FINAL REPORT

DEVELOPMENT OF PETROLUUM RESIDUA SOLUBILITY MEASUREMENT METHODOLOGY

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ABSTRACT

In the present study an existing spectrophotometry system was upgraded to provide high-resolution ultraviolet (UV), visible (Vis), and near infrared (NIR) analyses of test solutions to measure the relative solubilities of petroleum residua dissolved in eighteen test solvents. Test solutions were prepared by dissolving ten percent petroleum residue in a given test solvent, agitating the mixture, followed by filtration and/or centrifugation to remove insoluble materials. These solutions were finally diluted with a good solvent resulting in a supernatant solution that was analyzed by spectrophotometry to quantify the degree of dissolution of a particular residue in the suite of test solvents that were selected. Results obtained from this approach were compared with spot-test data (to be discussed) obtained from the cosponsor.

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EXECUTIVE SUMMARY

Western Research Institute (WRI) has proposed to develop methodology for the measurement of the solubility of whole petroleum residua in various solvents. The goal of the described work is to determine whether the optical absorption properties of petroleum residua in various solvents are such that existing off-the-shelf combinatorial equipment might be adapted to the rapid measurement of solubility. In addition, centrifugation and filtration systems have been evaluated for their effectiveness in separating insoluble from soluble materials. The work has been performed in conjunction with AB Nynäs Petroleum, Nynäshamn, Sweden, who has participated as the corporate cosponsor for the Jointly Sponsored Research (JSR) task proposed herein.

Western Research Institute has developed an automated flocculation titrimeter (AFT) for the accurate, reproducible determination of Heithaus parameters and asphaltene solubility in petroleum residua (Pauli 1996). AFT has been applied to the characterization of petroleum residua during thermal treatment at WRI and to the multidimensional modeling of residua solubility at AB Nynäs Petroleum. In a previous project, visualization software was developed at WRI for modeling the 3-dimensional solubility space resulting from applying the Hansen solubility parameter approach to petroleum residua. The input data sets for this software are in the form of solubility measurement results for petroleum residua in many solvents. The acquisition of these solubility data currently requires relatively large amounts of residua, is labor intensive, and sometimes provides ambiguous results. This work described in the present report discusses research results that could lead to the adaptation and use of modern “combinatorial” type laboratory instrumentation to perform the same solubility tests with small amounts of residua, in very short times, with less uncertainty. In addition, micro-scale solubility testing would reduce problems and costs associated with solvent disposal.

INTRODUCTION

Background

Through support from the Federal Highway Administration (FHWA) and the United States Department of Energy (USDOE), Western Research Institute (WRI) has developed an automated flocculation titrimeter (AFT) for the accurate, reproducible determination of Heithaus (solubility-related) parameters (Heithaus 1962) in petroleum residua (Pauli 1996). This titration apparatus and method has been refined and improved, and is finding application in the characterization of petroleum residua during pyrolysis, oxidative aging, and upgrading (Pauli 1996; Pauli and Branthaver 1998, 1999; Schabron and Pauli 1999; Schabron et al. 2001a, 2001b, 2001c). Recently, with USDOE and Nynäs AB support, WRI has developed solubility visualization software, named **sp3D**, to aid the visualization and analysis of petroleum-residua solubility in three solubility dimensions.

Currently used techniques for obtaining petroleum residua solubility include the above-mentioned AFT when solubility in a few solvent systems are desired, and simple laboratory solubility tests incorporating filter paper spot tests when solubilities in many solvent systems are desired. The AFT is a robust, flexible titration system with many research and characterization applications. It is more adept at determining precipitation points with solvent pairs than in determining absolute solubility.

In the more standard spot test protocol (Redelius 2004), used when solubilities in many solvents are needed, 0.5 grams of petroleum residuum is agitated in a test tube containing 5 milliliters of solvent. The tube is sealed to prevent solvent evaporation, and is stored, with periodic agitation, for forty eight hours. Solubility is classified into three groups: soluble, uncertain, and not soluble. Because of the opacity of the solutions, a small amount of the “uncertain” mixtures may be removed with a capillary and spotted onto a filter paper. If a dark spot is observed in the center of the resulting spot, the petroleum residuum is said to be not soluble in that solvent. If no dark spot is observed, the petroleum residuum is soluble. “Uncertain” samples may also be examined in thin films with an optical microscope to detect precipitate particles. After filter paper and microscopic examinations, “uncertain” samples are reclassified as soluble or not soluble. Like the AFT, this solubility testing system also uses relatively large volumes of solvent, requires grams of petroleum residue (for multiple solvent testing), and sometimes yields ambiguous results. Turn-around times for both described techniques might be two weeks for forty solvents.

