The Oil Compatibility Model and Crude Oil Incompatibility

Irwin A. Wiehe*,† and Raymond J. Kennedy

Exxon Research and Engineering Co., Corporate Research Laboratories, Route 22 East, Annandale, New Jersey 08801

Received June 22, 1999. Revised Manuscript Received September 20, 1999

Although incompatible crude oils have not been previously discussed in the scientific literature, they are discovered to be relatively common. Consequently, with the need of a predictive method, the Oil Compatibility Model was derived from two hypotheses. One hypothesis is that asphaltenes precipitate from the oil at the same mixture solubility parameter, no matter that the oil is blended with noncomplexing liquids or another oil. The other hypothesis is that the solubility parameter of a mixture is the volumetric average solubility parameter. As a result, the solubility parameter of a crude oil and its flocculation solubility parameter on a toluene−*n*-heptane scale can be determined based upon mixing the crude oil with toluene and *n*-heptane and determining if each mixture dissolves or precipitates asphaltenes. Thereafter, the correct proportions and correct order of blending oils to ensure compatibility can be specified. A refinery example is given where determining the correct order of blending potentially incompatible crude oils mitigated the coking of vacuum pipestill furnace tubes.

Introduction

Today, the rate of fouling and coking in crude preheat trains, heat exchangers and pipestill furnace tubes, have appeared to increase as the purchase of worldwide opportunity crudes has become more common. As a result, the hypothesis that incompatible blends of crudes might precipitate asphaltenes and cause this fouling and coking was investigated. Surprisingly, the first two blends selected of asphaltic crudes with paraffinic crudes were found to be incompatible. Although it is well-known that visbreaker tars and other processed oils can deposit asphaltenes when blended with paraffinic oils and that some suspected incidents of incompatible crude oils are in the patent literature,[1] no previous evidence of incompatible blends of crude oils appears to be in the scientific literature. Therefore, it was decided to develop laboratory tests and a model to predict which mixtures of crudes are incompatible. Consequently, not only was it discovered that incompatible crudes are relatively common but also that the order of mixing is important.

Physical Model of Petroleum. The phase behavior of petroleum is complex because of the large mixture of diverse molecules and because petroleum has some properties of a colloidal dispersion and some properties of a solution. Previously,[2] following the model of Pfeiffer and Saul[3] and on the basis of X-ray and neutron scattering data, the million or so different molecules in petroleum were simplified to just four types. A variation of the previous physical structure is shown in Figure 1. The largest, most aromatic molecules, the asphaltenes (capital A) are actually submicroscopic solids dispersed in the oil by the resins (R), the next largest, most aromatic group of molecules. This asphaltene−resin dispersion is dissolved into petroleum by small ring aromatics (lower-case a) that are solvents but opposed by saturates (s) that are nonsolvents. Thus, asphaltenes are held in petroleum in a delicate balance, and this balance can be easily upset by adding saturates or by removing resins or aromatics. Blending of oils can greatly change the overall concentrations of these molecular types to upset this balance and precipitate asphaltenes. By simplifying the resins and asphaltenes always to be associated with each other, the phase behavior is based upon solubility and upon aromatics−saturates balance. This assumption provides both the power and the limitation of the resulting model. The power is the ability to describe a complex system with a relatively simple model, while the limitation is that the predictions will be conservative.

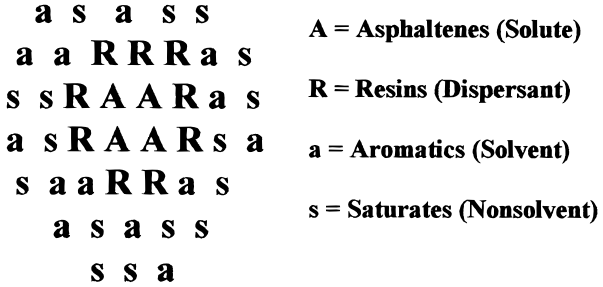

Figure 1. Physical model of petroleum.

* Corresponding author. Fax: (908) 470-0939. E-mail: wiehe@nac.net.
† Present address: Soluble Solutions, 3 Louise Lane, Gladstone, New Jersey 07934.

