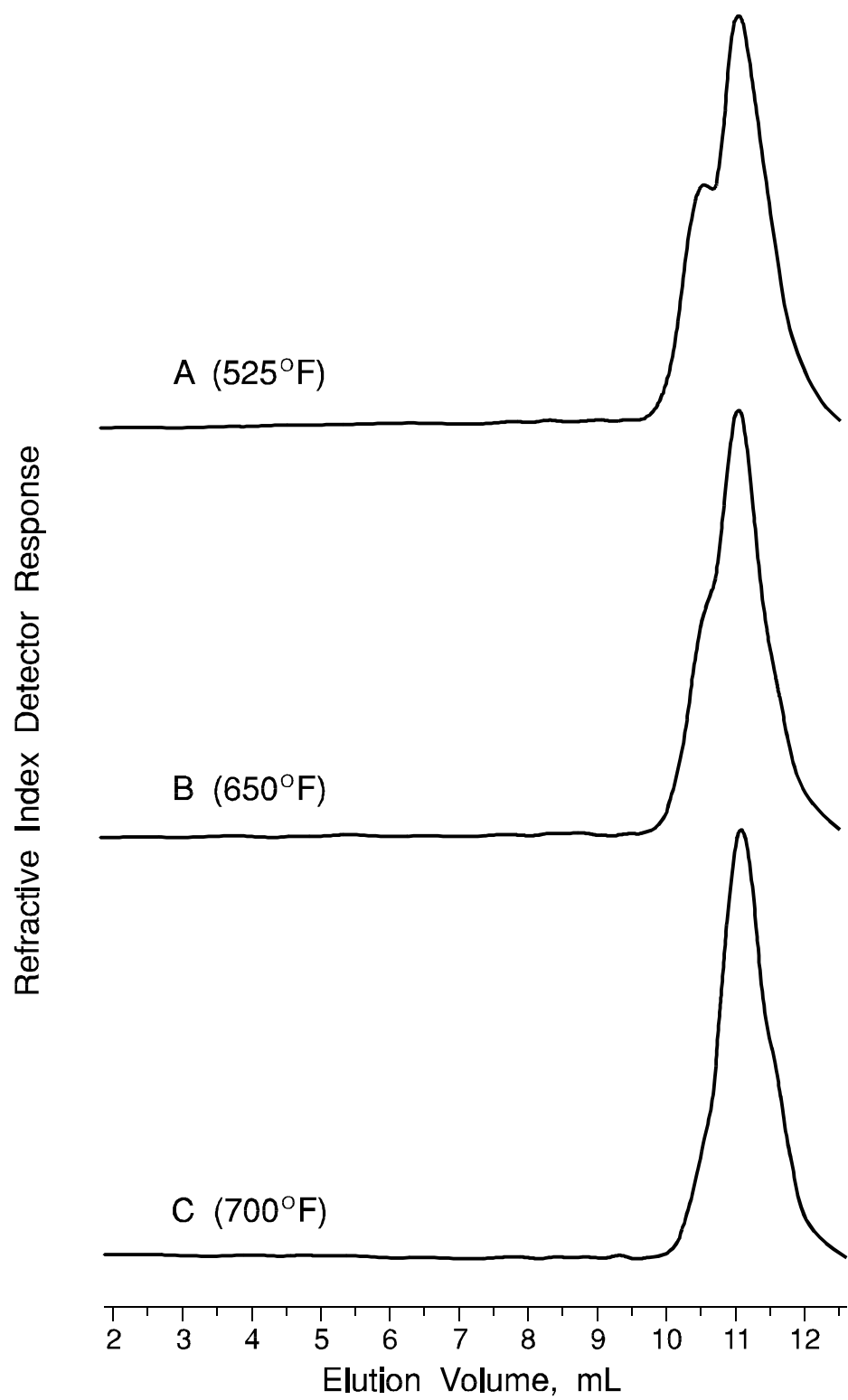
Except for the number average molecular weight values for the isooctane maltenes for all three materials (Fraction 1), the values are significantly lower than the number average molecular weight values determined by VPO. The discrepancy cannot be wholly attributed to the use of polystyrene standards and the non-uniform response with refractive index detection from residual components of differing functionality. Some adsorption of materials on the polystyrene-divinylbenzene stationary phase may be occurring also. The values determined by VPO represent the apparent number average molecular weights in 1 - 4 wt.% toluene solutions. An additional possible effect is that the colloidal complexes that give apparent high VPO molecular weight values in solution break down during the SEC separation for Fractions 4-5 for all three materials, resulting in significantly lower apparent number average molecular weight values than the corresponding VPO values. This has been observed in previous work (WRI 1998). To check this further, various amounts of one of the fractions for which sufficient material was available were injected onto the high-performance SEC column. The fraction was Material A, Fraction 4 which gave an apparent VPO molecular weight of 17,000 g/mole and a SEC number average molecular weight of 618 g/mole (Table 2).