A needed improvement in solubility mapping is in speeding the acquisition of solubility data while reducing sample sizes and solvent waste disposal costs. Test methodologies and equipment similar to those developed for combinatorial spectrophotometric solubility testing in the life sciences might be applicable to petroleum residua testing if some criteria are met. Typically, in life science research, aqueous solubilities of up to 120 drug compounds can be

measured in one day, with one instrument (Millipore protocol note PC2445EN00 Rev. 09/03 03-236). Solubility measurements are performed by mixing an excess of drug with water, agitating until the solution is saturated, filtering the solution, and measuring light absorption at several wavelengths. Concentration is determined from the absorption and calibration with standard solutions.

For petroleum residua solubility testing, the combinatorial scale of testing is desirable, but there are several technical problems that must be solved. The first of these is related to sample uniformity: Is the soluble portion of the sample the same as the insoluble portion? Certainly, the chemical compositions are somewhat different. Are the differences large enough to interfere with accurate concentration measurements? Can absorption wavelengths be selected to minimize differences? A second problem concerns the ability to reproducibly filter out the insoluble matter. In most drug solubility tests, the insoluble materials are solid particulates that are easily filtered. In petroleum residua, the insoluble materials are tarry, viscous liquids that may plug filters. Preliminary centrifugation or other adaptations may be necessary. A third potential problem is related to the relatively large number of solvents in which measurements must be performed. Selecting appropriate wavelengths and subtracting solvent backgrounds will be a complex exercise.

WRI has been actively involved in the development and validation of test methods and models for describing and upgrading petroleum residua and asphalts (Western Research Institute 2001a, 2001b). Recently, with USDOE and Nynäs AB support, WRI has developed solubility visualization software to aid the visualization and analysis of petroleum residua solubility in three solubility dimensions (Redelius 2004).

The goal of the current work is to remove barriers to implementing off-the-shelf, combinatorial test equipment in the solubility testing of petroleum residua.

Theory

In past studies conducted at WRI (Schabron and Pauli 1999; Schabron et al. 2001a, 2001b, 2001c), the state of stability of petroleum residua has been modeled in terms of ideal solutions, where dissolution of petroleum residua is quantified in terms of the heat of mixing, ΔH_m . The Gibbs free energy of mixing of two ideal solvents which constitute a binary solvent system, ΔG_m , may then be expressed as

$$\Delta G_m = \Delta H_m - T \Delta S_m \quad (1)$$

where T is the temperature, and ΔS_m is the change in entropy of mixing. In a typical ideal solution, the change in the entropy of mixing is found to be positive, resulting in a negative value contribution to the free energy. Spontaneous mixing of species comprising the solution is then

defined by the magnitude in ΔH_m , which is always a positive value based on Hildebrand's definition of the term. The Hildebrand definition of ΔH_m thus describes the enthalpy or heat of mixing as

$$\Delta H_m = V(\delta_1 - \delta_2)^2 \Phi_1 \Phi_2 \quad (2)$$

where V is the total solution volume, $\Delta(\text{CED}) = (\delta_1 - \delta_2)^2$ is the effective change in the cohesive energy density defined in terms of the square of the difference in solubility parameters, δ_1 , and δ_2 , for solvents designated one and two, and Φ_1 and Φ_2 are the volume fractions in each solvent, where $\Phi_1 + \Phi_2 = 1$. The volume fraction for each solvent present in the solution may be further defined as

$$\Phi_i = \frac{\bar{V}_i}{\bar{V}_i + \bar{V}_j} \quad (3)$$

The solubility parameters for each solvent is thus defined as

$$(\delta_i)^2 = \frac{\Delta H_i + RT}{\bar{V}_j} = (\text{CED})_i \quad (4)$$

where the square of the solubility parameters defines the cohesive energy density, CED, for a given species, designated by subscript-“i”, and R is the ideal gas constant. The Hildebrand approach describing the spontaneity of free energy of mixing postulates that when the solubility properties of petroleum residua, as measured by solubility parameters, becomes more like that of the solvent in which it is being dissolved in, the system approaches a state in the enthalpy of mixing characterized as if an ideal solvent were effectively mixed with itself. This situation subsequently is found to be equal to zero, i.e., $\Delta(\text{CED}) = (\delta_1 - \delta_2)^2 = 0$. Under such a condition, the free energy of mixing is found to be solely a function of the entropy contribution, with the species comprising the system are generally found to be mutually soluble.

An extension to this model was proposed by Hansen (1967) in which more complex solutions were considered. In this extended model, both hydrogen-bonding forces and polar interactions were incorporated into the description of solubility parameters by proposing that the solubility parameter of a non-ideal solvent could be divided into three types of interactions, including, dispersive hydrogen-bonding and polar interaction. Thus, the Hansen solubility parameter for non-ideal solvents may be expressed as

$$(\delta_H)^2 = (\delta_d)^2 + (\delta_h)^2 + (\delta_p)^2 \quad (5)$$

The enthalpy or heat of mixing of complex solvents (i.e., solvents which exhibit both hydrogen-bonding and polar interactions in addition to dispersive interactions) may then be expressed in terms of the extended Hansen solubility parameter model as

$$\Delta H_m = V((\delta_{d1} - \delta_{d2})^2 + (\delta_{h1} - \delta_{h2})^2 + (\delta_{p1} - \delta_{p2})^2)\Phi_1\Phi_2 \quad (6)$$

Subscripts in equation 6 then represent solubility parameter components of the total solubility parameter for either species in a two component solvent system, which have been labeled “1” or “2”.

