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Energy Fuels, **2005**, 19 (4), 1261-1267 • DOI: 10.1021/ef0496956 • Publication Date (Web): 21 April 2005

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The Paradox of Asphaltene Precipitation with Normal Paraffins[†]

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Received November 24, 2004. Revised Manuscript Received March 19, 2005

For bitumens and crude oils, the volume of *n*-paraffin at the flocculation point, which is the point of incipient asphaltene precipitation, increases as the *n*-paraffin carbon number increases, reaching a maximum at a carbon number of 9 or 10, and then decreases. Thus, asphaltenes often can begin precipitating with a smaller volume of *n*-hexadecane than with *n*-pentane, even though large volumes of *n*-hexadecane precipitate much less (and more aromatic) asphaltenes than large volumes of *n*-pentane. How can *n*-hexadecane be both a better and a poorer solvent than *n*-pentane for asphaltenes? This paradox of solvent quality can be resolved by combining the entropy of mixing of molecules of different sizes with the heat of mixing from solubility parameters, as expressed by the regular Flory–Huggins model. With sufficient characterization data, the approximations and methods of Yarranton et al. can quantitatively describe asphaltene precipitation from the flocculation point to large excesses of *n*-paraffins from pentane to hexadecane. To describe only the flocculation point data of bitumens and crude oils, the oil compatibility model of Wiehe can be used. Although the oil compatibility model was derived on the basis that the solubility parameter is constant for a given oil at the flocculation point, using “effective” solubility parameters, flocculation points can be predicted with little characterization data.

Introduction

The mitigation of fouling in petroleum production, transportation, upgrading, and refining requires the prevention of asphaltenes from precipitating¹ or even being close to the onset of precipitation.² The oil compatibility model¹ has proven to be useful in predicting both the incompatibility and near incompatibility² of oil mixtures for fouling mitigation. This model is based on the assumption that the onset of asphaltene precipitation occurs at the same solubility parameter of the mixture, whether the oil is blended with other oils or nonpolar liquids. However, Hotier and Robin³ found that the volume of *n*-paraffin at the onset of asphaltene precipitation of a crude oil with increasing carbon number of the *n*-paraffin reaches a maximum at a carbon number of 7 (*n*-heptane). This suggests that higher-carbon-number *n*-paraffins can be poorer solvents for petroleum asphaltenes than lower-carbon-number *n*-paraffins, even though the solubility param-

eters of *n*-paraffins increase continuously with increasing carbon number.⁴ In addition, at high *n*-paraffin:oil volume ratios and with increasing *n*-paraffin carbon numbers, lower amounts of more-aromatic asphaltenes are precipitated.⁵ This indicates that *n*-paraffins are better solvents for asphaltenes with higher carbon numbers, in agreement with their solubility parameters. This contradiction is the paradox of asphaltene precipitation with *n*-paraffins. Thus, one objective of this research is to determine if this maximum *n*-paraffin volume, with increasing *n*-paraffin carbon number at the onset of asphaltene precipitation, is general for all crude oils and bitumens. If this maximum is general, other objectives are to determine an explanation for its occurrence and to establish the consequences of contradicting the basic assumption of the oil compatibility model.

Cimino et al.⁶ offered an explanation for the maximum in volume of *n*-paraffins at the onset of asphaltene precipitation, and claim it is due to the entropy of mixing of molecules of different sizes. They used the regular Flory–Huggins model (RF–HM) that describes

[†] Presented at the 5th International Conference on Petroleum Phase Behavior and Fouling.