Portions of 100  $\mu$ L of toluene solutions containing 0.3 - 15 mg were injected. The results are shown in Figure 5. As more material was injected, the retention volume decreased, indicating an increase in associations/apparent molecular weight. For the 7.5 mg injected, the peak split into two peaks, suggesting the presence of significant associations. This peak splitting and elution volume shortening phenomenon was not observed when a polystyrene standard with a molecular weight of 400 g/mole was injected under identical conditions. For injections of 0.3 to 7.5 mg, the material eluted in about 3 mL of toluene. The concentration at which significant complex formation begins for this asphaltenic material is estimated to be at the point where the peak splits. This occurs somewhere between 1.5 and 7.5 mg injected diluted into about 3 mL toluene elution solvent, which is between about 0.06 - 0.3 wt. %. This is consistent with the results of Andersen and Birdie (1991), who reported a critical micelle concentration of asphaltenes in toluene near 0.38 wt.% using calorimetric titration.

As with the VPO data, the SEC number average molecular weights for a particular fraction generally decrease with increasing severity of thermal treatment. The polydispersity  $M_w/M_n$ , an indicator of molecular weight distribution, also decreases for a particular fraction with increasing severity of thermal treatment. The chromatograms appeared as essentially symmetrical peaks with one exception — the isooctane maltenes (Fraction 1). These showed a leading high molecular weight shoulder component in the 273 °C (525 °F) material, which was smaller for the 343 °C (650 °F) material and was not evident for the 371 °C (700 °F) material (Figure 6). This could represent a high molecular weight associated component of the isooctane maltenes that is destroyed with increasing



**Figure 5. High-Performance Size Exclusion Chromatography of 100  $\mu$ L Portions of Material A Solutions, Fraction 4 at Various Amounts Injected**



**Figure 6. High-Performance SEC Profiles for Isooctane Maltenes**

severity of thermal treatment. Perhaps this is another indicator of the loss of resinous-type components as thermal treatment progresses to coke formation.

### Heithaus Titration Results

Heithaus titration plots for the three bottoms materials are provided in Figure 7. The Heithaus parameters for these three materials are provided in Table 4. The residua are colloidal-/micellar-type systems. The results show that the materials are becoming less stable with increasing severity of thermal treatment. The results also show a significant difference between Material C, which is producing coke, and Materials A and B, which are not yet near coke production.