EXPERIMENTAL

Overview of the Study

Activities performed during the course of the study have been described in two stages. The research procedure described here uses the same initial petroleum residuum concentration as described above in the standard spot test protocol (Redelius 2001). While both of the AFT and spot test methods attempt to determine solubility through the detection of insoluble materials, the procedure developed in the current study determines solubility directly. In addition, in cases where the residuum is not completely soluble in a solvent, the limiting solubility may still be determined. Through an additional quantitative dilution in a good solvent, optical absorbance is then adjusted to provide the best concentration measurement.

Apparatus

The experimental apparatus developed in the present study is comprised of a high resolution UV-Visible computer-based spectrometer (OceanOptics™ HR2000) equipped with a 210-1700 nm Deuterium-Tungsten light source, a 0.10-mm path length Starna™ Quartz flow cell (Figures 1 and 2) housed in a temperature controlled cuvette holder, and a Neslab™ RTE-110 water bath circulator. A 2.0-mL syringe was further used to deliver flushing solvents as well as sample solutions to the 0.1 mm path length quartz cell by injection of either solvents or solution into a Teflon tube attached to one end of the flow cell. With one tubing end selected as the injection port, which was mounted in a small hole bored through a cork test tube stopper (Figure 3), and held in place by a laboratory ring stand using a test tube clamp, the other tubing end, further attached to the out flow port of the flow cell could be conveniently placed in a disposal reservoir. The present setup ultimately allowed for rapid sampling of test solutions by simple of injection of test solution, followed by flushing of the flow cell with wash solvents after each sample was analyzed.

Figure 1. HR2000 UV-VIS Spectrometer w/Deuterium-Tungsten Light Source, NesLab RTE-110 Water-bath Circulator, Temperature Controlled Cuvette Holder w/0.10 mm Quartz Flow Cell And Cork Septum Injection Port w/Sample Syringe

Figure 2. Deuterium-Tungsten Light Source, Temperature Controlled Cuvette Holder w/0.10 mm Quartz Flow Cell and Cork Septum Injection Port

Figure 3. Deuterium-Tungsten Light Source And Temperature Controlled Cuvette Holder w/0.10 mm Quartz Flow Cell And Cork Septum Injection Port. Sampling Syringe Pictured Positioned Sitting In Cork Septum Sample Injection Port

For the test procedure specifically involving measurements of dissolution of petroleum residua in a suit of organic solvents, a 0.45- μm syringe filter attached to a 5.0-mL glass syringe, equipped with a stopcock positioned between the syringe and the syringe filter (Figure 4), was used to filter test solutions prior to spectroscopic analysis. In certain cases a centrifugation procedure was further performed for specific samples prior to filtration to insure that the filtration procedure work properly. Once a test solution had sufficient time to dissolve, not less than 24-hours in each case, it was transferred from the original vial in which it was first prepared to a centrifuge test tube. Excess insoluble materials were then separated from the solution, via centrifugation, to the bottom of a centrifuge test tube. These solutions were then filtered and analyzed. A Neslab™ RTE-110 water bath circulator was used to maintain constant temperature of the cuvette holder and flow cell portions of the spectrometer at 25°C throughout testing.

Figure 4. 5-mL Syringe with Stopcock and Syringe Filter

Standardization of Test Method

Standardization of the experimental method was carried out by measuring the UV-visible spectra of several model compound systems in the wave length range of 200 nm to 1100 nm. UV-visible spectra were obtained for several model systems; solvents prepared as a mixture with a second solvent, or as a solution in one model compound, naphthalene, prepared in a number of different solvents. Solutions of toluene and carbon disulfide (CS_2) were prepared in four different solvents to provide baseline spectra to determine wave length and absorbtivity values for the appropriate peaks corresponding to electronic transitions of interest (i.e., $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$, respectively). Toluene-in-solvent solutions were prepared by adding different volumetric amounts (measured in volume) of HPLC grade toluene to four 5-mL volumetric flasks, then adding carbon disulfide, isooctane, or isopropyl alcohol to each flask to attain molar concentrations of 1.0, 0.5, 0.2, 0.1, and 0.01 mol/L. (For example, to prepare a 1.0 mol/L toluene-in-carbon disulfide solution, the volume of toluene needed to produce 5-mL of a 1.0 mol/L solution is calculated based on the known formula weight and density of toluene. This calculated volume of toluene is then added to the 5-mL flask volumetric flask. Carbon disulfide is finally added to the remaining volume of the 5-mL flask to attain 5.0 mL of the 1.0 mol/L solution). Carbon disulfide-in-solvent solutions were also prepared by adding different volumetric amounts of HPLC grade carbon disulfide to four 5-mL volumetric flasks, then adding toluene, isooctane, isopropyl alcohol, or methyl ethyl ketone (MEK) to each flask to attain molar concentrations of 1.0, 0.5, 0.2, 0.1, and 0.01 mol/L. A model compound, naphthalene, which was selected to represent asphaltene-like materials, was prepared by dissolution in either toluene or carbon disulfide at the same five molar concentrations that were used for preparing the solvent mixtures, namely; 1.0, 0.5, 0.2, 0.1, and 0.01mol/L.