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qualitatively, but not quantitatively, the low solubility of polymers in solvents.⁷ In reality, the Flory–Huggins equation is a lower limit on the entropy of mixing of noncomplexing, chain liquids, whereas the ideal entropy of mixing is an upper limit.⁸ Nevertheless, the RF–HM equations require tedious trial-and-error calculations to solve for even three components: asphaltenes, maltenes, and *n*-paraffin. As a result, Cimino et al.⁵ approximated that the solvent separates as the second phase from the mixture, rather than asphaltenes. Although this happens with polymers of very high molecular weights⁷ (>100 000), optical microscopy shows that asphaltenes precipitate, as expected for their moderate molecular weights (1000–5000). Hirschberg et al.⁹ approximated the RF–HM by assuming that the volume fraction of asphaltenes is small, compared to unity, and by assuming the precipitating phase is only asphaltenes without maltenes or solvent. Wang and Buckley¹⁰ approximated the RF–HM by assuming that asphaltenes, maltenes, and *n*-paraffin mixtures are a binary mixture, with maltenes and *n*-paraffin acting as a single solvent in the same proportion in both the light and heavy phases. Although much better than the other approximations, this pseudo-binary approximation has been criticized for polymer solutions.¹¹ Nevertheless, the approximation of Wang and Buckley^{10,12} has successfully been applied to describe quantitatively the change of refractive index of crude oils in *n*-paraffins at the onset of asphaltene precipitation. Wang and Buckley¹⁰ calculated the onset condition when the Gibbs free energy of mixing, as a function of the asphaltene mole fraction curve, has an inflection point with a horizontal tangent line at the low asphaltene concentration end. Although the variation of refractive index at the onset of asphaltene precipitation with *n*-paraffins indicates that the solubility parameter of the mixture also varies, Wang and Buckley did not mention the maximum in *n*-paraffin volume. Yarranton and co-workers^{13–15} have used similar approximations as Hirschberg et al. for the RF–HM, except that Yarranton et al. greatly increased the number of pseudo-components to include *n*-paraffin, saturates, aromatics, resins, and associated asphaltenes with a molecular weight distribution and included resins with asphaltenes in the precipitated phase. As a result, their model is capable of quantitatively describing the fractional precipitation of asphaltenes from Athabasca and Cold Lake bitumens with volume fractions of *n*-paraffin from *n*-pentane through *n*-hexadecane. Because the aromaticity of the precipitated phase varies significantly with yield, it is necessary to have several

Table 1. Flocculation Points at the Same Solubility Parameter of Mixture for Solvents and Nonsolvents of Similar Molar Volumes

crude oil	toluene equivalence	cyclohexane equivalence	TE/CE
A	30	64	0.47
B	12	23	0.52
C	27	58	0.47
average			0.49
predicted by eq 3			0.48

asphaltene pseudo-components. More details are discussed below.

Experimental Section

For the toluene equivalence, 2 g of oil are weighed into individual small bottles and 10 mL of test liquid composed of varying ratios of toluene and *n*-heptane are added to each bottle and mixed well. After waiting 5 min at room temperature, a drop from each bottle is examined between a glass slide and a cover slip at 100× with an optical microscope in transmitted light for evidence of asphaltene precipitation. Using a trial-and-error procedure, the minimum volume percent toluene in the test liquid required to keep the asphaltenes in solution is determined, and this is the toluene equivalence. If toluene is replaced by cyclohexane, otherwise keeping the procedure the same, the minimum volume percent of cyclohexane in the test liquid required to keep the asphaltenes in solution is called the cyclohexane equivalence. A comparison of toluene equivalence and cyclohexane equivalence is presented in Table 1 for three different crude oils.

The onset of asphaltene precipitation for two crude oils and two bitumens were determined at room temperature for *n*-paraffins from *n*-pentane through *n*-hexadecane. Using the same procedure, one laboratory performed measurements on Maya crude and Cold Lake bitumen, whereas a different laboratory performed measurements on a diluted Alberta heavy oil, an Athabasca bitumen, and a much different Cold Lake bitumen sample. The diluted Alberta heavy oil (DAHO) is a heavy crude oil from Alberta Providence in Canada that is diluted with gas condensate to reduce the viscosity so that it can be transported by pipeline to refineries. The procedure used increments of *n*-paraffin addition (5 mL, 1 mL, and then 0.1 mL) to 5 mL of oil in a small bottle, with a 5-min wait period, after each increment before examining a drop under an optical microscope at 100× for evidence of asphaltene precipitation. By not adding more than 2 mL of *n*-paraffin at a time before mixing and using the 5-min wait period before looking for asphaltene precipitation, the common problem of the onset value changing with the rate of *n*-paraffin addition was avoided. After asphaltene precipitation was observed, a new bottle of oil was then used (containing the maximum volume of *n*-paraffin previously observed without asphaltene precipitation) as the starting point for adding the next smallest increment. The recorded volume of *n*-paraffin at the onset of asphaltene precipitation was the average of the maximum volume of *n*-paraffin added without observing precipitation and the minimum volume of *n*-paraffin added when precipitation was observed. The volume fractions of *n*-paraffin at the onset of asphaltene precipitation are shown in Table 2, with properties of the oils given in Table 3. The precision of this method is ~0.1 vol %.

