ELSEVIER

Fuel 80 (2001) 529–537

FUEL

www.elsevier.com/locate/fuel

Molecular weight polarity map for residua pyrolysis

J.F. Schabron*, A.T. Pauli, J.F. Rovani Jr.

Western Research Institute, 365 North 9th Street, Laramie, WY 82072, USA

Received 13 March 2000; revised 6 June 2000; accepted 9 June 2000

Abstract

A new molecular weight/polarity map was developed for petroleum residua based on the Scatchard–Hildebrand solubility equation. A series of extractions is performed with solvents of increasing solubility parameter, and the fractions are analyzed by vapor pressure osmometry for number average molecular weight, and analytical scale size exclusion chromatography for molecular weight spread. The results are diagnostic of the layers of solvation by resin-type molecules around a central asphaltene core. As thermal treatment progresses, the solubility parameter of the components of residua fractions increases, and the apparent molecular weight decreases. Coking onset appears to coincide with the depletion of resin-type asphaltene solubilizing components of residua and the formation of a bimodal system. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Residua; Pyrolysis; Solubility parameter

1. Introduction

1.1. Solubility parameters and petroleum residua

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 ΔG is the free energy, ΔH the heat of mixing, T the temperature, and ΔS 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 [1]. 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 ΔH is the heat of mixing, V the total volume, ΔE_x the molar energy of vaporization of component x, V_x the molar volume of component x, and Φ_x is the volume fraction of component x in the solution [2]. The term $(\Delta E/V)^{1/2}$ is called the solubility parameter δ, 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, ΔE and the molar volume V. Other means of estimating solubility parameters have been described [2]. 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 [3].

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 ΔH to oppose the entropy term. If the entropy term is less than the energy term, mixing or dissolution will not occur.

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 [4–6]. For such systems, solubility is maximized when all the various components for the solvent and material being dissolved are as similar as possible. For petroleum residua and fractions isolated therefrom, bulk solubility characteristics can be best described by the single component dispersion solubility parameter [5]. Solubility parameters of heavy oils also have been related to refractive index values [7]. The isolation of asphaltenes is a solvent separation

* Corresponding author. Tel.: +1-307-721-2011; fax: +1-307-721-2345.

0016-2361/01/$ - see front matter © 2001 Elsevier Science Ltd. All rights reserved.
PII: S0016-2361(00)00100-9

procedure, which is based on the solubility difference between the precipitating solvent and the precipitated material [8]. The solubility (or lack thereof) of asphaltenes is dependent on both molecular weight and polarity considerations [9].

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 [10,11].

1.2. Asphaltene solubility

The solubility parameter difference which 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 which take into account both the heat of mixing and entropy terms [4]:

$$\ln a_a = \ln x_a + M_a/RT\rho_a \cdot [N_s^2(\delta_s - \delta_a)^2]$$

where a_a is the activity of the solute a, x_a the mole fraction solubility of a, M_a the molecular weight of a, ρ_a the density of a, N_s 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 which can be used to gain insight into the solubility of asphaltenes:

$$\ln x_a = -M_a/RT\rho_a \cdot [(\delta_s - \delta_a)^2]$$

Solubilities as a function of the differences between asphaltene and solvent solubility parameters were calculated for hypothetical asphaltene molecules with molecular weights of 750 and 1500 g/mol [12]. The results showed that the solubility of an individual asphaltene moiety decreases as the difference between solubility parameters increases. Also, a lower molecular weight moiety is more soluble than the higher molecular weight molecule for a particular difference in solubility parameter. It is apparent that the solubility depends on both molecular weight and polarity of the particular asphaltene molecule or associated specie. Additional insight was gleaned by calculating the solubility parameter difference at several molecular weights ranging from 100 to 10,000 g/mol at which the solubility of asphaltenic or other material is a mole fraction of 0.001 (0.1%, or 1000 ppm). A phase diagram was developed which showed that both polarity and molecular weight of asphaltenes in a solvent define the solubility boundaries. This tends to explain conceptually how asphaltenes are precipitated from the mixture in crude oils, which can be considered a continuum of molecular weights and polarities. As the molecular weight of a particular solute decreases, there is an increased tolerance of polarity difference between solute and solvent under miscible conditions [12].