UV-visible spectrophotometric analysis conducted for either model solvents or the model compound naphthalene, prepared in several test solvents at different molar concentrations, was carried out as follows; Background spectra were initially collected, as a reference spectrum, of the representative “solvating” solvent (i.e., reference spectra of carbon disulfide, isooctane, or isopropyl alcohol were collected in the case of toluene-in-solvent solutions testing). Each sample comprising a solvent mixture, was analyzed by transferring a portion of the solvent mixture to the test apparatus by drawing up approximately 1 mL of the sample into a 2.0-mL syringe and then injecting just enough of the sample into a 0.1 mm path length quartz cell through an injection port, (i.e., tubing attached to a cork-stopper to act as an injection septum [Figure 3]) to fill the flow cell. A spectrum was then obtained of the sample in the wavelength range from 200 nm to 1100 nm. Directly following acquisition of the spectrum of the sample, the 2.0-mL syringe was again used to inject air through the flow cell to blow the sample out of the system into a waste reservoir. This step was promptly followed with two rinsings of the flow cell system conducted by first injecting 5.0 mL of toluene, followed by a second injection of 5.0 mL of acetone through the system. The system was then completely evacuated using a vacuum line to draw the remaining solvent from the tubing line and flow cell.

As a proof of concept, a “model” petroleum residuum; SHRP asphalt AAD-1, which has been characterized as being of lower compatibility and high in asphaltenes, ~ 20% by mass (Western Research Institute 2001a), was selected for analysis by the methodology developed from the previous studies involving the model compounds. Test samples were prepared by weighing out $0.500 \pm 0.001\text{g}$ of the material into seven re-sealable 30-mL sample vials. Seven solvents; toluene, carbon disulfide, iso-octane, methyl ethyl ketone, cyclohexane, acetone, isopropyl alcohol were individually added ($5.00 \pm 0.01\text{mL}$) to each of the seven vials containing the sample then capped under an argon gas purge. These solutions were allowed 24-hours, undisturbed, to allow for complete dissolution of sample. In certain cases, (for example, samples of AAD-1 dissolved in iso-octane, methyl ethyl ketone, cyclohexane, and acetone where partial dissolution of the sample was visually observed to occur), following sample dissolution, a 5.0-mL glass syringe was used to decant-transfer approximately 4.0 mL of each solution to 8.0-mL centrifuge test tubes. Test tubes containing sample solutions were covered with aluminum foil and centrifuged at 3200 rpm for 5 to 15 minutes and periodically inspected throughout the centrifuge procedure to visually observe the amount of material which had settled. A 0.45- μm syringe filter was then attached to a 5.0-mL glass syringe equipped with a stopcock positioned between the syringe and the syringe filter, to filter a portion of the centrifuged solution prior to spectroscopic analysis. Approximately 2.0 mL of centrifuged sample was drawn up through the syringe filter into the 5.0-mL glass syringe, at which point the stopcock was shut and the filter removed. The filtered solution was then transferred to a 25-mL vial and capped prior to spectroscopic analysis. For samples of AAD-1 which were visually observed to be completely dissolved in toluene or carbon disulfide solution, and assumed to comprise homogeneous solutions, or for samples of AAD-1 prepared in isopropyl alcohol, which appeared not to dissolve any material at all based on visual observation, and hence were observed to remain clear, the centrifuge step was omitted, and only the filtration step was conducted.

These original seven solutions, which were referred to as the “parent” solutions, were finally diluted in a “good” reference solvent at specific volume-to-volume concentrations. The reference solvent chosen for this step was carbon disulfide. A 5.0 mL Teflon-plunger syringe was used to transfer exactly 0.3, 0.2, and 0.1 mL of each of the parent solutions into three 5-mL volumetric flasks. Each 5 mL flask was filled with carbon disulfide to the “5-mL” mark such that the bottom of the meniscus was level with the top of the fill mark. Two additional dilutions of 0.5 mL of the parent solution was prepared in 5-mL volumetric flasks from the cyclohexane and isooctane parent solutions. Furthermore, an additional 0.05 mL dilution was prepared from the ethyl methyl ketone and acetone parent solutions. UV-visible spectrophotometric analysis of each of the samples was ultimately carried out employing the same procedure that applied to the model solvents and model compound naphthalene.