The separation of saturates, aromatics, resins, and asphaltenes was as described previously,¹⁵ using the procedure of ASTM Standard D2007M. The molecular weights were measured by vapor pressure osmometry in toluene at 50 °C with those of asphaltenes being extrapolated to zero concentration. Densities were measured with an Anton Paar model DMA 46 density meter. Asphaltene densities were calculated indirectly

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Table 2. Volume Fractions of *n*-Paraffin at the Onset of Asphaltene Precipitation for Five Oils

<i>n</i> -paraffin carbon number	Volume Fraction				
	Cold Lake bitumen 1	Cold Lake bitumen 2	Athabasca bitumen	Maya crude	diluted Alberta heavy oil, DAHO
5	0.587	0.645	0.650	0.412	0.587
6	0.608	0.669	0.669	0.438	0.618
7	0.623	0.669	0.671	0.462	0.640
8	0.636	0.669	0.669	0.474	0.645
9	0.649	0.669	0.673	0.474	0.653
10	0.636	0.669	0.669	0.462	0.667
11	0.623	0.669	0.669		0.645
12	0.608	0.645	0.669	0.438	0.640
13	0.592	0.632	0.660	0.438	0.624
14	0.574	0.621	0.645		0.618
15	0.556	0.612	0.630		0.600
16	0.550	0.590	0.618	0.412	0.590

from the densities of mixtures of asphaltenes and toluene, as described previously.¹³

Results

Solvents and Nonsolvents of Similar Size. The molar volumes of toluene (106.3 mL/g-mol), *n*-heptane (146.5 mL/g-mol), and cyclohexane (108.1 mL/g-mol) are of the same order of magnitude. Thus, a comparison of toluene equivalence and cyclohexane equivalence of the same oil determines if solvent and nonsolvents of approximately the same molar volume have flocculation points at the same solubility parameter. Assuming this is true and using the mixing rule that the solubility parameter of a mixture is the solubility parameter of each component times its volume fraction in the mixture yields

$$\left[\frac{2/\rho_{\text{oil}}}{10 + (2/\rho_{\text{oil}})} \right] \delta_{\text{oil}} + \frac{10\text{TE}\delta_{\text{T}}/100}{10 + (2/\rho_{\text{oil}})} + \frac{10(100 - \text{TE})\delta_{\text{H}}/100}{10 + (2/\rho_{\text{oil}})} = \left[\frac{2/\rho_{\text{oil}}}{10 + (2/\rho_{\text{oil}})} \right] \delta_{\text{oil}} + \frac{10\text{CE}\delta_{\text{C}}/100}{10 + (2/\rho_{\text{oil}})} + \frac{10(100 - \text{CE})\delta_{\text{H}}/100}{10 + (2/\rho_{\text{oil}})} \quad (1)$$

$$\text{TE}(\delta_{\text{T}} - \delta_{\text{H}}) = \text{CE}(\delta_{\text{C}} - \delta_{\text{H}}) \quad (2)$$

$$\frac{\text{TE}}{\text{CE}} = \frac{\delta_{\text{C}} - \delta_{\text{H}}}{\delta_{\text{T}} - \delta_{\text{H}}} = \frac{8.19 - 7.50}{8.93 - 7.50} = 0.482 \quad (3)$$

where ρ_{oil} is the density of the oil (in units of g/mL), TE the toluene equivalence, δ_{oil} the solubility parameter of the oil (in units of (cal/mL)^{1/2}), δ_{T} the solubility parameter of toluene (in units of (cal/mL)^{1/2}), δ_{H} the solubility parameter of *n*-heptane (in units of (cal/mL)^{1/2}), δ_{C} the solubility parameter of cyclohexane (in units of (cal/mL)^{1/2}), and CE the cyclohexane equivalence.

As shown in Table 1, the ratio of the toluene equivalence to the cyclohexane equivalence for three different crude oils (referenced as A, B, and C) average 0.49. This is within experimental error of that predicted by eq 3, based on the assumption that the flocculation point occurs at the same solubility parameter of the mixture. Previously,¹⁶ the ratio of the toluene equivalence to chlorobenzene equivalence for fluid catalytic cracker

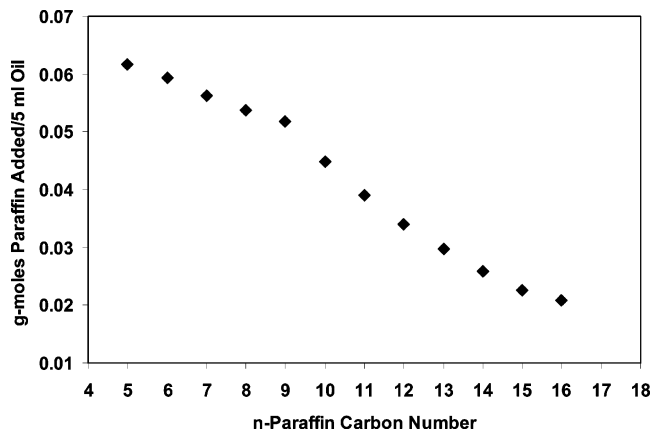


Figure 1. Experimental data describing the number of g-moles of *n*-paraffin per 5 mL of oil at the onset of asphaltene precipitation for Cold Lake bitumen 1.