The absolute difference in solubility parameters, which will result in a two-phase system or precipitation for a particular system, is not straightforward, however some generalizations can be made. For a polymer to dissolve in a solvent, the solubility parameter of the solvent should be within about 2 $MPa^{1/2}$ of the solubility parameter of the polymer [3]. For a non-polymeric solid material such as naphthalene to dissolve in a solvent, the difference in solubility parameters should be less than about 4 $MPa^{1/2}$ [13]. And finally, for two liquids to be miscible, the difference in their solubility parameters should be less than about 14 $MPa^{1/2}$ [1].

1.3. The Heithaus titration

The 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 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 [14]:

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

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

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 [14]:

$$p_a = 1 - FR_{max} \qquad \text{Peptizability of Asphaltenes}$$

$$p_o = FR_{max} \times (1/C_{min} + 1) \qquad \text{Solvent Power of Maltenes}$$

$$P = P_o/(1 - P_a) = 1/C_{min} + 1$$

Overall Compatibility of Residuum

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

1.4. Stability evaluations

In the current study, three atmospheric stripper bottoms subjected to increasing severity of pyrolysis 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 towards the goal of diagnosing how close these materials are to coke formation, and to recommend a relatively simple and inexpensive approach to measuring the nearness to coke formation during future pilot and demonstration runs.

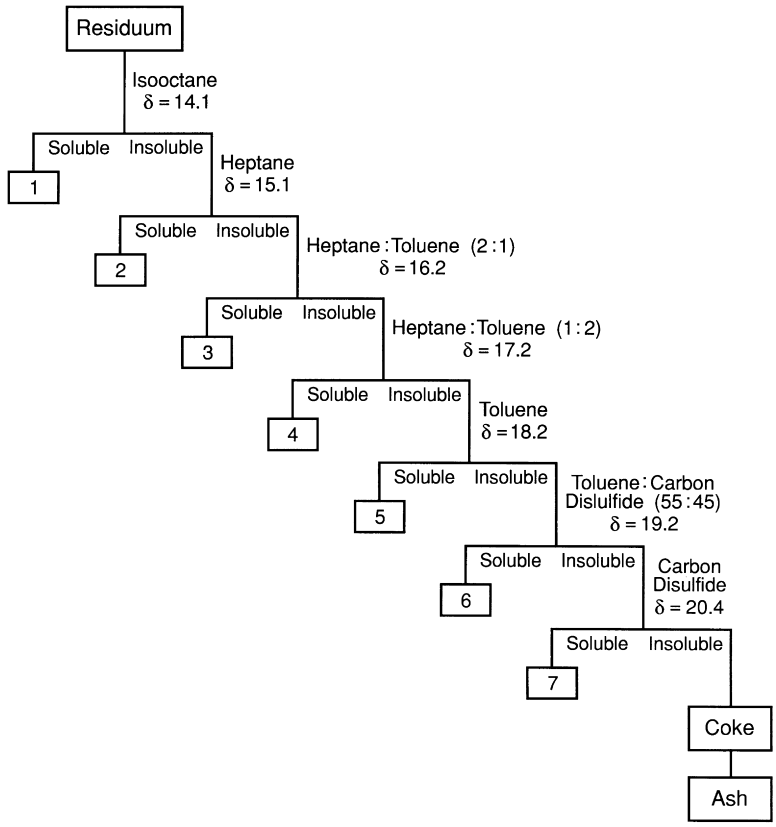

Fig. 1. Solvent extraction sequence and solubility parameters of solvents $MPa^{1/2}$.

2. Experimental

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

A. Stripper Bottoms — 275°C
B. Stripper Bottoms — 340°C
C. Stripper Bottoms — 370°C

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 and the Heithaus titration apply to pyrolyzed 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. 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.

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 Fig. 1. Isooctane asphaltenes were obtained by heating the whole residuum with a 40:1 (v:w) portion of isooctane to about 70°C for 1 h with stirring. The mixture was stirred at room temperature overnight, then allowed to set for at least 0.5 h prior to vacuum filtering through a medium frit (10–15 μm) sintered glass filter. Solvent was removed from the insolubles by passing air through the filter for 5 min, followed by placing them in a vacuum oven at 120°C and 77×10^3 Pa vacuum for 1 h, and weighed after cooling. 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 Fig. 1. 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.

