

PRECIPITATION AND FOULING IN HEAVY OIL-DILUENT BLENDS

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ABSTRACT

Heavy oil fractions rich in asphaltenes were mixed with diluents containing from 0.6-25% aromatics, and the resulting blends subjected to batch precipitation experiments at 85°C, and thermal fouling tests at surface temperatures in the range 230-310°C. Deposit compositions were determined, and are compared with suspended asphaltene composition. When the heavy oils were blended with the most aromatic diluents, precipitation and fouling were negligible. As the aromaticity of the diluents was decreased, the extent of asphaltene precipitation and the fouling rates increased. The solubility parameter of the blends, δ_{mix} , and the flocculation solubility parameter for asphaltenes, δ_f , were determined from measurements of the asphaltene flocculation onset by titration with heptane at temperatures from 25 to 50°C. Literature models predict no asphaltene precipitation (and presumably little fouling) will occur when $[\delta_{\text{mix}} - \delta_f] > 0$. Both the amount of asphaltene precipitated in the batch experiments, and the rate of thermal fouling decreased as the solubility parameter difference $[\delta_{\text{mix}} - \delta_f]$ increased from negative to positive values. However some precipitation and fouling was observed at the expected condition for mixture stability $\delta_{\text{mix}} \geq \delta_f$. As the temperature of the flocculation titration was raised towards the bulk temperatures of the experiments, values of $[\delta_{\text{mix}} - \delta_f]$ decreased, and the agreement of the data with prediction of the point for zero precipitation and fouling improved. For unstable oil blends, the solubility parameter provides a good predictive measure of the tendency for asphaltene precipitation, and for heat exchanger fouling.

INTRODUCTION

Hydrocarbon components of oils may be divided into several classes of increasing polarity: saturates, aromatics, resins, and asphaltenes. Asphaltenes are defined as the fraction of oil that is soluble in toluene and insoluble in an alkane, usually pentane or heptane. Asphaltenes are high molecular mass polar molecules, which normally are present in heavy oils in a colloidal state, but which can be partially precipitated when the solubility properties of the surrounding fluid changes due to blending of oils, or

changes in temperature or pressure. Asphaltene precipitation may result in deposition of asphaltenes onto equipment and piping, and the fouling of heated surfaces.

In unstable asphaltene mixtures, a fraction of the asphaltenes is present as precipitated particulate matter, and the remainder is present in "solution". In deposition, some of the suspended solids must transfer to a surface by fluid motion or by sedimentation, and then adhere to the surface in question. Hence, deposition depends not only on the asphaltene suspended solids concentration, but on other variables as well. Asomaning and Watkinson (1999) have shown that fouling rate increases with surface temperature, and decreases with increases in velocity, and bulk temperature. The latter effect was attributed to the decrease in insoluble asphaltene concentration with increased temperature. To understand and predict fouling from unstable oil mixtures, the factors which govern the amount of solids which precipitate must be known. If such fouling is particulate deposition, the state of aggregation of the precipitated asphaltenes is expected to be a factor of importance. For a given total concentration of asphaltenes in a system, the colloidal instability index

$$\text{CII} = [(\text{Saturates} + \text{Asphaltenes}) / (\text{Aromatics} + \text{Resins})] \quad [1]$$

provided a correlating parameter for fouling rate under otherwise fixed conditions (Asomaning and Watkinson, 1999). However, the C.I.I. by itself can not encompass the effects of oil quality on fouling. On a more fundamental basis, the solubility parameter provides a guide to whether precipitation and fouling is to be expected (Wiehe and Kennedy, 2000), however quantitative agreement is lacking (Al-Atar and Watkinson, 2002; Brons and Rudy, 2002). The aims of this work were to investigate the effect of different diluents on the stability of colloiddally dispersed heavy oil systems, and to determine the effects of instability on asphaltene precipitation and thermal fouling. Blends of heavy oils with diluents of different aromaticity were tested for their asphaltene flocculation or precipitation onset, and the solubility parameters determined. The resulting characteristics for the oil blend were then correlated with separate measurements of extent of

precipitation in batch experiments, and with the rate and extent of thermal fouling in a test heat exchanger loop.

Experimental Materials, Apparatus and Methods

The sources of asphaltene are Cold Lake vacuum residue (VR) and Athabasca atmospheric tower bottoms (ATB). The diluents include a commercial lube oil basestock—Paraflex (PFX) of which two samples designated PFX1 and PFX2 were used, a heavy vacuum gas oil (HVGO), and a resin-enriched fraction (REF) recovered from Cold Lake vacuum residue by supercritical fluid extraction and fractionation (E,Hong 2005). The aromatics content of the individual diluents varied from 0.6 to 63 %. Properties of all streams are shown in Table 1.