Analysis of Heavy Oil Residua

Analyses employing the present methodology were conducted for five test samples, two of which were supplied by the co-sponsor (AB Nynäs Petroleum); designated B20/30F and T59-05, and three supplied by WRI designated SHRP asphalts; AAG-1, AAM-1 and ABG were prepared by weighing sample sets of 0.500 ± 0.001 g of petroleum residua into eighteen 25-mL sample vials. Each set of samples (18 time 5 in total) was subsequently dissolved in 5.0 mL of eighteen different solvents (Tables 1 and 2). These particular eighteen solvents were selected based on referenced work previously conducted by Nynäs (Redelius 2000): toluene, 2, 2, 4-trimethyl pentane, 2-ethyl-1-hexanol, methyl ethyl ketone, cyclohexane, cyclohexanol, cyclohexanone, n-heptane, carbon disulfide, acetonitrile, 1-butanol, 2-methyl-2-propanol alcohol, acetone, iso-propyl alcohol, ethyl acetate, methyl acetate, tri-decane, and decahydronaphthalene. In cases where samples were observed to comprise a partially dissolved solution, both centrifugation and filtration procedures were conducted, as previously discussed, whereas, with solutions that constituted completely dissolved, homogeneous solutions, only the filtration procedure was conducted. Finally, for solutions which remained clear, where virtually no dissolution of sample was observed, neither centrifugation or filtration procedures were conducted prior to standard dilution in carbon disulfide followed by acquisition of spectra.

Solvent	#	B20/30F	T59-05	AAG-1	ABG	AAM-1
toluene	1	0.622	0.389	0.307	0.421	0.463
iso-octane	2	0.164	0.164	0.166	0.103	0.384
2-ethyl,1-hexanol	3	0.091	0.05	0.208	0.034	0.046
methyl ethyl ketone-MEK	4	0.329	0.136	0.286	0.133	0.086
cyclohexane	5	0.509	0.385	0.331	0.385	0.441
cyclohexanol	6	0.015	-0.011	0.084	0.005	0.003
cyclohexanone	7	-0-	0.323	0.315	0.377	0.416
heptane	8	0.234	0.178	0.234	0.167	0.443
carbon disulfide	9	0.6	0.384	0.411	0.404	0.444
acetonitrile	10	0.005	-0.04	0.056	0.004	0.003
1 butanol	11	0.013	-0.04	-0.008	0.004	0.003
2 methyl-2 propanol	12	-0-	-0.04	-0.012	0.002	0.001
acetone	13	0.088	0.045	0.063	0.008	0.071
isopropyl alcohol	14	-0.001	-0.042	-0.011	0.043	0
ethyl-acetate	15	0.22	0.051	0.219	0.062	0.036
methyl-acetate	16	0.103	0.008	0.1	0.01	0.023
tri-decane	17	0.219	0.284	0.265	0.096	0.422
decalin	18	0.568	0.555	0.283	0.403	0.438

Table 1. Sample Solution Light Absorption at 400-nm in Eighteen Test Solvents Measured for Five Petroleum Residua Test Samples

Solvent	#	B20/30F	T59-05	AAG-1	ABG	AAM-1
toluene	1	104	101	75	104	104
iso-octane	2	27	43	40	25	86
2-ethyl,1-hexanol	3	15	13	51	8	10
methyl ethyl ketone	4	55	35	70	33	19
cyclohexane	5	85	100	81	95	99
cyclohexanol	6	3	-3	20	1	1
cyclohexanone	7	No data	84	77	93	94
heptane	8	39	46	57	41	100
carbon disulfide	9	100	100	100	100	100
acetonitrile	10	1	-10	14	1	1
1 butanol	11	2	-10	-2	1	1
2 methyl-2 propanol	12	No data	-10	-3	0	0
acetone	13	15	12	15	2	16
isopropyl alcohol	14	0	-11	-3	11	0
ethyl-acetate	15	37	13	53	15	8
methyl-acetate	16	17	2	24	2	5
tri-decane	17	37	74	64	24	95
decalin	18	95	145	69	100	99

Table 2. Sample Solution Light Absorption at 400-Nm in Test Solvent Divided by Sample Solution Light Absorption at 400-nm in CS₂, Multiplied by 100 for Five Petroleum Residua Test Samples

At the time of preparation of solutions for UV-Visible spectrophotometric analysis, each solution was visually inspected to ascertain whether the solution required centrifugation followed by filtration, filtration alone, or whether the solution could be diluted as is with neither centrifugation nor filtration. In cases where centrifugation was required, a 5.0-mL glass syringe was used to decant transfer approximately 4.0 mL of the solution to an 8.0-mL test tube. The test tube was covered with aluminum foil and centrifuged at 3200 rpm for 20 minutes (solutions requiring centrifugation were generally centrifuged in batches of 4 samples to save time). A 0.45- μ m syringe filter was then attached to a 5.0-mL glass syringe equipped with a stopcock positioned between the syringe and the syringe filter. Approximately 2.0 mL of the upper portion of the centrifuged sample (or sample not requiring centrifugation, but only filtration) was drawn up through the syringe-filter, the stopcock was shut and the filter removed. The filtered solution was then deposited in a small vial and capped.