(1) Dickakian, G. U.S. Patent 4,853,337, 1989.
(2) Wiehe, I. A.; Liang, K. S. *Fluid Phase Equilib.* **1996**, *117*, 201−210.
(3) Pfeiffer, J. P.; Saul, R. N. J. *J. Phys. Chem.* **1940**, *44*, 139−145.

10.1021/ef990133+ CCC: $19.00
Published on Web 12/14/1999

Solubility Parameters. The solubility parameter was derived by Hildebrand[4] and Scatchard[5] as part of the regular solution model. However, it is much more general and useful[6,7] than the regular solution model. Although the solubility parameter has been expanded to two[6] or three[7] components to account for hydrogen bonding and other charge transfer complexes, petroleum and noncomplexing solvents were found to need only one component.[8] The solubility parameter, δ, is defined as

$$\delta = \sqrt{\frac{E_v}{V}} \tag{1}$$

where E_v is the energy of vaporization to an ideal gas in cal/g-mol and V is the molar volume in mL/g-mol.

This square root definition of solubility parameter results from the regular solution model. Since the regular solution model is not used here, the cohesive energy density, the energy of vaporization divided by the molar volume, could be used instead. However, the rule for calculating the solubility parameter for a mixture is well established to be the volumetric average.[6,7] Although the solubility parameters at 25 °C for pure liquids are well-known because the energy of vaporization and the molar volume can be directly measured, they are not for asphaltenes that do not evaporate. The solubility parameter of an asphaltene has been estimated[8] to be about 9.5 $(cal/mL)^{1/2}$, the highest solubility parameter of any component in an unprocessed oil. Nevertheless, what is more important is the solubility parameter at which asphaltenes just begin to precipitate, the flocculation solubility parameter.

The use of flocculation testing of oils by adding various amounts of a solvent, such as toluene, and titrating with a nonsolvent alkane to predict the compatibility of processed oils, such as visbreaker tars, has been common in the petroleum industry.[9,10] However, the compatibility predictions are either empirical or based upon the regular solution model. This work takes advantage of flocculation testing but uses a model with a clear basis without the known limitations of the regular solution model. Although the resulting model also has limitations, the predictions will be conservative for well-understood reasons.

Results

Flocculation and Oil Solubility Parameters. The basic hypothesis of the Oil Compatibility Model is that the asphaltene/resin dispersion has the same flocculation solubility parameter, no matter that the oil is blended with noncomplexing liquids or other oils. While this hypothesis has been used previously,[11−13] only the present authors have applied it to predict the compatibility on mixing oils. Support for this hypothesis is the observation by Buckley[14,15] that the onset of precipitation of asphaltenes occurs over a narrow range of solution refractive index. If one orders the liquids that contain only hydrogen, carbon, and sulfur atoms in increasing solubility parameter, it is common that all liquids below a certain solubility parameter precipitate asphaltenes and all liquids of higher solubility parameter dissolve the oil completely at the given concentration.[8] For Souedie crude (Figure 2) the flocculation solubility parameter lies between 7.80 (for methylcyclohexane, highest of the nonsolvents) and 8.19 (for cyclohexane, lowest of the solvents) but can only be determined exactly by testing the oil with mixtures of solvents and nonsolvents. However, to be even more precise, one needs to account for the solubility parameter of the oil to determine the flocculation solubility parameter because the oil contributes to the solvency of the mixture. Thus, by varying the oil-to-liquid volume ratio, one can actually measure both the flocculation and the oil solubility parameters. However, since asphaltenes are defined as toluene soluble and *n*-heptane insoluble, it makes sense to stretch out the solubility parameter scale of interest by putting the solubility parameters on a reduced *n*-heptane−toluene scale. Therefore, two such reduced solubility parameters, the insolubility number, I_N, and the solubility blending number, S_{BN} are defined as:

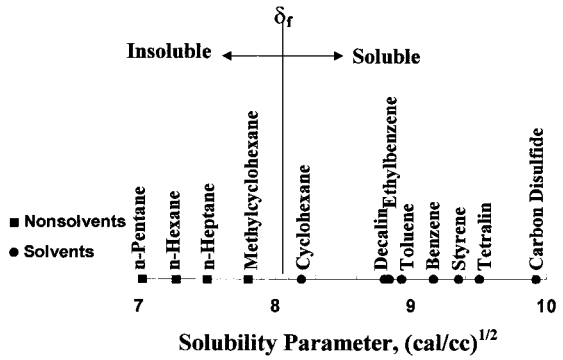

Figure 2. Solvents and nonsolvents for Souedie crude oil at 0.1 g of oil and 25 mL of liquid.

$$I_N \equiv 100\frac{(\delta_f - \delta_H)}{(\delta_T - \delta_H)} \tag{2}$$

$$S_{BN} \equiv 100\frac{(\delta_{oil} - \delta_H)}{(\delta_T - \delta_H)} \tag{3}$$

where $\delta_f \equiv$ the flocculation solubility parameter, $\delta_H \equiv$ the solubility parameter of *n*-heptane, $\delta_T \equiv$ the solubility parameter of toluene, and $\delta_{oil} \equiv$ the solubility parameter of the oil.

If the oil is completely soluble in *n*-heptane and thus contains no asphaltenes the insolubility number is 0, but if the asphaltene−resin dispersion is barely soluble in toluene the insolubility number is 100. Likewise, an oil that is as poor a solvent as *n*-heptane has a solubility blending number of 0, and an oil that is as good a solvent as toluene has a solubility blending number of 100.

(4) Hildebrand, J. H.; Wood, S. E. *J. Chem. Phys.* **1933**, *1*, 817−822.
(5) Scatchard, G. *Chem. Rev.* **1931**, *8*, 321−333.
(6) Wiehe, I. A. *Ind. Eng. Chem. Res.* **1995**, *34*, 661−673.
(7) Hansen, C. M. *Ind. Eng. Chem. Prod. Res. Dev.* **1969**, *8*, 2−11.
(8) Wiehe, I. A. *Fuel Sci. Technol. Int.* **1996**, *14*, 289−312.
(9) Heithaus, J. J. *J. Inst. Pet.* **1962**, *48*, 45−53.
(10) Griffith, M. G.; Sigmund, C. W. In *Marine Fuels;* Jones, C. H., Ed.; ASTM, Philadelphia, 1985; pp 239−245.
(11) De Boer, R. B.; Leerlooyer, K.; Eigner, M. R. P.; van Bergen, A. R. D. *SPE* 24987 **1992**, 259−270.
(12) Wiehe, I. A.; Kennedy, R. J. U.S. Patent 5,871,634, 1999; World Patent WO 98/26026.
(13) Andersen, S. I. *Energy Fuels* **1999**, *13*, 315−322.
(14) Buckley, J. S. *Fuel Sci. Technol. Int.* **1996**, *14*, 55−74.
(15) Buckley, J. S. *Energy Fuels* **1999**, *13*, 328−332.

Mixtures of Oil and Test Liquid. To measure the solubility parameters, one blends the oil with various volume ratios of test liquids composed of various volume ratios of toluene and *n*-heptane and determines if each dissolves or precipitates asphaltenes. The easiest method to detect insoluble asphaltenes is to look at a drop of the mixture between a cover slip and a glass slide in transmission light with an optical microscope at about 100−200×. Insoluble asphaltenes are seen throughout the entire view in the form of brownish chain agglomerates. At each volume ratio of oil to test liquid, the minimum volume percent toluene in the test liquid to keep the asphaltenes in solution is determined. The solubility parameter of the mixture of oil, toluene, and *n*-heptane at this point is the flocculation solubility parameter, δ_f, determined with the volumetric mixing rule:

$$\delta_f = \frac{V_T\delta_T + V_H\delta_H + V_{oil}\delta_{oil}}{V_T + V_H + V_{oil}} \quad (4)$$

Cross-multiplying, rearranging, and substituting yields

$$\frac{100\ V_T}{V_{TL}} = I_N + \frac{100\ V_{oil}}{V_{TL}}\left[\frac{I_N - S_{BN}}{100}\right] \quad (5)$$