Number average molecular weights were determined with a Knaur 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 was performed with a 300 × 7.8 mm Phenomenex Linear-2 size exclusion column maintained at 40°C. Elution was with toluene at 1 ml/min. Portions of 150 μl of 0.1 wt.% standards and 0.2 wt.% samples in toluene were injected using a Waters 717 autosampler. Calibration was with a series of polystyrene standards from Waters Associates. Polystyrene calibration was used to monitor the performance of the system. The chromatograms were interpreted

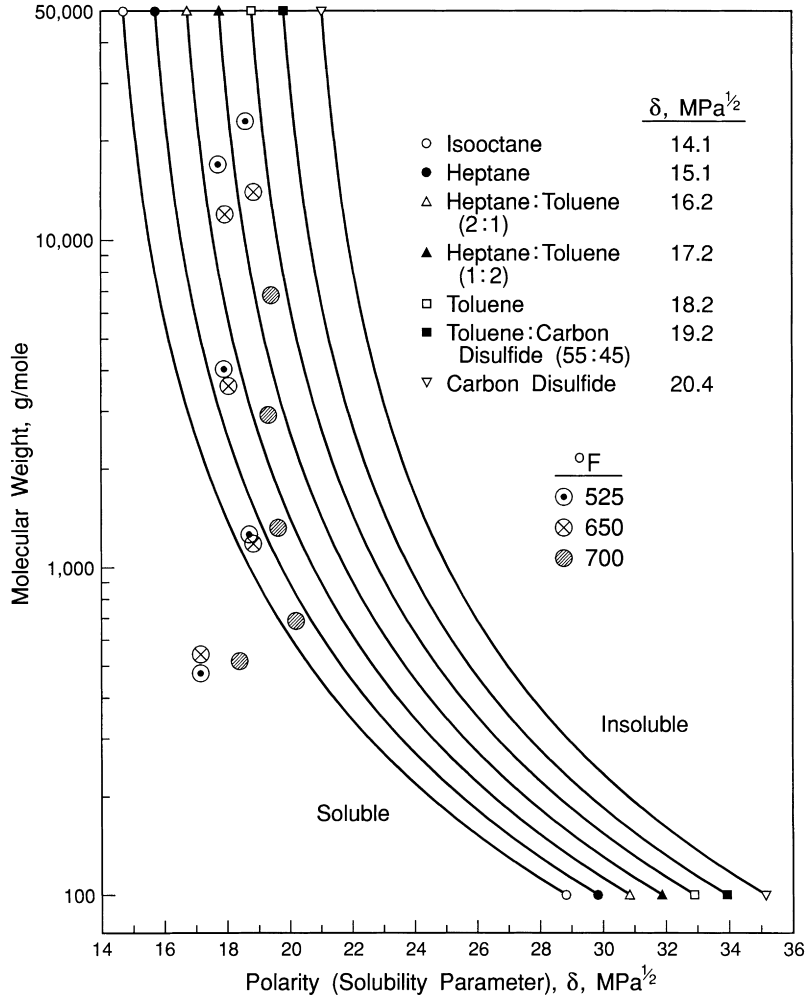

Fig. 2. Molecular weight/polarity map for three stripper bottoms.

using ChromPerfect size exclusion chromatography software, version 3.5.

Automated Heithaus titrations were performed in toluene solutions using isooctane as titrant. The instrument and procedure used are described in detail elsewhere [15].

3. Results and discussion

3.1. 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 Section 1. The phase diagram map was developed by calculating the regions of asphaltene solubility/insolubility in a variety of solvents ranging from isooctane, with a solubility parameter of 14.1 $MPa^{1/2}$ to carbon disulfide, with a solubility parameter of 20.4 $MPa^{1/2}$ (Fig. 1). The map is based on solubility-parameter-tuned solvent mixtures providing even spacing between contour lines of 1.0 $MPa^{1/2}$ except for the last series between toluene:CS_2 (55:45) (v:v) and CS_2, where the spacing is 1.2 $MPa^{1/2}$. The calculations assume a series of individual molecules with apparent molecular weights ranging from 100 to 50,000 g/mol and a density of 1.3 g/cm^3 [16]. The border between the soluble and insoluble regions is defined arbitrarily as the solubility of a mole fraction of 0.001 (0.1% or 1000 ppm). This border is actually a point on a solubility gradient, where solubility increases towards the left-hand portion of a particular curve, and decreases to the right [12].