bottoms was calculated to be 1.52 from solubility parameters using eq 3 and measured to be 1.48. Chlorobenzene has a molar volume (101.8 mL/g-mol) of the same order of magnitude of toluene, *n*-heptane, and cyclohexane. Thus, evidence is mounting that for solvents and nonsolvents of the same order of magnitude of molar volume the flocculation point indeed occurs at the same solubility parameter of the mixture.

Paraffins of Varying Size. Normal paraffins from *n*-pentane (molar volume of 115.2 mL/g-mol) to *n*-hexadecane (molar volume of 292.8 mL/g-mol) vary in molar volume by a factor of 2.5 and are chain molecules. From Table 2, for four different bitumens and crude oils with properties in Table 3, it is concluded as a general phenomenon for petroleum oils that the volume of *n*-paraffins at the onset of asphaltene precipitation goes through a maximum with *n*-paraffin carbon number. However, where the maximum can be distinguished, it occurs at *n*-paraffin carbon numbers of 8, 9, or 10 (for this study), rather than at carbon number 7, as observed by Hotier and Robin.³ Because the solubility parameter increases as the *n*-paraffin carbon number increases,⁴ the flocculation point for mixtures of *n*-paraffins and a given petroleum oil cannot occur at the same solubility parameter of the mixture.

When the number of g-moles of *n*-paraffin per 5 mL of oil at the onset of asphaltene precipitation is plotted against the *n*-paraffin carbon number, as in Figure 1 for Cold Lake bitumen 1, no maximum is observed (thanks to a reviewer for pointing this out). However, even on this basis, one would conclude that *n*-paraffins become poorer solvents for asphaltenes with increasing

Table 3. Properties of the Five Oils in This Study

property	Value				
	Cold Lake bitumen 1	Cold Lake bitumen 2	Athabasca bitumen	Maya crude	diluted Alberta heavy oil, DAHO
saturates					
yield (wt %)	19.5 ^a	19.5	16.4		38.4
density (g/mL)	0.882 ^a	0.882	0.885		0.882 ^a
molecular weight	508 ^a	508	524		508 ^a
aromatics					
yield (wt %)	38.2 ^a	38.2	40.1		37.9
density (g/mL)	0.995 ^a	0.995	1.003		0.995 ^a
molecular weight	522 ^a	522	550		522 ^a
resins					
yield (wt %)	26.8 ^a	26.8	28.7		12.1
density (g/mL)	1.037 ^a	1.037	1.04		1.037 ^a
molecular weight	930 ^a	930	976		930 ^a
C ₅ asphaltenes					
yield (wt %)	15.5 ^a	15.5	14.8		11.6
density (g/mL)	1.203 ^a	1.203	1.203 ^a		1.203 ^a
molecular weight	2850 ^a	2850	2910		2600
density (g/mL)	0.991	1.001	0.9952	0.876	0.9327
toluene equivalence	19	19.5	18.5	38	21.0
insolubility number	28.5	33	31.4	47	34
solubility blending number	76	99.7	95.5	71	94.5

^a Not measured but assumed to be the same as that for Cold Lake bitumen 2.

paraffin carbon number. On the other hand, high dilutions of *n*-paraffins precipitate less insolubles with increasing paraffin carbon number,⁵ which would lead one to conclude that *n*-paraffins become better solvents for asphaltenes with increasing carbon number. Therefore, the paradox still remains on either the molar basis or the volume basis, even though the maximum does not appear on the molar basis.

Yarranton Approximation to RF–HM. The multicomponent (*n* components) RF–HM^{17,18} for the chemical potential of component *i* (μ_i) is given by

$$\frac{\mu_i - \mu_i^*}{RT} = \ln(\phi_i) + 1 - \sum_{j=1}^{j=n} r_{ij}\phi_j + \frac{x_i(\delta_i - \delta_M)^2}{RT} = \ln(x_i\gamma_i) \quad (4)$$

where μ_i^* is the standard chemical potential of pure component *i*, *R* the gas constant, *T* the absolute temperature, x_i the mole fraction of component *i*, v_i the molar volume of component *i*, ϕ_i the volume fraction of component *i* ($\phi_i = x_i v_i / (\sum x_i v_i)$), $r_{ij} = v_i / v_j$, δ_i the solubility parameter of component *i*, δ_M the solubility parameter of the mixture ($\delta_M = \sum \phi_i \delta_i$), and γ_i the activity coefficient of component *i*.