Table 1 Properties of Fluids

	VR	ATB	PFX1	HVGO	REF
Sa	11.0	21.2	99.4	68.3	0.9
(Wt%)					
Ar	38.7	45.5	0.6	15.9	62.8
(Wt%)					
Re	32.6	19.8	0.0	15.8	36.3
(Wt%)					
As	17.7	13.5	0.0	0.0	0.0
(Wt%)					
C.I.I.	0.40	0.53	165.7	2.15	0.01
C (wt%)	83.64	82.82	85.66	86.55	81.99
H (wt%)	10.0	10.32	13.73	12.65	9.70
N (wt%)	0.53	0.45	0.0	0.03	0.56
S (wt%)	4.88	4.47	0.0	0.98	5.47
Ash (%)	1.4	1.77	-	-	-
H/C	1.42	1.49	1.92	1.76	1.42
(atomic)					
Mw	756	581	314	285	905
SG	1.040	1.016	0.855	0.869	1.044

*: ATB: Athabasca atmospheric tower bottom (Syncrude Canada Ltd.), VR: Cold Lake vacuum residue (Imperial Oil Ltd.), HVGO: Heavy vacuum gas oil (Imperial Oil Ltd.), PFX: Paraflex (Petro-Canada Ltd.), REF: Resin enriched fraction. Sa=saturates, Ar=aromatics, Re=resins, As=asphaltenes (Toluene soluble-heptane insoluble).

Asphaltene precipitation experiments are described in E.,Hong and Watkinson (2004) and E.,Hong (2005). A 10 g. blend of heavy oil and diluent was made up at 85°C, by adding the latter to the former, mixing the fluids for a period of 30 minutes, and then filtering the mixture under vacuum through a 47 mm dia., 1 or 3 micron pore size glass fiber filter. After rinsing the filter, the amount of precipitated solids was determined by weighing. Results were expressed as either weight percent of heavy oil which precipitated W (g asphaltenes/g feed oil), or as suspended asphaltene concentration $C_{As, s}$ (g asphaltenes/L of liquid mixture).

The onset point of asphaltene flocculation was determined for VR and ATB by titration with n-heptane, using the automated flocculation titrimeter developed by Western Research Institute, Inc. and described in ASTM

D 6703-01. Samples of between 0.5 and 1.0g heavy oil were transferred into specially designed reaction vials containing 3.0ml toluene, to form three different concentrations of heavy oil in toluene. With a given solution of heavy oil and toluene, different amounts of the diluents were added. The mixture was then titrated with n-heptane precipitant at 0.5ml/min and the light transmission of the sample first increases due to the dilution effect of the titrant, and then decreases with the occurrence of precipitating asphaltenes. The onset is taken as the volume of titrant added when a maximum light transmission occurs.

Fouling experiments were conducted in a flow loop (Watkinson *et al.*, 2000), and equipped with an annular electrically heated Heat Transfer Research Incorporated probe, supplied by Ashland Drew Chemicals. The test fluid was prepared by mixing the diluent into the heavy oil sample, and placed in the supply tank, which was then purged with nitrogen for one hour under 410 kPa abs. to eliminate any dissolved oxygen. The pump and tank heater were then turned on. Once the desired temperature of 85°C and pressure were reached, the flow control valve was set to yield the desired bulk velocity. Before the probe heater was started, a sample of the test fluid was taken for analysis. The power to the heat transfer probe was adjusted to achieve the desired initial surface temperature (T_{s0}). A data-logger and computer were activated to record system variables at a scanning interval of 10 minutes over the ~40 hour experiment. A small flow of cooling water was used to maintain a constant bulk temperature throughout the run.

At the end of 40 hours or when power to the probe was cut off due to high surface temperatures, a sample of the test fluid was taken once again for analysis. The cooling water flow rate was increased to cool the system, the pressure of the system released and the test fluid drained. The probe was taken out of the test section and rinsed with varsol solvent (Esso Chemicals), to dissolve the oil, followed by n-pentane. The deposit was then recovered mechanically. The flow loop was cleaned by re-circulating varsol for one hour. The probe was cleaned with varsol and n-pentane prior to each run.

The fouling probe operates at constant heat flux over time, with a power input $Q = \text{Volts} * \text{Amps}$. Four thermocouples embedded within the wall measure the temperature, which is then corrected to give the metal surface temperature, and then averaged to give T_s . Under constant heat flux the fluid/deposit interface is assumed to be constant at T_{s0} . The thermal fouling resistance which is a function of time is calculated from the decline in heat transfer coefficient given by

$$R_f = \frac{1}{U} - \frac{1}{U_0} \quad [2]$$

$$\text{where } \frac{1}{U} = \frac{T_s - T_b}{Q/A}, \text{ and } \frac{1}{U_0} = \frac{T_{s0} - T_b}{Q/A}$$