The location of a particular material on the map was determined by three measurements. These are (I) obtaining a solubility or solvent spectrum of the material to determine between what lines on the map the material lies. This is 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. Then (II) 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

Table 1
Solubility map data for three stripper bottoms

Sample	Measurement	Fraction (see Fig. 1)								
		1	2	3	4	5	6	7	Coke	Ash
A	Weight percent	85.9	0.8	6.3	5.1	0.7	1.1	0.1	< 0.1	< 0.1
	VPO Mn g/mol	474	1260	4040	17,000	23,000	–	–	–	–
	δ MPa$^{1/2}$	17.2	18.8	18.0	18.0	18.8	–	–	–	–
B	Weight percent	83.4	0.9	6.7	5.5	1.0	2.2	0.1	0.2	< 0.1
	VPO Mn g/mol	542	1180	3580	12,000	14,000	–	–	–	–
	δ MPa$^{1/2}$	17.2	18.8	18.0	18.0	18.8	–	–	–	–
C	Weight percent	64.0	2.0	5.3	5.8	2.9	4.5	1.5	11.5	2.5
	VPO Mn g/mol	516	684	1320	2920	6800	–	–	–	–
	δ MPa$^{1/2}$	18.4	20.2	19.6	19.4	19.4	–	–	–	–

60°C, followed by (III) analytical scale size exclusion chromatography.

A particular molecule or associated specie in an actual residuum or asphaltenes 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 or 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 will cause the points representing these materials to move to a different region of the map. Thus, the map can be used to evaluate 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 relatively more polar materials during petroleum production.

Table 2
High performance size exclusion chromatography results

Fraction	Size exclusion chromatography				VPO
	M_w	M_n	Range[a]	M_w/M_n	M_n
A (525°F)					
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	17,000
5	2120	523	210–5300	4.05	23,000
B (650°F)					
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	12,000
5	1930	510	210–4800	3.78	14,000
C (700°F)					
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 10–90% of peak area.

3.2. Pyrolysis series map

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) for the three stripper bottoms (Fig. 2). The data for the three stripper bottoms materials are presented in Table 1. 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). The data also show that the number average molecular weights of the isooctane soluble maltenes is about the same for all three oils, while the molecular weights of each of the respective 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 the polarity of the associated complexes as closely as possible to the solvent matrix (isooctane maltenes). This appears to occur by automatic adjustment of the apparent molecular weights of the complexes.

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 relative to Materials A and B. The solubility