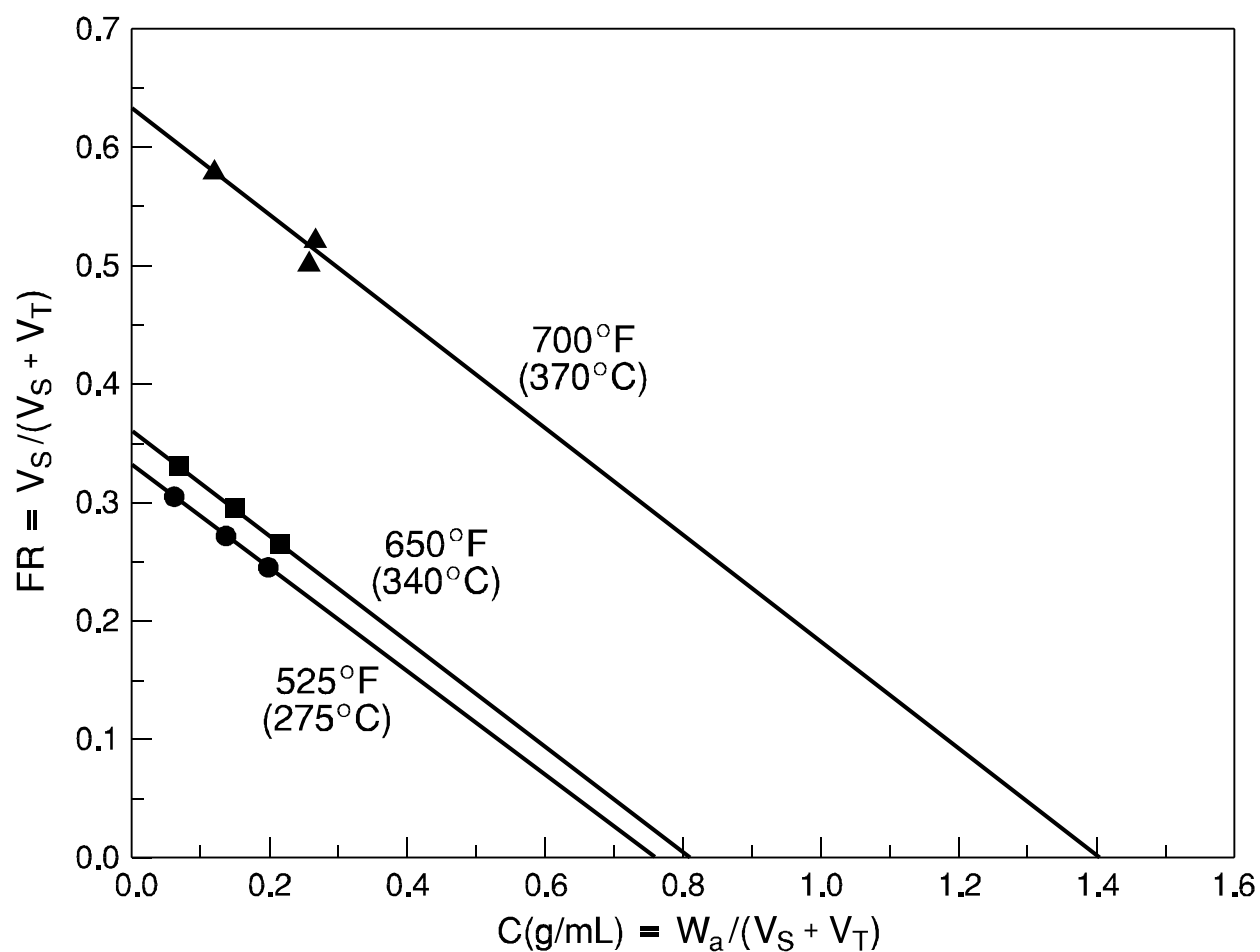


Figure 7. Heithaus Titration Results for Three Stripper Bottoms

**Table 4. Heithaus Titration Results for Three Stripper Bottoms**

<u>Heithaus Parameter</u>	<u>Material</u>		
	<u>A (525 °F)</u>	<u>B (650 °F)</u>	<u>C (700 °F)</u>
$p_a$	0.668	0.638	0.364
$p_o$	0.766	0.805	1.09
P	2.31	2.23	1.71
$p_a/C_{min}$ Ratio	0.872	0.783	0.259

### Solubility Parameter and Heithaus Data

Another way of evaluating  $FR_{max}$  is that it is the volume fraction of toluene in a toluene and isooctane mixture, assuming additive volumes. By knowing the solubility parameter of both solvents, the solubility parameter at  $FR_{max}$  can be calculated.  $FR_{max}$  is thus a measure of the solubility parameter at infinite dilution at which asphaltenes begin to precipitate. A relatively larger  $FR_{max}$  indicates a less soluble asphaltene. Since solubility depends on both molecular weight and polarity, this can be due to a higher molecular weight or more polar asphaltene, or both.  $C_{min}$  is the ratio of residuum to titrant (isooctane) at which asphaltenes begin to precipitate. A larger  $C_{min}$  indicates a less compatible system (smaller P). Assuming that asphaltene flocculation occurs at a particular solubility parameter for a particular residuum, it is apparent that both  $FR_{max}$  and  $C_{min}$  and the line connecting them are at the same solubility parameter. The solubility parameter and molecular weight of the asphaltenes, whole residuum, and maltenes relate to Heithaus terms as shown in Table 5.

The solubility parameter at which asphaltenes begin to precipitate (at  $FR_{max}$ ) and the solubility parameters of the residuum matrix (at  $C_{min}$ ) were calculated and are listed in Table 6 for the three stripper bottoms. Both the solubility parameter for the whole residuum and the solubility parameter of the onset of asphaltene flocculation increase with increasing severity of thermal treatment. The material that has been heated to the point of coke production is significantly more polar than the same material prior to coke production. This is also reflective of cracking and the removal of less polar distillates with heating.