Where V_{TL} is the volume of test liquid (toluene and *n*-heptane). Therefore, this model predicts that if the minimum percent toluene in the test liquid to keep asphaltenes soluble is plotted against 100 times the volume ratio of oil to test liquid, the data will fall on a line and the *y*-axis intercept will be equal to the insolubility number. If the *x*-axis intercept of the line is H_D, then:

$$S_{BN} = I_N\left[1 + \frac{100}{H_D}\right] = I_N\left[1 + \frac{V_H}{V_{oil}}\right]_{V_T=0} \quad (6)$$

This *x*-axis intercept can be evaluated directly by determining the maximum *n*-heptane that can be added to the oil without precipitating asphaltenes. This is called the heptane dilution test. As shown above, the volume ratio of *n*-heptane to oil measures the reserve solvency of the oil beyond that required to dissolve the asphaltenes ($S_{BN} = I_N$).

For crude and processed petroleum oils, the plot of the minimum percent toluene in the test liquid to keep asphaltenes soluble against 100 times the volume ratio of oil to test liquid has indeed been found to lie on straight lines with Figure 3 for Arab Light crude being an example. However, for experimental efficiency the minimum two measurements are commonly done. The heptane dilution with 5 mL of oil is usually one test, unless the viscosity of the oil is high. The other test is commonly the toluene equivalence test[10] at a concentration of two grams of oil and 10 mL of test liquid.

Mixtures of Oils. The solubility blending number of a mixture of oils from the mixing rule for solubility parameters is the volumetric average:

$$S_{BNmix} = \frac{V_1S_{BN1} + V_2S_{BN2} + V_3S_{BN3} + ...}{V_1 + V_2 + V_3 + ...} \quad (7)$$

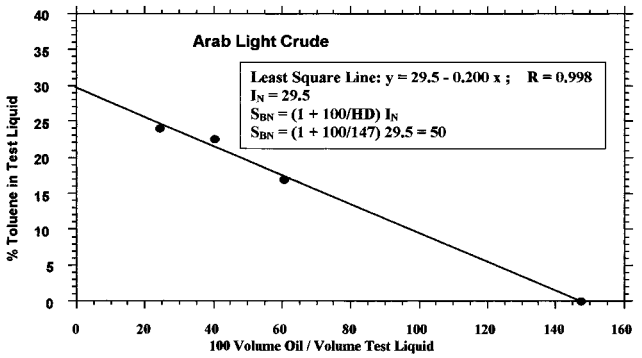

Figure 3. As predicted, a plot of percent toluene in the test liquid versus volume ratio of oil to test liquid for Arab Light falls on a line.

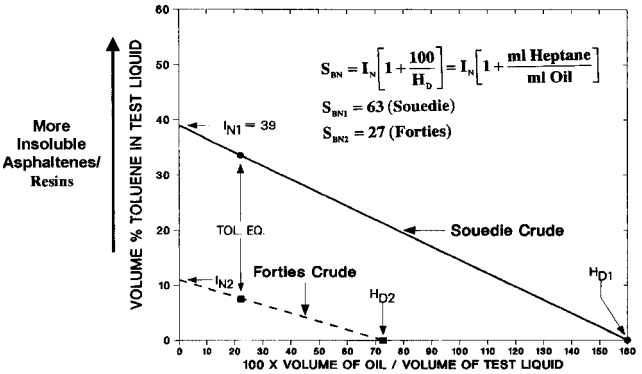

Figure 4. The evaluation of the compatibility numbers for Souedie and Forties crudes.

Since for compatibility the solubility parameter of the mixture of oils must be higher than the flocculation solubility parameter of any oil in the mixture, the maximum insolubility parameter of all the oils in the mixture is the only one required. Thus, for a mixture of oils:

$$\text{Compatibility Criterion: } S_{BNmix} > I_{Nmax} \quad (8)$$

While it is theoretically possible to also get incompatibility if the solubility parameter of the oil is too high, in practice this does not happen with oils because the asphaltenes-resin dispersion always has the highest solubility parameter.

Blending of Souedie and Forties Crudes. Figure 4 shows the evaluation of the insolubility numbers and solubility blending numbers for Souedie and Forties crudes from the heptane dilution and toluene equivalence tests. The insolubility numbers are the *y*-axis intercepts. Mathematically the insolubility number can be calculated from

$$I_N = \frac{TE}{\left[1 - \frac{V_{Hmax}}{25d}\right]} \quad (9)$$

where TE = toluene equivalence, V_{Hmax} = the maximum mL of *n*-heptane that can be blended with 5 mL of oil without precipitating asphaltenes from the heptane dilution test, and d = density of the oil in g/mL. The solubility blending number can be calculated from eq 6.