With the assumptions discussed above, Yarranton et al.^{13–15} determined that the ratio of the equilibrium mole fractions of each of the asphaltene and resin species in light (L) and heavy (H) phases is given by

$$K_i = \phi_i^L = \exp \left[\ln \left(\frac{v_i^L}{v_M^L} \right) + 1 - \frac{v_i^L}{v_M^L} + \frac{v_i^L}{RT} (\delta_i - \delta_M^L)^2 \right] = \frac{x_i^H}{x_i^L} \quad (5)$$

where v_M^L = molar volume of the mixture in the light phase ($v_M^L = \sum x_i v_i^L$).

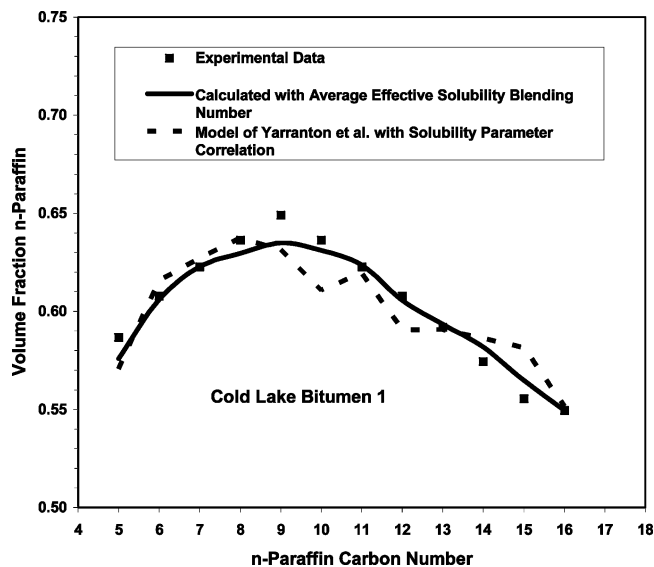


Figure 2. Comparison of experimental data of the volume fraction of *n*-paraffin at the onset of asphaltene precipitation with two methods of calculation for Cold Lake bitumen 1.

The RF–HM is extremely sensitive to the values of the solubility parameters with differences in the fourth significant figure being important. This requires higher accuracy than is typically measured for solubility parameters, including for *n*-paraffins. Yarranton et al.¹⁵ calculated solubility parameters for *n*-paraffins from a correlation based on heat of vaporization and molar volume data, whereas Wang and Buckley^{10,12} used a correlation with refractive index data. As is shown in Figures 2–5, the model of Yarranton et al. correctly predicts the volume maximum with the carbon number of *n*-paraffins at the onset of asphaltene precipitation (calculated for 0.5 wt % yield of precipitate) for four different oils with either the solubility parameters of Yarranton et al. and those of Wang and Buckley. Therefore, the cause of this volume maximum is consistent with mixing molecules of much different sizes, as predicted by the Flory–Huggins model.

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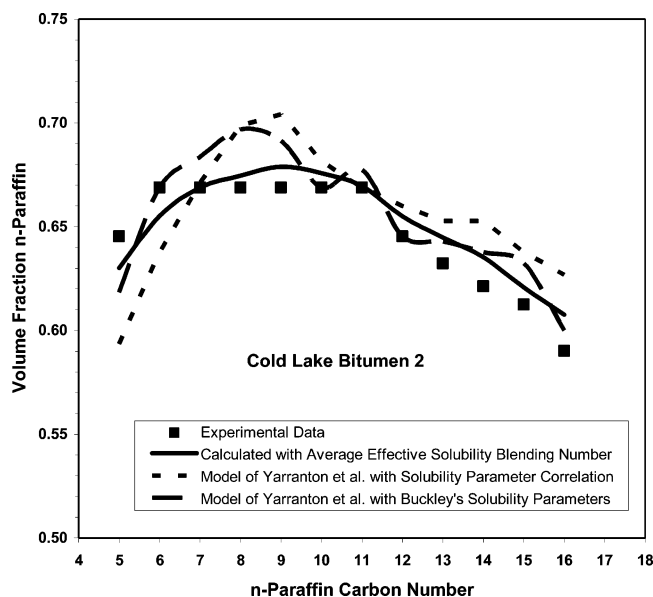


Figure 3. Comparison of experimental data of the volume fraction of *n*-paraffin at the onset of asphaltene precipitation with three methods of calculation for Cold Lake bitumen 2.