To prepare standard dilution samples, a second 5.0-mL Teflon-plunger syringe was used to transfer exactly 0.3 mL of centrifuged and filtered or used-as-is solutions to 5-mL volumetric flasks. Each 5-mL flask was subsequently filled with carbon disulfide to the "5-mL" mark such that the bottom of the meniscus was level with the top of the fill mark. Sample spectra were finally collected by initially collecting a background spectrum of the reference solvent (carbon disulfide) that was used to dissolve the sample asphalt, followed by flushing of the cell with

acetone and drying of the cell with a vacuum hose. The sample was then analyzed by adding approximately 1 mL of the solvent solution, which was drawn into a 2.0 mL syringe and deposited into the 0.1 mm path length quartz cell through tubing attached to a cork septum. A spectrum was then acquired of the sample. The cell was again rinsed, first with the reference solvent (approximately 5-mL to clear the cell), then with acetone (approximately 5-mL to remove excess reference solvent). Vacuum was applied to one end of the tubing to dry the cell. The syringe was also rinsed with toluene or carbon disulfide to remove residual asphalt material, then rinsed with acetone and dried after each sample analysis.

Analysis of Heavy Oil Residua: Repeatability Study of Test Method

In one final set of studies, three addition samples, two supplied by the co-sponsor (AB Nynäs Petroleum); designated B20/30F and T59-05, and one supplied by WRI, designated SHRP asphalt AAG-1, and were prepared by weighing 0.500 ± 0.001 g of sample into 20 25-mL vials, then dissolving the samples in 5.0-mL of twelve different solvents (Tables 3 and 4), which comprised a subset of the original sweet of eighteen solvents. Again, in cases where samples were observed to comprise a partially dissolved solution, both centrifugation and filtration procedures were conducted, as previously discussed, whereas, with solutions that constituted completely dissolved, homogeneous solutions, only the filtration procedure was conducted. Finally, for solutions which were observed to remain clear, where virtually no dissolution of sample was observed, neither centrifugation nor filtration procedures were conducted prior to standard dilution in carbon disulfide followed by acquisition of spectra. The same standard dilution procedure used to prepare the original five samples (see previous section) was employed in the present set of samples.

Solvent #	Solvent	B20/30F	T59-05	AAG-1
1	toluene	101	102	102
2	iso-octane	27	42	67
3	2-ethyl-1-hexanol	19	16	100
4	MEK	58	39	94
6	cyclohexanol	3	1	52
7	cyclohexanone	99	98	101
8	n-heptane	40	59	83
9	carbon disulfide	100	100	100
11	1-butanol	3	2	6
15	ethyl-acetate	37	25	65
16	methyl-acetate	16	8	35
19	decalin	46	95	97

Table 3. Sample Solution Light Absorption at 400-nm in Test Solvent Divided by Sample Solution Light Absorption at 400-nm in CS₂, Multiplied by 100 for Three Test Asphalt (duplicate set)

Solvent #	Solvent	B20/30F	T59-05	AAG-1
1	toluene	104	101	75
2	iso-octane	27	43	40
3	2-ethyl-1-hexanol	15	13	51
4	MEK	55	35	70
6	cyclohexanol	3	-3	20
7	cyclohexanone	No Data	84	77
8	n-heptane	39	46	57
9	carbon disulfide	100	100	100
11	1-butanol	2	-10	-2
15	ethyl-acetate	37	13	53
16	methyl-acetate	17	2	24
19	decalin	95	145	69

Table 4. Sample Solution Light Absorption at 400-nm in Test Solvent Divided by Sample Solution Light Absorption at 400-nm in CS₂, Multiplied by 100 for Three Test Asphalt (original data set)

RESULTS AND DISCUSSION

Standardization of the experimental methodology initially consisted of determining the range of wavelengths in the ultra violet-visible-near infrared frequency band which would be applicable to detection of petroleum residua, specifically molecular species processing an aromatic and or dipole moment nature. Furthermore, interferences in wavelengths in the ultra violet-visible-near infrared frequency band affiliated with solvents used to dissolve the samples of interest would initially need to be identified. It is understood that various chemical species in residua have different optical absorbtivities. Figures 5 through 8 depict absorption versus wavelength plots (UV-VIS spectra) of toluene in 2,2,4-trimethyl pentane (solvent mixture) solution prepared at five molar concentrations, carbon disulfide in 2,2,4-trimethyl pentane (solvent mixture) solution prepared at five molar concentrations, naphthalene in carbon disulfide solution prepared at five molar concentrations , and naphthalene in toluene solution prepared in at five molar concentrations (mol/L = M). In all four of the present cases, absorption occurred below a wavelength of 350 nm. Additional sample-solvents were also tested and found to absorb light at or below the same wavelength. It was thus determined that if petroleum residua exhibited strong absorption above a wavelength of 350 nm, the present approach should be applicable for determining the amount of material dissolved in a given solvent.