**Table 5. Heithaus Parameter and Solubility Parameter Trends**

<u>Term, Definition</u>	<u>Value</u>	<u>Effect of <math>\delta</math> and/or MW (Material)</u>
$FR_{\max} = V_S / (V_S + V_T)$ $W_A \rightarrow 0$	↓	↓ (Asphaltenes)
$C_{\min} = W_A / (V_S + V_T)$ $V_S \rightarrow 0$	↑	↓ (Resid Matrix/Maltenes, for the same $FR_{\max}$ ) ↑ (Resid Matrix/Maltenes as $FR_{\max}$ increases)
$p_a = 1 - FR_{\max}$	↑	↓ (Asphaltenes)
$p_o = FR_{\max} (1/C_{\min} + 1)$	$FR \downarrow, P_o \downarrow$ $C_{\min} \uparrow, P_o \downarrow$	↓ (Asphaltenes) ↓ (Resid Matrix/Maltenes, for the same $FR_{\max}$ ) ↑ (Resid Matrix/Maltenes as $FR_{\max}$ increases)
$P = P_o (1 - P_a)$ $= (1/C_{\min} + 1)$	$P_o \uparrow, P \uparrow$ $P_a \uparrow, P$ -none $C_{\min} \uparrow, P \downarrow$	(See $p_o$ above) ↓ (Asphaltenes) (See $C_{\min}$ above)

**Table 6. Solubility Parameters for Whole Residua and Asphaltene Precipitation Onset**

<u>Material</u>	<u>Solubility Parameter, <math>\delta</math> (cal/cc)<sup>1/2</sup></u>	
	<u>Whole Residuum</u>	<u>Asphaltene Precipitation Onset</u>
A (525 °F)	8.4	7.6
B (650 °F)	8.5	7.6
C (700 °F)	9.1	8.2

## New Coking Index Ratio

In the current work, we are experimenting with the concept of a new “Coking Index Ratio,” defined as  $p_a/C_{\min}$ . This is based on the above consideration that  $p_a$  increases as the solubility parameter and/or molecular weight of the asphaltenes decrease and  $C_{\min}$  decreases as the overall stability of the residuum matrix/maltenes increases. Some preliminary studies suggest that a ratio near 1 is indicative of a relatively stable system and that the onset of coking occurs at a  $p_a/C_{\min}$  of about 0.3. The proposed Coking Index Ratio,  $p_a/C_{\min}$  is essentially at the suggested coke onset threshold value of 0.3 for the coke-producing Residuum C in Table 4. More residuum systems need to be studied to determine how universal this concept is. Such an index opens the possibility of optimizing distillate yield by continuing a distillation to a coking index value of 0.4, for example.

## The Gaestel Stability Index

The Gaestel index is a calculation made from the results of a SAPA (saturates, aromatics, polars, and asphaltenes) gravimetric analysis (Gaestel et al. 1971). Asphaltenes were precipitated from Materials A and B, which were completely soluble in toluene, and the toluene-soluble portion of Material C with a 40:1 (v:w) ratio of heptane. The saturates fraction was obtained by eluting a portion of the heptane-soluble maltenes on calcined aluminum oxide using a scaled-down version of ASTM D-4124 (5). The index is calculated as follows:

$$G = (\text{saturates} + \text{asphaltenes}) \div (\text{aromatics} + \text{polars}).$$

The saturates and asphaltenes are the lowest- and highest-polarity components of the residuum, respectively, and the solubility of the asphaltenes in a colloidal system is enhanced by the presence of intermediate polarity species such as aromatics and polars. The wt. % (aromatics + polars) is essentially equal to 100 - wt. % (saturates + asphaltenes). Thus, the higher the G value, the less stable the overall system is.

The weight percentages of the fractions and the G values for the toluene-soluble portions of the three stripper bottoms materials are listed in Table 7. Material C shows the highest G value, which is consistent with an unstable residuum that is producing coke. The G index is not as diagnostic as the Heithaus titration procedure, since it deals only with the quantity of fractions and not their chemical nature. It can, however, provide some indication of the nearness to coke production for a particular residuum.