RESULTS AND DISCUSSION

Thermal Fouling-Composition Effects

Fouling data were taken in the present study, using both ATB and VR feedstocks at 10 % wt. in various blends, chosen to cover both stable and non-stable conditions. For unstable asphaltene blends the fouling rate has been found to depend on initial surface temperature, bulk temperature, and velocity as well as composition of the mixture (Asomaning and Watkinson, 1999). This prior work showed that at constant surface temperature, as velocity was increased over a narrow range, the fouling rate decreased in a near linear fashion (Watkinson, 2007). In the present work, where composition and temperature effects are explored, the velocity was held constant at 0.75m/s. Figures 1 and 2 show typical plots of the fouling resistance versus time. For both VR and ATB, as might be expected, fouling is much higher when the aliphatic diluent is used, and decreases as the aromaticity of the diluent is raised. For VR, at a surface temperature of 260°C, rapid fouling occurred when blended with PFX (<1 % aromatics), and almost negligible fouling with HVGO (16 % aromatics). ATB fouling rates were lower than with VR, due to the relatively lower asphaltene content for ATB of 1.35 % vs 1.77 % for VR in the blends. Therefore surface temperatures for ATB were raised to 290°C, as shown in Figure 2. This figure includes one run for VR, and shows that at the same temperature, the fouling rate of VR is about 40 % greater than for ATB. With the addition of increasing amounts of the aromatics (63%) and resin (36%) rich REF, the extent of fouling of ATB blends at any time decreases substantially. As will be shown below, this appears to be a bulk concentration effect, not a surfactant effect. Initial fouling rates were taken from the data by fitting a linear equation over times of 0 to 5 hours, or in a few appropriate cases, such as curves A and C in Figure 1 and curve E in Figure 2 by fitting an asymptotic curve to the R_f versus t .

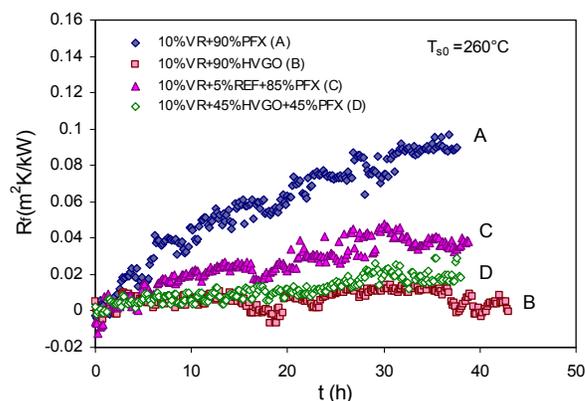


Figure 1 Fouling resistance versus time for the mixtures of VR and various diluents

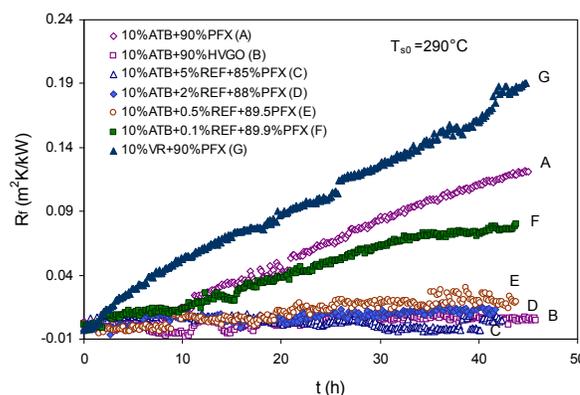


Figure 2 Fouling resistance versus time for the mixtures of ATB and various diluents

Thermal fouling-surface temperature effects

The effect of surface temperature on thermal fouling was investigated over the range of 230-310°C, yielding film temperatures (average of bulk and surface temperatures) in the range 158 to 198°C. With the velocity held constant at 0.75 m/s, Reynolds numbers were roughly 2400 evaluated at bulk temperature, and above 10,000 evaluated at film temperatures due to the strong temperature dependence of the viscosity. At the temperatures in question, fouling rates double for a 25°C increase in surface temperature. The dependence of the initial fouling rates on surface temperature (Figure 3) was expressed by an Arrhenius type equation of the form $(dR_f/dt)_0 = A \exp(-E/RT_{s0})$, where E is an apparent activation energy. An average fouling activation energy of ~68 kJ/mol which was similar for both oils represents the overall fouling process. This value is higher than expected for a physical process. If chemical processes are absent, then a high activation energy may indicate a

temperature-sensitive adhesion step in the attachment of deposits.

The diluents PFX1 and PFX2 were different samples of Paraflex HT 10. Mixtures of VR with PFX1 showed higher fouling rates than with PFX2 at the same conditions. Subsequent PNA analysis (ASTM D-2786, 3239) showed that PFX1 had a higher paraffin content of 34.7% than for PFX2 (23.0%), and a corresponding lower naphthene content. Simulated distillation showed that PFX1 was slightly heavier than PFX2.