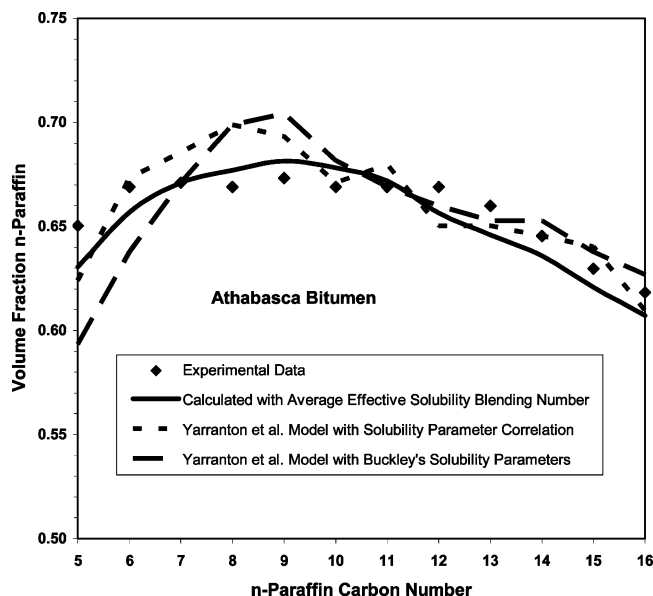


Figure 4. Comparison of experimental data of the volume fraction of *n*-paraffin at the onset of asphaltene precipitation with three methods of calculation for Athabasca bitumen.

Oil Compatibility Model Approximation. Using the definition of asphaltenes as being soluble in toluene but insoluble in *n*-heptane, the oil compatibility model¹ defines two dimensionless solubility parameters: the insolubility number (I_N), which is defined as

$$I_N \equiv 100 \times \frac{\delta_f - \delta_H}{\delta_T - \delta_H} \quad (6)$$

and the solubility blending number (S_{BN}), which is defined as

$$S_{BN} \equiv 100 \times \frac{\delta_{oil} - \delta_H}{\delta_T - \delta_H} \quad (7)$$

where δ_f is the solubility parameter of the mixture at

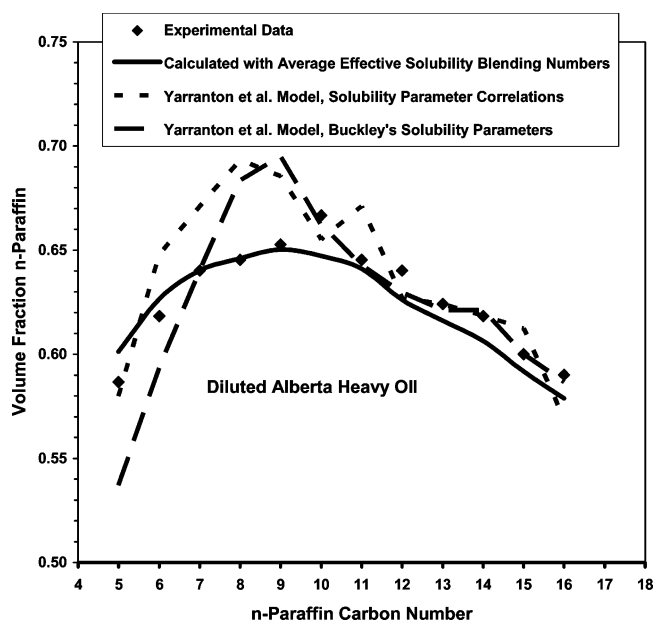


Figure 5. Comparison of experimental data of the volume fraction of *n*-paraffin at the onset of asphaltene precipitation with three methods of calculation for diluted Alberta heavy oil.

the flocculation point and the others are as defined previously. These dimensionless solubility parameters eliminate the need for awkward square root units and expand the solubility parameter scale over the region of interest between *n*-heptane and toluene. If the oil compatibility model is applied to an oil-containing asphaltene, based on the assumption that the flocculation solubility parameter is the same whether the oil is blended with nonpolar solvents or other oils, the insolubility number and the solubility blending number are determined by

$$I_N = \frac{TE}{1 - [V_H/(25\rho_{oil})]} \quad (8)$$

$$S_{BN} = I_N \left(1 + \frac{V_H}{5} \right) \quad (9)$$

where V_H is the maximum volume (in milliliters) of *n*-heptane that can be blended with 5 mL of oil without precipitating asphaltenes (the heptane dilution test). The compatibility criterion for a mixture of oils is that the volume-average solubility blending number must be greater than the insolubility number of each oil in the mixture.