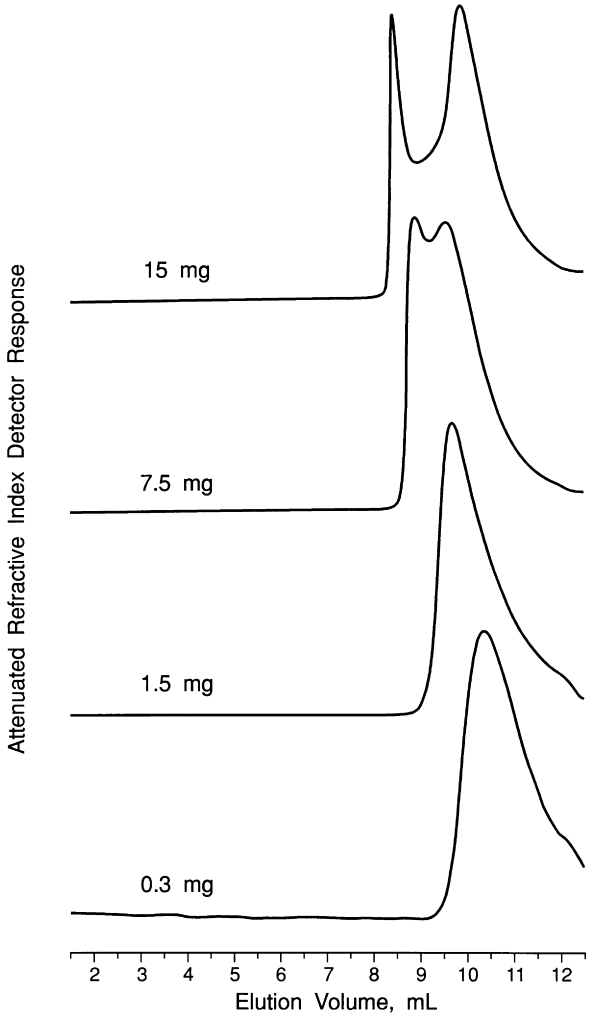

Fig. 3. High performance size exclusion chromatography of 100 μl portions of material A solutions, fraction 4 at various amounts injected.

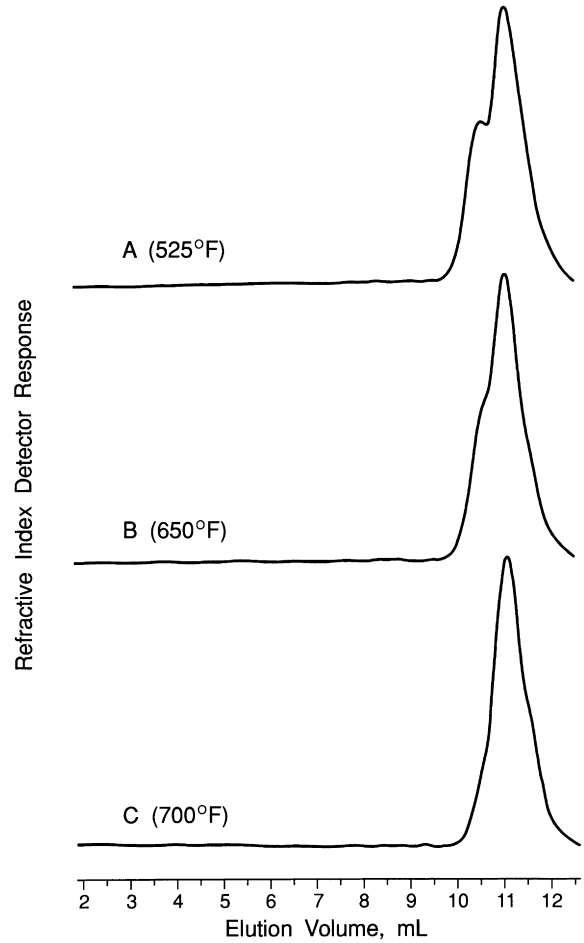

Fig. 4. High performance SEC profiles for isooctane maltenes.

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.

3.3. Size exclusion chromatography

The high performance analytical scale size exclusion chromatography (SEC) results for the fractions are listed in Table 2. Portions of 150 μl 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. Toluene was used as the eluting solvent to provide a basis of comparison with the VPO data, which was obtained in toluene. Also, it is important to note that in general, residua asphaltenes are not fully soluble in basic solvents such as pyridine [8]. They are fully soluble in toluene.

The number average molecular weight values for the isooctane maltenes for all three materials (Fraction 1) are similar to the values obtained by VPO. For all the other more polar fractions, 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 potential for non-uniform response with refractive index detection from residua components of differing functionality. Some adsorption of materials on the polystyrene–divinylbenzene stationary phase can 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 which 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 phenomenon has been observed in previous work [17]. 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/mol and a