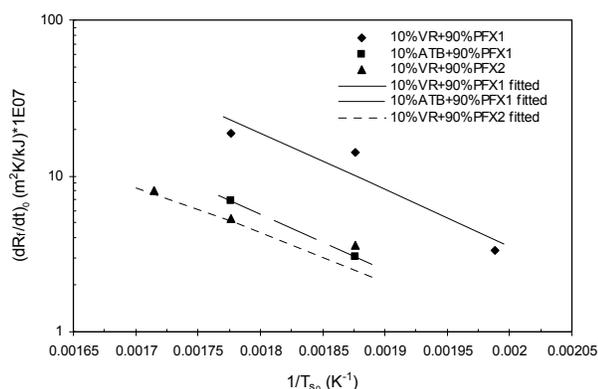


Figure 3 Dependence of initial fouling rate on surface temperature

Characterization of thermal fouling deposits

Thermal fouling deposits were characterized by elemental analysis, thermo-gravimetric analysis (TGA), and scanning electron microscopy with energy dispersion X-ray (SEM-EDX). Deposit analyses are compared in Table 2 with results for insolubles recovered by hot filtration of the blends used in fouling, and for asphaltenes precipitated by heptane. Fixed carbon contents ranging from 22.3 to 49.0 wt% were observed for all samples. Ash contents were markedly higher (7.7-14.2 wt%) for the fouling deposits originating from ATB, than for the deposits originating from VR (1.3-4.7wt%), which reflects the differences in processing of the two streams. The high ash content suggests that inorganic particulates in the bulk fluid or that the heteroatoms, especially sulphur, combine with some components of the solids to form inorganic salts on the probe surface. Elemental analysis shows that the H/C atomic ratios were very high for the fouling deposits originating from ATB (1.51-1.70), and much lower for the deposits and the precipitates (0.94-1.20) originating from VR. The higher H/C ratios, and lower S contents for the ATB deposits suggest that some PFX is

incorporated in the ATB deposits in spite of the rinsing step used to remove oil. Physically, deposits from ATB appeared loose, while those from VR were hard. The fouling deposits and hot filtration solids show a significant difference in their microstructure under SEM (E., Hong 2005). The hot filtration solids show fine grain-mosaic structure while the fouling deposits show some coarse grain-mosaic structure and some degree of spherical agglomeration. The EDX results showed noticeable silicon and aluminum content for the deposits originating from ATB, which indicated that clay particles may be present in ATB and contribute to the fouling of ATB blends.

Table 2 Fouling deposits and solids from hot filtration and precipitation tests*

Solid	Oil Blend	F.C. wt%	Ash wt%	C Wt%	H wt%	N wt%	S wt%	H/C
D	VR-PFX	39.9	3.1	82.5	8.2	0.9	4.4	1.19
D	VR-PFX	61.1	1.3	82.6	6.5	1.0	5.5	0.94
I	VR-PFX	49.0	4.3	80.6	7.4	1.1	6.1	1.10
HI	VR-Hep	40.1	2.2	81.2	8.0	1.0	5.6	1.17
D	ATB-PFX	22.3	14.2	72.8	9.2	0.5	2.3	1.51
D	ATB-PFX-REF	13.0	7.7	75.0	10.6	0.4	1.9	1.70
HI	ATB-Hep	32.9	4.7	77.7	7.8	1.2	5.6	1.20

*: D=heated probe deposit, I= filtration insolubles, Hep=heptane, HI=heptane insolubles (asphaltenes), Blends contain 10 wt % VR or ATB

Precipitation and Precipitation Onset

Batch precipitation results at 85°C were presented in E., Hong and Watkinson (2004), and E., Hong (2005). As expected, the amount of asphaltene precipitated increased with R, the ratio of diluent volume to feed mass, and decreased with increasing aromatics concentration in the diluent. Results are discussed below with Figure 5. Typically, 1-8% of the feed oil (which contained 13.5 or 17.7 % asphaltenes) precipitated, and the remainder of the asphaltenes remained in solution. Flocculation onset results using n-heptane titrations at temperatures of 25-50°C confirmed these trends. Adding the highly aromatic diluents, toluene and REF to the VR or ATB resulted in larger amounts of heptane needed for the precipitation onset (E., Hong, 2005).