When the oil compatibility model¹⁶ is applied to an oil without asphaltenes, this unknown oil is blended with five times the volume of a standard oil-containing asphaltene for which the insolubility number (I_N) and the solubility blending number (S_{BN}) have been determined. If this blend is found to contain insoluble asphaltenes, the oil is termed a nonsolvent oil. The maximum volume ($V_{Nonsolvent}$) of the nonsolvent oil that can be blended with 5 mL of the standard oil without precipitating asphaltenes is determined and compared with the heptane dilution test on the standard oil with result V_H . From the assumption of equal solubility parameters of the mixture at the onset of asphaltene

Table 4. Effective Solubility Blending Numbers for *n*-Paraffins and Five Oils

<i>n</i> -paraffin carbon number	Effective Solubility Blending Number, S_{BN}					average
	Cold Lake bitumen 1	Cold Lake bitumen 2	Athabasca bitumen	Maya crude	diluted Alberta heavy oil, DAHO	
5	-4.62	-3.63	-3.04	-10.74	-8.62	-6.13
6	-1.84	0.00	-0.31	-4.82	-3.36	-2.07
7	0.00	0.00	0.00	0.00	0.00	0.00
8	1.63	0.00	-0.31	2.09	0.75	0.83
9	3.08	0.00	0.30	2.09	1.81	1.46
10	1.63	0.00	-0.31	0.00	3.74	1.01
11	0.00	0.00	-0.31	0.00	0.75	0.11
12	-1.84	-3.63	-0.31	-4.82	0.00	-2.12
13	-3.93	-5.76	-1.62	-4.82	-2.46	-3.72
14	-6.33	-7.65	-3.80		-3.36	-5.28
15	-9.12	-9.19	-6.26		-6.35	-7.73
16	-10.05	-13.29	-8.14	-10.74	-8.03	-10.05

precipitation, the solubility blending number of the nonsolvent oil is calculated by

$$S_{\text{Nonsolvent}} = I_N \left(1 - \frac{V_H}{V_{\text{Nonsolvent}}} \right) \quad (10)$$

This equation is applied to the oils in Table 2 using the insolubility numbers in Table 3 and treating all *n*-paraffins as nonsolvent oils, except *n*-heptane. The calculated effective solubility blending numbers are given in Table 4, along with the average values. These average effective solubility blending numbers of the *n*-paraffins are used to calculate the volume of *n*-paraffin at the onset of asphaltene precipitation using eq 10. As shown in Figures 2–6, the average effective solubility blending numbers can describe well the asphaltene onset data for all the oils. This demonstrates why the oil compatibility model with compatibility numbers measured by asphaltene onset titrations has been successful at predicting oil compatibility, although the onset does not strictly occur at the same solubility parameter of the mixture. The effective solubility parameter (solubility blending number) of the oil measured with toluene and *n*-heptane is a good approxima-

tion of the effective solubility parameter of the oil, when blended with other oils.

Discussion of Results

In this paper, we have determined that the maximum in volume of *n*-paraffin, as a function of the carbon number of the *n*-paraffin at the onset of asphaltene precipitation, is general for crude oils and bitumens. This phenomenon is a result of mixing liquids of greatly different molecular sizes, and, as a result, the precipitation of asphaltenes from the onset to large excesses of nonsolvent can be quantitatively described by the Yarranton et al. approximations to the RF–HM. This model works even better for petroleum oils than for organic polymers. Part of the reason this model works is because only van der Waals interactions are important for petroleum oils;¹⁹ however, the complete reason is unknown. Nevertheless, our work confirms the conclusion of Wang and Buckley^{10,12} that the onset of asphaltene precipitation does not necessarily happen at the same solubility parameter of the mixture for a given petroleum oil, but can be influenced by the molar volumes of the components in the mixture. When the solvent and nonsolvent blended with oil is kept at the same order of magnitude of molar volume, the solubility parameter of the mixture at the flocculation point is found to be constant. However, if the solvent and nonsolvent blended with the oil varies significantly in molar volume, one should expect the solubility parameter at the flocculation point to vary. Although this contradicts the basic assumption of the oil compatibility model, the practice of determining effective solubility parameters (solubility blending numbers) using asphaltene onset titrations directly on petroleum oils accounts for the size effect.