Figure 5. Absorption versus Wavelength Plots (UV-VIS Spectra) of Toluene in 2,2,4-Trimethyl Pentane (Solvent Mixture) Solution Prepared at Five Molar Concentrations (mol/L = M)

Figure 6. Absorption versus Wavelength Plots (UV-VIS Spectra) of Carbon Disulfide in 2,2,4-Trimethyl Pentane (Solvent Mixture) Solution Prepared at Five Molar Concentrations (mol/L = M)

Figure 7. Absorption versus Wavelength Plot (UV-VIS Spectra) of Naphthalene in Carbon Disulfide Solution Prepared at Five Molar Concentrations (mol/L = M)

Figure 8. Absorption versus Wavelength Plots (UV-VIS Spectra) of Naphthalene in Toluene Solution Prepared at Five Molar Concentrations (mol/L = M)

Based on the results obtained for model systems, a model petroleum residuum was considered. Seven solutions containing SHRP asphalt AAD-1 originally prepared in seven different solvents were analyzed spectroscopically as standard dilution solutions prepared in carbon disulfide was conducted. Original solutions prepared in toluene, CS₂ and cyclohexane each appeared to have gone into solution and no appearance of sediment was ever observed after centrifuging, but it was often observed that the material remaining in the syringe filters used for filtering the toluene and CS₂ solutions were usually found to be a little darker than, for example, the material remaining in the syringe filter after filtering the cyclohexane solution. Original solutions prepared in MEK and iso-octane were observed to be the next darkest solutions in appearance. The MEK solution appeared a little darker than the iso-octane solution and both solutions clearly had significant amounts of undissolved material (much greater than 50% of original residuum initially weighed into the vial) present in the original vial. The acetone solution with notably colored, but transparent and not nearly as dark as the previous two samples. Finally, the iso-propanol solution was essentially clear; the entire sample was simply stuck in a lump at the bottom of the vial where it was initially weighted into the flask.

After conducting centrifugation and filtration of these seven samples, followed by standard dilution in carbon disulfide, spectrophotometric analysis was conducted. The wavelength Figure 9 depicts a plot of the absorption versus wavelength spectra of the seven samples, each representative of the 0.2 mL of sample in a 5-mL CS₂ solution. Absorption at 400 nm was ultimately selected as the wavelength of choice for comparative analysis and quantification of the degree of dissolution. This wavelength was selected because it represented a frequency band that was shifted up-field just off of the maximum absorption peak, but also shifted down-field just off of the shoulder that was present in each spectrum, which could be observed around 425 nm. This selection of wavelength would then insure that repeatable data could be obtained for different residua material, given that the molar absorptivity of materials did not differ significantly from that of the AAD-1 sample. Based on the results depicted in Figure 9, it appears that cyclohexane was the best solvent for completely dissolving AAD-1, simply based on visual inspection of the spectra, where it was noted as having the highest absorption at around 350-400nm, followed by the CS₂ solution then the toluene solution. Furthermore, sample solutions containing methyl ethyl ketone, iso-octane, and acetone as solvent all showed decreasingly lower absorption, and essentially no absorption for the alcohol solution, as compared to the first three solvents. The data were found to correlate closely with visual observation of each solution, suggesting that the method should work adequately for quantitatively measuring the degree of solubility of asphalts in a suite of solvents. For reference samples of Nynäs petroleum bitumen, designated T59-05, were photographed after standard dilution in carbon disulfide solutions were prepared. Figures 10, 11, and 12 depict photographs of this sample originally dissolved in three solvents; carbon disulfide, 2-ethyl-1-hexanol, and acetonitrile, respectively. The carbon disulfide soluble sample is opaque, the 2-ethyl-1-hexanol soluble solution is transparent and orange in color, and the acetonitrile soluble solution is clear, hence, the transparency of the solution correlated with the amount of absorption.

Figure 9. Absorption versus Wavelength Plot (UV-VIS spectra) of 0.20 mL Petroleum Residue; SHRP Asphalt AAD-1 Solutions Prepared in 5.0 mL (volumetric) of CS_2 , for Seven Different Dissolution Sample Solutions Originally Dissolved in Seven Different Solvents

Figure 10. Standard-dilution Carbon Disulfide Solution of Petroleum Residue; Nynäs T59-05 Originally Dissolved in Carbon Disulfide

**Figure 11. Standard-dilution Carbon Disulfide Solution of Petroleum Residuum;
Nynäs T59-05 Originally Dissolved in 2-ethyl-1-hexanol**

**Figure 12. Standard-dilution Carbon Disulfide Solution of Petroleum Residuum;
Nynäs T59-05 Originally Dissolved in Acetonitrile**

Analyses employing the present methodology were conducted for five test samples. Table 1 lists absorbance values measured at a wavelength of 400 nm for five asphalts dissolved in 18 different solvents, then re-diluted in carbon disulfide and analyzed using UV-Vis spectrophotometry. Table 2 lists values of percent absorbance of samples relative to absorbance in carbon disulfide, (i.e., $[A(\text{sample})/A(\text{sample diluted in CS}_2)] \times 100$, where solvent No. 9 (carbon disulfide) samples each represent exactly 100% relative to the remaining seventeen samples of a given set). To conveniently observe differences among samples derived from different crude sources, Figures 13-17 depict bar charts of solvent designation number (listed in Tables 1 and 2) plotted versus $[A(\text{sample})/A(\text{sample diluted in CS}_2)] \times 100$, for the five asphalts previously listed.