To predict the stability of various oil mixtures, literature models (Andersen and Pedersen, 1999; Wiehe and Kennedy, 2000) were applied to results from the

titrations to calculate the solubility parameter of the feedstock blends. Asphaltenes should precipitate when the solvent phase or oil reaches conditions where the average solubility parameter of the phase equals a critical solubility parameter obtained through the titration. The critical or flocculation solubility parameter for the mixture, δ_f , is given as

$$\delta_f = \phi_o\delta_o + \phi_p\delta_p + \phi_s\delta_s \quad [3]$$

where δ_o , δ_p , and δ_s are the solubility parameters of oil, precipitant and solvent respectively and ϕ_o , ϕ_p , ϕ_s are volume fractions of the corresponding components such that $\sum \phi_i = 1$. Assuming that Equation 3 describes the onset of asphaltene precipitation, a plot of V_p/V_o vs V_s/V_o at flocculation conditions is a linear function, where the slope, $s = (\delta_s - \delta_f) / (\delta_f - \delta_p)$, and the intercept, $I_y = (\delta_o - \delta_f) / (\delta_f - \delta_p)$. The criterion for the oil blend to be stable is that $\delta_o > \delta_f$. The Oil Compatibility Model of Wiehe and Kennedy (2000) suggests that asphaltene will precipitate from an oil at the same mixture solubility parameter when blended with other non-complexing liquids or oils, and that the solubility parameter of any oil mixture is given by its volumetric average, whence

$$\delta_{\text{mix}} = \sum \phi_j \delta_j \quad [4]$$

Since for compatibility, the solubility parameter of a blend of oils must be greater than the flocculation solubility parameter of any oil in the mixture, the maximum insolubility or flocculation solubility parameter of all the oils in the mixture is the only one required. Thus, for a mixture of oils, the compatibility criterion is $\delta_{\text{mix}} > \delta_f$.

Table 3 shows that the calculated solubility parameters of all the components of the present blends at 25°C, lie in the range of 15.6-21.2 (MPa)^{0.5}, which is in agreement with the values reported in the literature (Lian, H. et al., 1994; Laux, H et al., 1997; Andersen, S.I. and Pederson, C., 1999). Based on the acquired solubility parameter for each feedstock, the solubility parameters and model parameters for test fluids used for batch hot filtration experiments were calculated on the volumetric average rule. Since the bulk temperatures in the precipitation and fouling studies were 85°C, and the titrations were done at 25°C, it was of interest to determine their temperature dependence. The titrations were repeated at temperatures of 35°C and 50°C, and the results shown in Figure 4 for δ_o fitted to linear temperature relationships (Table 3), where a and b are dimensional constants

$$\delta_o \text{ (MPa)}^{0.5} = a - b T(\text{K}) \quad [5]$$

The values of the coefficients for temperature variation are within reasonable agreement with literature values. Akbarzadeh *et al.*, (2005), give “b” values of 0.022 for saturates, and 0.0204 for aromatics, compared to values of 0.026 in this work for Paraflex, and 0.0344 for HVGO. For the asphaltene-containing fractions, and the resin-derived fluid, δ_o values were relatively more strongly dependent on temperature, showing “b” values of 0.043-0.045. For the blended mixtures, δ_{mix} “b” values are therefore higher than the 0.028 of the PFX, or the 0.0344 of the HVGO. As can be seen from Table 3, values of δ_f were almost identical for VR and for ATB, and decreased only slightly with temperature. All six readings could be expressed within $R^2 = 0.9838$ by

$$\delta_f = 23.328 - 0.0238 T (\text{K}) \quad [6]$$

Since δ_o decreases more strongly with temperature than does δ_f , then $[\delta_{\text{mix}} - \delta_f]$ will also decrease as temperature increases. Thus a mixture which was calculated to be unstable at a low temperature could become stable at higher temperatures as the value of the difference in solubility parameters becomes smaller as temperature is increased. As has been stated by Wiehe and Kennedy (2000), the stability criterion calculated from 25°C solubility parameters is conservative, in that mixtures which are stable from the 25°C calculation will become more stable as temperatures are raised.

Table 3 Calculated solubility parameters [MPa]^{0.5} and Eq'n 5 constants (a [MPa]^{0.5}, b [MPa]^{0.5}·K⁻¹)

	δ	δ_f	δ	δ_f	Eq'n5 A	Eq'n5 10 ² b
T (°C)	25	25	50	50		
ATB	19.57	16.20	18.46	15.59	32.36	4.32
VR	19.53	16.23	18.38	15.66	32.77	4.47
REF	21.12	-	19.86	-	35.93	4.98
PFX1	15.67	-	15.0	-	23.71	2.69
PFX2	16.09	-	15.34	-	25.01	2.99
HVGO	16.82	-	15.96	-	27.06	3.44

Relation of Precipitation and Thermal Fouling Data to Instability Parameters

Figure 5 shows the batch precipitation results (E., Hong and Watkinson, 2003) where W, the percentage of the feed oil precipitated as asphaltenes at 85°C in 30 minutes is plotted versus the driving force for precipitation ($\delta_{\text{mix}} - \delta_f$) evaluated at temperatures of 25°C and 50°C. Clearly there is a good correlation of the

precipitation amount for both ATB and VR with the solubility parameter difference. Further, as the temperature at which the driving force is evaluated is raised towards the temperature of the precipitation experiments, the condition of zero precipitation at $\delta_{\text{mix}} > \delta_f$ is better approximated. The fact that some precipitation was found even at $[\delta_{\text{mix}} - \delta_f] > 1$, may be due to the presence of some non-asphaltene solids such as clays in the ATB.