The effect of molar volume ratio on the entropy of mixing in the RF–HM equation is well-known. Higher molar volume ratios result in a smaller entropy of mixing and a higher free energy of mixing. However, the enthalpy term in eq 4 has molar volumes multiplied by solubility parameter differences. As a result, the larger molar volumes of the components in the mixture give a higher enthalpy of mixing and, thus, a higher free energy of mixing and are more likely to be insoluble on mixing. This is why polymer blends are the least-compatible mixtures of nonpolar molecules.¹⁷ As one increases the carbon number of the *n*-paraffin that is

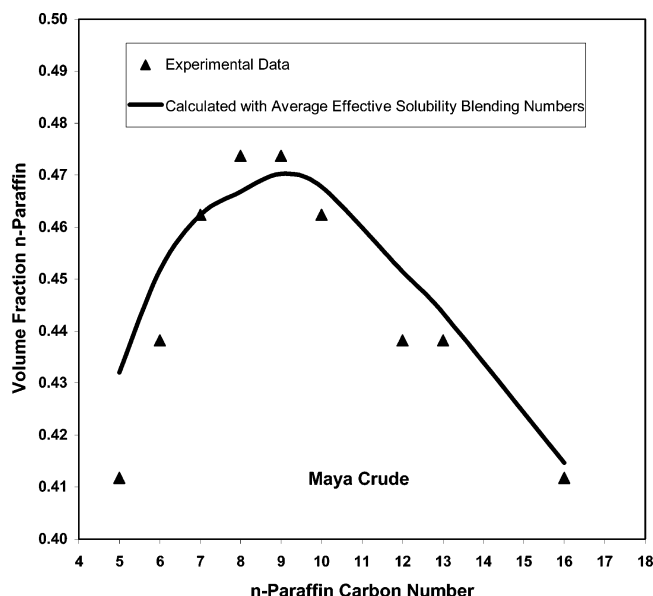


Figure 6. Comparison of experimental data of the volume fraction of *n*-paraffin at the onset of asphaltene precipitation with the approximate oil compatibility model for Maya crude oil.

blended with an oil, the solubility parameter difference between the n -paraffin and the asphaltene in the oil becomes smaller and the ratio of the molar volume of the asphaltene to the molar volume of the n -paraffin in the entropy of mixing becomes smaller. Both of these effects decrease the free energy of mixing and make the n -paraffin and asphaltene more compatible. This is why, at small-carbon-number n -paraffins, the volume of n -paraffin at the flocculation point increases as the n -paraffin carbon number increases. However, as the carbon number of the n -paraffin increases, the rate of increase of the solubility parameter decreases, while the molar volume increases linearly. Thus, the enthalpy of mixing increases as the molar volume of the n -paraffin increases and soon overcomes the effect of the decreasing solubility parameter difference between the n -paraffin and the asphaltene in the oil. This causes the free energy of mixing to increase with increasing n -paraffin carbon number at higher carbon numbers and results in decreases in the volume of n -paraffin at the flocculation point, relative to increasing n -paraffin carbon number. The consequence is a maximum in the volume of n -paraffin at the flocculation point as one increases the carbon number of the n -paraffin blended with an oil-containing asphaltene.

The model of Yarranton et al. and the oil compatibility model fit different needs. The model of Yarranton et al. is more scientifically satisfying and can explain quantitatively why the maximum in the onset volume is observed while the precipitation at large dilutions is

described by the solubility parameter of the nonsolvent. This ability to describe the complete precipitation of asphaltenes with increasing dilution should find applications to deasphalting processes. The oil compatibility model is better-suited for cases where there is a minimum of characterization data and for fouling mitigation, where no asphaltene precipitation nor tendency for asphaltene precipitation is desired. Maya crude is an example where the oil compatibility model can describe the asphaltene onset data with only density and toluene equivalence data. The ability of each of the models to describe the asphaltene onset data could not be compared impartially, because the data were used to determine the average effective solubility blending numbers for the n -paraffins and the approximate oil compatibility model was forced to fit for n -heptane. Actually, the n -paraffin solubility parameters of Wang and Buckley described the data slightly better than the solubility parameters of Yarranton et al. There is a definite need for more-accurate solubility parameters for pure liquids.

Acknowledgment. Partial funding for NCUT has been provided by the Canadian Program for Energy Research and Development (PERD), the Alberta Research Council (ARC) and the Alberta Energy Research Institute (AERI).

EF0496956