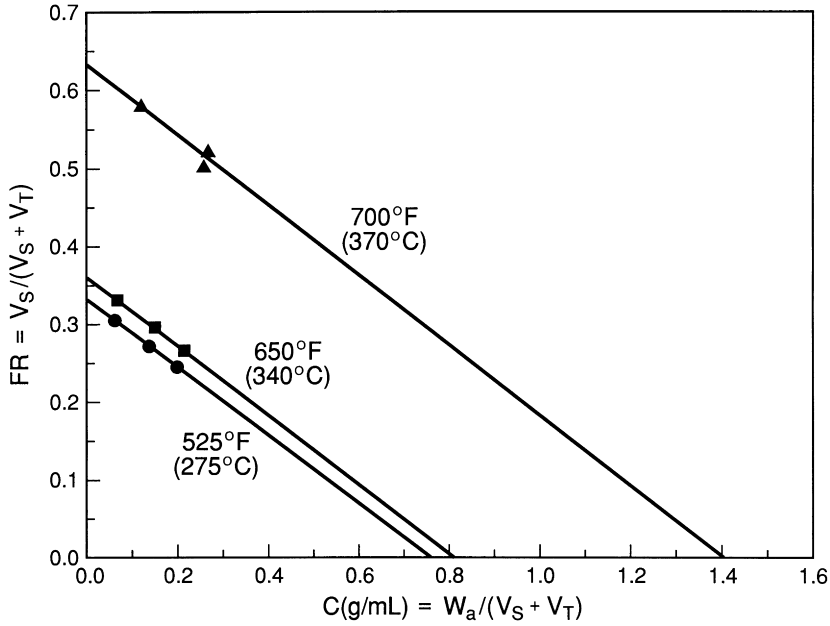

Fig. 5. Heithaus titration results for three stripper bottoms.

SEC number average molecular weight not much greater than the isoocatne maltenes (Fraction 1) of 618 g/mol (Table 2).

Portions of 100 μl of toluene solutions containing 0.3–15 mg were injected. The results are shown in Fig. 3. As more material is injected, the retention volume decreases, indicating an apparent increase in associations/apparent molecular weight. For the 7.5 mg injected, the peak splits 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/mol was injected under identical conditions. Thus, this is not a column overloading phenomenon. For injections of 0.3–7.5 mg, the material elutes in about 3 ml of toluene. An estimate of the concentration at which significant complex formation begins for this asphaltenic material possibly can be considered 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 and 0.3 wt.%. This is consistent with the results of Andersen and Birdi [18], who reported a critical micelle concentration of asphaltenes in toluene near 0.38 wt.% using calorimetric titration.

Table 3
Heithaus titration results for three stripper bottoms

Heithaus parameter	Material		
	A (525°F)	B (650°F)	C (700°F)
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	0.87	0.78	0.26

As with the VPO data, the apparent SEC number average molecular weights for a particular fraction generally decreases 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 show a leading high molecular weight shoulder component in the 525°F material, which is smaller for the 650°F material and is not evident for the 700°F material (Fig. 4). This could represent a high molecular weight associated component of the isooctane maltenes, which is destroyed with increasing severity of thermal treatment. Perhaps this is another possible indicator of the loss of resinous type components as thermal treatment progresses to coke formation.

3.4. Solubility parameter and Heithaus data

Heithaus titration plots for the three bottom materials are provided in Fig. 5. The Heithaus parameters for these three materials are provided in Table 3. 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.

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

Table 4
Solubility parameters for whole residua and asphaltene precipitation onset

Material	Solubility parameter, δ MPa$^{1/2}$	
	Whole residuum	Asphaltene precipitation onset
A (525°F)	17.2	15.5
B (650°F)	17.4	15.5
C (700°F)	18.6	16.8

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 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 4 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 which 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 a less polar distillate with heating.

3.5. Coking indexes

In the current work, we define a new Coking Index ratio as p_a/C_{min}. This is based on the observation that p_a decreases and C_{min} increases as pyrolysis progresses. The ratio for the stripper bottoms decreases from 0.87 to 0.26, the latter value representing the coke producing Residuum C in Table 4. More residua systems are being 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.

Another 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 5.

Table 5
Solubility of heptane asphaltenes in two solvents with $\delta = 16.8$ MPa$^{1/2}$

Material	wt.% Heptane	wt.% Asphaltenes soluble in	
	Asphaltenes	Cyclohexane	Heptane:toluene (1:1) (v:v)
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 a diagnostic of 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 a solvent mixture of identical solubility parameter as cyclohexane, 16.8 MPa$^{1/2}$, heptane:-toluene (1:1) (v:v) gives a larger yield of soluble material relative to 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 [19]. This is a plausible explanation of the data in Table 5. 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 weight percent 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 525, 650, and 700°F treated materials, respectively. Work in progress with additional residua systems suggests that this is a universal phenomenon, independent of residuum source.