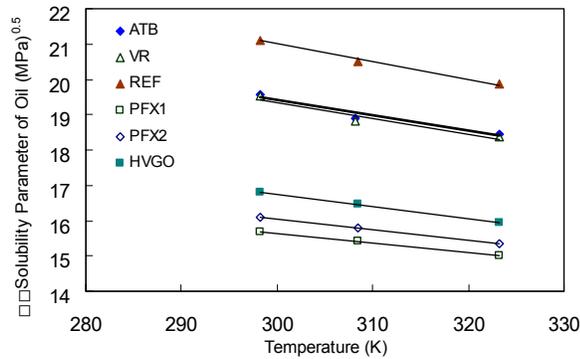


Figure 4 Temperature dependence of oil solubility parameters

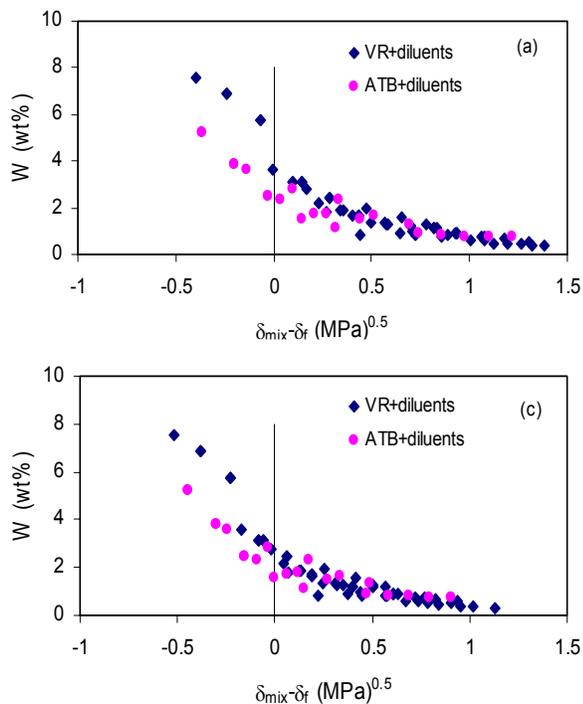


Figure 5 Weight percent of feed precipitated at (a) 25°C and (c) 50°C versus solubility parameter difference

Figures 6 and 7 shows plots of initial fouling rate versus the mixture stability criteria parameter, for the current experiments. For diluted Cold Lake Vacuum Residue, the asphaltene concentration was 1.77% and the initial surface temperature was 260°C, whereas for Athabasca atmospheric tower bottom blends, the asphaltene concentration was held constant at 1.35 % and the initial surface temperature was 290°C. Good correlations of rate of fouling with the instability parameters are obtained for both sets of blends. Again, the prediction of conditions of zero of the fouling is more closely approached as the driving force is evaluated at temperatures more closely approaching the bulk temperature of the experiments.

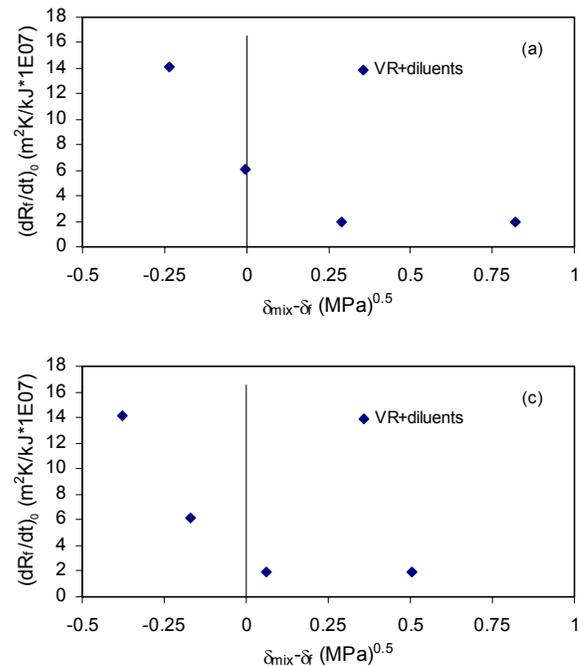


Figure 6 Correlation of initial fouling rate with stability criterion for VR and diluents with solubility parameter determined at (a) 25°C, and (c) 50°C