Since the insolubility number of each crude is less than its solubility blending number, each crude is

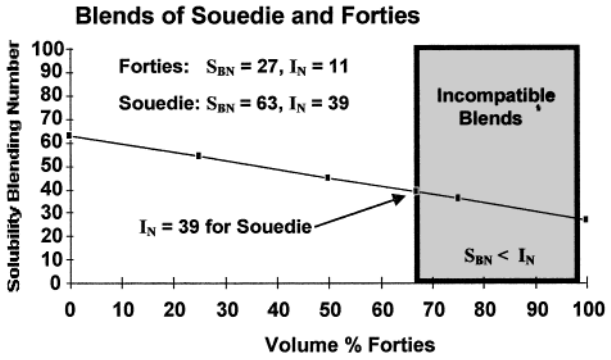

Figure 5. Both the proportions and the order of blending are important for compatibility.

compatible with itself. However, since the insolubility number of Souedie, 39, is greater than the solubility blending number of Forties, 27, there will be some mixtures of the two crudes that are incompatible.

Souedie and Forties crudes are graphically blended in Figure 5. If we start with a tank partially filled with Souedie crude and start adding Forties crude, the blend remains compatible but the solubility blending number of the mixture decreases until reaching 39 at 67% Forties when it equals the insolubility number of Souedie. Thereafter, any additional Forties that is added is predicted and found experimentally to precipitate asphaltenes. Now, if we start with a tank partially filled with Forties and start adding Souedie, the first drop of Souedie will precipitate asphaltenes and this will continue until adding 33% Souedie. Although the precipitated asphaltenes will eventually go back in solution, it might take days or weeks because petroleum is both a dispersion and a solution. Meanwhile, such a blend has high potential for fouling and coking in the refinery time scale of minutes. Since coke formation is triggered by the phase separation of asphaltenes at thermal cracking temperatures,[16] insoluble asphaltenes that hit a metal surface above 350 °C, almost immediately form coke.

Refinery Processing of Souedie and Forties Crude Blends. Souedie and Forties crudes were blended in a tank in the correct proportions for compatibility but in the wrong order at a refinery. The result was black sludge in the desalter, high fouling of preheat exchangers, and rapid coking of vacuum pipestill furnace tubes. Once the problem was analyzed, this refinery continued to mix these crudes but in the correct order and proportions without unusual fouling or coking. Therefore, *blending order is important*. One should blend potentially incompatible oils in the order of decreasing solubility blending number. The process of blending oils to ensure compatibility based upon the Oil Compatibility Model is the subject of a recent patent[10] by the authors.

Incompatible Pairs of Crude Oils. Once the insolubility and the solubility blending numbers of a number of crude oils have been measured, the set of potentially incompatible pairs of crudes can be predicted and compared with experimentally blending a number of pairs of crudes in a number of proportions. The prediction is found to be conservative in that no incompatible crude blends were predicted to be compatible. However, there are a number of crude pairs that were predicted to be incompatible but found to be compatible. This happens when the low-insolubility-number crude has an excess of resins and little or no asphaltenes and the high-insolubility-number crude has a low resin-to-asphaltene ratio. This causes the maximum insolubility number to decrease on blending because of the dispersion effect. To predict this effect is clearly outside the scope of the present model but the subject of future investigations. Nevertheless, since reality is always equal or better than the prediction, the present model provides a useful tool for preventing high rates of fouling and coking caused by incompatible oils.

In the next paper, the Oil Compatibility Model will be applied to solve the problem of the rapid plugging of a fixed bed hydrotreater. This example will demonstrate the utility of the Oil Compatibility Model to mitigate the fouling and coking of processed oils within the refinery. The evaluation of the solubility blending numbers for oils without asphaltenes also will be discussed.

EF990133+

(16) Wiehe, I. A. *Ind. Eng. Chem. Res.* **1993**, *32*, 2447−2454.