**Table 7. Gaestel Index Values for Three Stripper Bottoms Materials**

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<u>Material</u>	<u>Weight Percent of Fractions</u>		<u>G Index</u>
	<u>Saturates</u>	<u>Asphaltenes</u>	
A (525 °F)	22.9	11.9	0.534
B (650 °F)	18.7	14.2	0.490
C (700 °F)	19.3	22.4	0.715

---

### **Cyclohexane-Soluble Component of Asphaltenes**

Another, simpler method for estimating the proximity to the coke formation onset in thermal treatment is to determine the cyclohexane-soluble portion of heptane asphaltenes. The data for the three stripper bottoms are provided in Table 8.

**Table 8. Solubility of Heptane Asphaltenes in Two Solvents with  $\delta = 8.2$  (cal/cc)<sup>1/2</sup>**

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<u>Material</u>	<u>wt.% Heptane Asphaltenes</u>	<u>wt.% Asphaltenes Soluble in:</u>	
		<u>Cyclohexane</u>	<u>Heptane:Toluene (1:1) (v:v)</u>
A (525 °F)	11.9	14.0	63.2
B (650 °F)	14.2	10.8	52.4
C (700 °F)	22.4	1.8	26.9

---

Both Materials A and B are fully soluble in cyclohexane, yet their heptane asphaltenes are only partially soluble. Again, this is due to the associated colloidal nature of these materials. The cyclohexane-soluble components of the asphaltenes probably reflect the state of the solubilizing resins in these materials. The disappearance of the cyclohexane-soluble portion of heptane asphaltenes appears to coincide with coke formation.

It is interesting to note that the solvent mixture heptane:toluene (1:1)(v:v), which has the same solubility parameter as cyclohexane, (8.2 (cal/cc)<sup>1/2</sup>), gives a larger yield of soluble material than cyclohexane from the heptane asphaltenes for each of the three stripper bottoms. A likely explanation is that in addition to the solubility parameter, there is a chromatographic effect due to the presence

of toluene in the mixed solvent. Possibly toluene is displacing some associated material from the associated asphaltene complex. Although solubility parameters of mixtures are additive with the volume fractions of the components, chromatographic solvent strengths are not. The first small portion of a stronger chromatographic solvent in a mixture with a weaker one increases the overall chromatographic solvent strength almost exponentially (Snyder 1968). This is a plausible explanation of the data in Table 8. This also provides additional evidence for the presence of associated species in a colloidal system.

Another possible coking index can be derived by dividing the weight percent cyclohexane-soluble material in the heptane asphaltenes by the weight percent of heptane asphaltenes. A larger wt % asphaltene value would indicate a greater coking tendency, as would a smaller wt. % cyclohexane-soluble portion of the asphaltenes. The ratio values for the three stripper bottoms are 1.2, 0.76, and 0.08 for the materials treated at 273, 343, and 371 °C (525, 650, and 700 °F), respectively. The value approaches zero as coking occurs. Additional residuum systems must be studied to see how universal this phenomenon is.

## CONCLUSIONS

A new molecular weight / polarity map based on the Scatchard-Hildebrand solubility equation has been developed for petroleum residua. Work was performed for a heavy oil material subjected to three increasing severities of thermal treatment, prior to and through the onset of coke formation. The results are diagnostic of the layers of solvations by resin-type molecules around a central asphaltene core.

Two additional stability diagnostic procedures were also used. These were the Heithaus titration “P-index” and Gaestel “G” index. In the present work, Heithaus data were developed in terms of the Hildebrand solubility parameter. The Heithaus results were combined with data from the new molecular weight / polarity map to provide additional insight. The solubility parameters for the toluene-soluble asphaltene components were measured and the solubility parameters of the maltenes were calculated. As thermal treatment progresses, the solubility parameters of the components of residuum fractions increase, and the molecular weights decrease. A new coking index was proposed ( $p_a/C_{\min}$ ) based on Heithaus titration data. Preliminary results suggest that an alternative, simpler coking index may be developed by measuring the weight percent cyclohexane solubles in heptane asphaltenes. Coking onset appears to coincide with the depletion of resin-type, asphaltene-solubilizing components of residua. An unstable system results when the depletion of the resins diminishes the ability of the asphaltene/resin complexes to increase their apparent molecular weights to auto-adjust their solubility parameter to closely match the solubility parameter of the matrix.

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