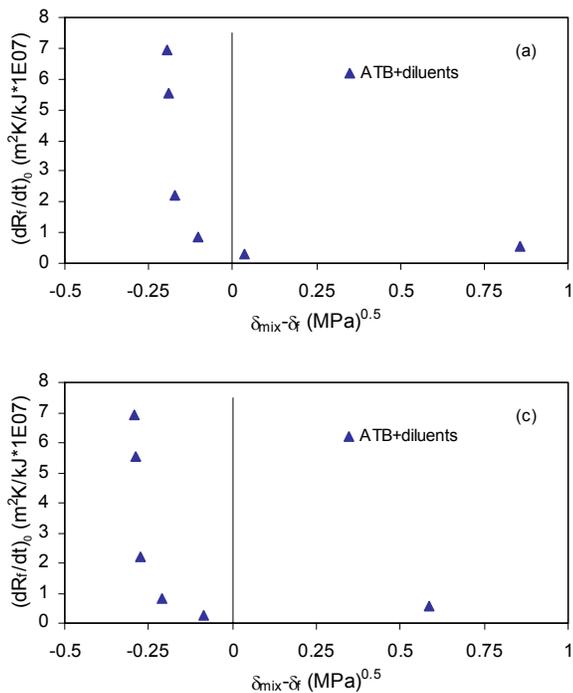


Figure 7 Correlation of initial fouling rate with stability criterion for ATB and diluents with solubility parameter determined at (a) 25°C, and (c) 50°C

As mentioned above, the colloidal instability index is a useful empirical parameter for correlating fouling and precipitation results. Figures 8a and b show the similarity of trends in both suspended asphaltene concentrations, and in initial fouling rate with the colloidal instability index. For each oil source, its blending components and amounts dictate the concentration of suspended asphaltene solids which will occur in the mixture. For the 10 wt % VR or ATB blends used here, at a given C.I.I., the suspended solids concentrations for the VR are 2.23 times that for the ATB. The suspended solids concentration then appears to dictate the fouling rate at the given temperature and velocity. Therefore it appears that in unstable mixtures, where asphaltene precipitation has occurred particulate fouling then follows. However at a given C.I.I. the ratio of fouling rates of Figure 8b, is greater than the ratio of suspended solids concentrations in Figure 8a, in spite of surface temperature differences.

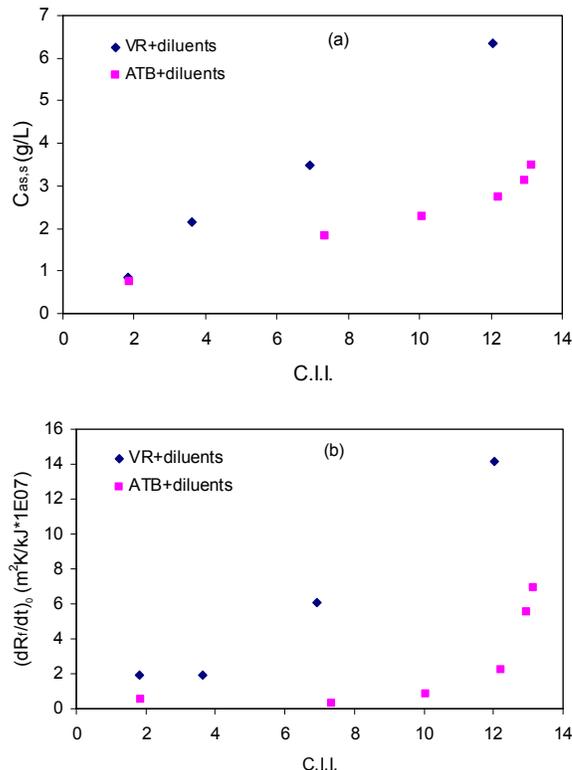


Figure 8 Dependence of (a)suspended asphaltene concentration and (b) initial fouling rate on colloidal instability index for VR and ATB blends.

The reason that the C.I.I. gives such a good correlation of fouling rates is indicated in Figure 9, where for the batch precipitation experiments of Figure 5, The C.I.I. is shown to correlate well with the solubility parameter difference. The inter-relationship of C.I.I. and $[\delta_{mix} - \delta_f]$, shows, at least for the mixtures tested, that either parameter can be expected to correlate with initial fouling rate. The C.I.I. can readily be determined from the SARA analysis of the blending components, whereas the solubility parameter requires a number of titrations, and may be less easy to evaluate.

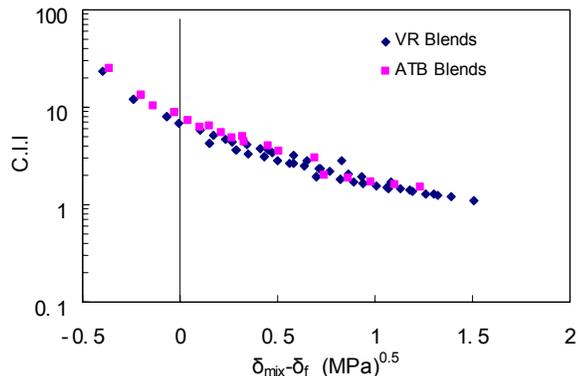


Figure 9 Correlation of C.I.I. with solubility parameter difference for the precipitation data of Figure 5