4. Conclusions

A new molecular weight/polarity map has been developed for petroleum residua. This is based on the Scatchard–Hildebrand solubility equation. A series of extractions is performed with solvents of increasing solubility parameter, and the fractions are analyzed by vapor pressure osmometry for number average molecular weight, and analytical scale size exclusion chromatography for molecular weight spread. The results are diagnostic of the layers of solvations by resin-type molecules around a central asphaltene core. 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. Additional insight is obtained when Heithaus results are combined with

data from the new molecular weight/polarity map. The solubility parameters for the toluene soluble asphaltene components were measured and the solubility parameters of the maltenes could be calculated. As thermal treatment progress, the solubility parameter of the components of residua fractions increases, and the molecular weight decreases. Two new Coking Indexes are proposed. The first is the p_a/C_{min} ratio based on Heithaus titration data. The second is obtained by measuring the weight percent cyclohexane solubles in heptane asphaltenes, and dividing this by the weight percent of heptane asphaltenes. An unstable system results when the depletion of the resins diminishes the ability of the asphaltene/resins complexes to increase their apparent molecular weights to auto-adjust their solubility parameter to closely match the solubility parameter of the matrix. At this point, a bimodal system forms and coking ensues.

Acknowledgements

Funding for this study was provided by the U.S. Department of Energy under cooperative agreement DE-FC26-98FT40322, and by BetzDearborn, Inc. Mobil Technology Co., Phillips Petroleum Co., and SGI International.

Disclaimer. This manuscript was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

References

[1] Burrell H. Solubility parameters. Interchem Rev 1955:3–16.
[2] Hildebrand JH, Prausnitz JM, Scott RL. Regular and related solutions. New York: Van Nostrand Reinhold, 1970.
[3] Small PA. Some factors affecting the solubility of polymers. J Appl Chem 1953:71–80.
[4] Barton AF. Solubility parameters. Chem Rev 1974;75(6):731–53.
[5] Wiehe IA. Two-dimensional solubility parameter mapping of heavy oils. Fuel Sci Technol Int 1996;14(1 and 2):289–312.
[6] Redelius PG. Solubility parameters and bitumen. Fuel 2000;79:27–35.
[7] Buckley JS. Microscopic investigations of the onset of asphaltene precipitation. Fuel Sci Technol Int 1996;14(1 and 2):55–74.
[8] Schabron JF, Gardner GW, Hart JK, Niss ND, Miyake G, Netzel DA. The characterization of petroleum residua. US Department of Energy Report DE/MC/1107-3539, 1993.
[9] Long RB. The concept of asphaltenes. Preprints, Div Petrol Chem, Am Chem Soc 1979;24:891.
[10] Long RB, Speight JG. Studies in petroleum composition. Revue de l'Institut Francais du Petrole 1989;44(2):205–17.
[11] Snyder LR. In: Kirkland JJ, editor. Modern practice of liquid chromatography. New York: Interscience, 1971.
[12] Schabron JF, Speight JG. The solubility and three-dimensional structure of asphaltenes. Petrol Sci Technol 1998;16(3–4):361–76.
[13] Scatchard G. Equilibria in non-electrolyte solutions in relation to the vapor pressure and densities of the components. Chem Rev 1931:321–33.
[14] Heithaus JJ. Measurement and significance of asphaltene peptization. J Inst Petrol 1962;48(458):45–53.
[15] Pauli AT. Asphalt compatibility testing using the automated Heithaus test. Preprints, Div Fuel Chem, Am Chem Soc 1996;41(4):1276–81.
[16] Parkash S, Moschopedis S, Speight JG. Physical properties and surface characteristics of asphaltenes. Fuel 1979;58:877–82.
[17] Western Research Institute, Fundamental properties of asphalts and modified asphalts, Volume 2, Final Report — New Methods, Report prepared for the Federal Highway Administration under Contract no. DTFH61-92C000170, 1998.
[18] Andersen SI, Birdi KS. Aggregation of asphaltenes as determined by calorimetry. J Colloid Interface Sci 1991;142:497–502.
[19] Snyder LR. Principles of adsorption chromatography. New York: Marcel Dekker, 1968 (p. 206–10).