The fouling rate data for the four least stable 10 % ATB blends warrants further examination. The ATB data points in Figure 8 with the highest four C.I.I. values (raw data shown in Figure 2) were obtained by adding Resin Enriched Fraction (REF) to 10% ATB-Paraflex mixtures. In Figure 10, fouling rates are plotted versus % REF in the mixture. Addition of REF results in dramatic decreases in fouling rate, which are detectable at % REF as low as 0.1-0.5 %. At 2 % addition, the fouling rate is decreased by a factor of 8.3. REF, which is derived from VR, contains 99% Aromatics + Resins (Table 1), and has a solubility parameter of 21.1 [MPa]^{0.5} (Table 2). Hence, even at low percentage additions as a diluent, it affects calculated values of δ_o and C.I.I. (Figures 7 and 8). Although addition of REF has a strong solvent effect in reducing fouling, commercial anti-foulants can reduce fouling rates by much larger extents and at much lower concentrations of about 0.01% (Watkinson and Wilson, 1997) in a similar unstable heavy oil system. At an additive concentration of < 0.01%, calculated values of C.I.I. or δ_o would not be affected, and the fouling reduction arises presumably from dispersant effects.

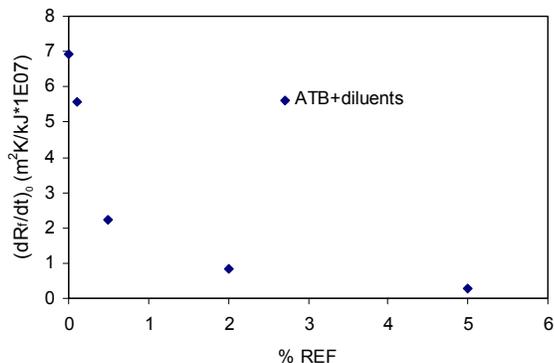


Figure 10 Effect of REF addition on fouling rate of 10% ATB-REF-PFX blends.

CONCLUSIONS

A study of asphaltene precipitation and fouling from blends of Cold Lake and Athabasca heavy oil cuts and diluents of varying aromaticities showed:

- When heavy oil cuts are blended with aliphatic diluents, asphaltenes are precipitated and heavy fouling occurs. With diluents containing significant aromatic content, much less precipitation occurs and fouling is reduced. A resin-rich fraction extracted from the heavy oil reduced fouling at concentrations of $\geq 0.1\%$.

- Fouling rates increase moderately with surface temperature; an increase of 25°C from 260 to 285°C resulted in a doubling of the initial fouling rate. With Cold Lake mixtures, deposits were of composition similar to suspended asphaltene solids, and with Athabasca blends were enriched in ash/clay and diluent constituents.

- Solubility parameter values for the heavy oil–diluent blend components could be readily obtained from automated flocculation titrations, and stability of oil blends predicted by literature models.

- Both the amount of asphaltenes precipitated in isothermal batch experiments, and the initial thermal fouling rate under fixed conditions can be related to the oil mixture solubility parameter, or to the more empirical colloidal instability index.

NOMENCLATURE

Abbreviations

ATB	Athabasca Atmospheric Tower Bottoms
C.I.I.	Colloidal Instability Index
HVGO	Heavy Vacuum Gas Oil
PFX	Paraflex
REF	Resin Enriched Fraction
VR	Cold Lake Vacuum Residue

Nomenclature

A	Surface area (m ²), Pre-exponent constant in Arrhenius equation (m ² K/kJ)
C _{as,s}	Suspended asphaltene concentration (g/L)
E	Activation energy (kJ/mol)
Mw	Molecular weight (g/mol)
Q	Electrical power (kW)
R _f	Thermal fouling resistance (m ² K/kW)
SG	Specific Gravity at 20°C (refer to water density at 4°C)
t	Time (s, minute, hour)
T	Temperature (°C, K)
T _b	Bulk fluid temperature (°C)

T_s, T_{s0}	Probe surface temperature under fouled and clean conditions ($^{\circ}\text{C}$)
U, U_0	Overall heat transfer coefficient under fouled and clean conditions ($\text{kW}/\text{m}^2\text{K}$)
V_o, V_p, V_s	Volume of oil, precipitant and solvent respectively (ml)
W	Weight percent of the feed which precipitated ($(\text{g asphaltene}/\text{g feed oil}) \times 100\%$)
δ	Solubility parameter (MPa) ^{0.5}
δ_f	Flocculation onset point solubility parameter, (MPa) ^{0.5}
δ_{mix} (MPa) ^{0.5}	Solubility parameter of the mixture,
$\delta_o, \delta_p, \delta_s$	Solubility parameter of oil, precipitant and solvent respectively
φ_i, φ_j	Volume fraction of component i and j

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