Figure 13. Bar Chart; Sample Solution Light Absorption at 400-nm in Test Solvent Divided by Sample Solution Light Absorption at 400-nm in CS₂, Multiplied by 100%, Plotted versus Solvent Designation Number for Petroleum Residuum; Nynäs B20/30F

Figure 14. Bar Chart; Sample Solution Light Absorption at 400-nm in Test Solvent Divided by Sample Solution Light Absorption at 400-nm in CS₂, Multiplied by 100%, Plotted versus Solvent Designation Number for Petroleum Residuum; Nynäs T59-05

Figure 15. Bar Chart; Sample Solution Light Absorption at 400-nm in Test Solvent Divided by Sample Solution Light Absorption at 400-nm in CS₂, Multiplied by 100%, Plotted versus Solvent Designation Number for Petroleum Residuum; SHRP Asphalt AAG-1

Figure 16. Bar Chart; Sample Solution Light Absorption at 400-nm in Test Solvent Divided by Sample Solution Light Absorption at 400-nm in CS₂, Multiplied by 100%, Plotted versus Solvent Designation Number for Petroleum Residuum; SHRP Asphalt ABG

Figure 17. Bar Chart; Sample Solution Light Absorption at 400-nm in Test Solvent Divided by Sample Solution Light Absorption at 400-nm in CS₂, Multiplied by 100%, Plotted versus Solvent Designation Number for Petroleum Residuum; SHRP Asphalt AAM-1

Initial inspection of the data listed in Table 1 suggests that samples prepared in solvents; toluene, cyclohexane, carbon disulfide (the designated standard solvent) and decalin (decahydronaphthalene) are all reasonably good solvents for heavy residua. It should be pointed out that absorption data obtained for s Nynäs bitumen T59-05 and SHRP asphalt AAG-1 may be in greater error than the remaining three samples. During the sampling of these two asphalts, care was not taken to lock down the shutter located on the cuvette holder, and subsequently may have been bumped during acquisition of spectra. With the remaining three sample residua care was then rigorously taken to ensure that the cuvette holder shutter was locked in place. Another observation that may be made is that hydrogen bonding solvents (alcohols) are all generally poor solvents for all of the materials tested. The remaining solvents appear to be intermediate in solvent quality for asphalts. Finally, SHRP asphalt AAM-1 appears to be the most non polar asphalt, based on good dissolution, particularly in aliphatic solvents, whereas, asphalt AAG-1 appears to be the most polar asphalt of the five asphalts tested, exhibiting better solubility in the polar solvents.

In one final set of studies, three addition samples, two supplied by the co-sponsor (AB Nynäs Petroleum); designated B20/30F and T59-05, and one supplied by WRI, designated SHRP asphalt AAG-1, and were prepared in twelve different solvents which comprised a subset of the original sweet of eighteen solvents. Table 3 and 4 lists values of absorption at 400 nm measured for duplicate samples; B20/30F, T59-05, and AAG-1, in twelve test solvents relative to absorption in carbon disulfide solutions. Comparison of results between data list in Table 3 to data listed in Table 4 shows that repeatability for sample B20/30F is extremely good, with the exception of the sample prepared in decalin, repeatability for sample T59-05 is fair, and repeatability for sample AAG-1 is poor (Figure 18). It is again pointed out that in the previous set of data (the original sample set of five materials) that absorption data obtained for samples T59-05 and AAG-1 may have been in greater error than remaining samples. It was speculated that during the sampling of these two asphalts, care was not taken to lock down the shutter located on the cuvette holder, and subsequently may have been bumped during scanning. Thus, data listed in Table 3, reported for samples T59-05 and AAG-1 should be used to replace data reported in Table 4. The results suggest that the method can be very repeatable if care is taken throughout the procedure.

CONCLUSIONS

In the present study a test procedure was developed to measure the percent of soluble petroleum residua as a function of their solubility in a suite of organic solvents. Testing protocol entailed initially dissolving samples of heavy oil residua in several different solvents, allowing contact between the residuum and solvent for a given period of time, and then preparing standard dilution solutions to measure absorption at 400 nm relative to the absorption of the sample in carbon disulfide. Preliminary results suggest that the present method may be used to accurately

and reproducibly quantify heavy oil solubility properties. A logical next-step on the research effort should be to research and evaluate potential modern “combinatorial” type laboratory instrumentation to perform the same solubility tests with small amounts of residua, in very short times.

Figure 18. Data Reproducibility Plot for Three Petroleum Residua, Percent Soluble Material (PSM), Measured in Terms of Sample Absorption at 400 nm (A) in Test Solvent per Absorption in Carbon Disulfide, Multiplied by 100%, of Original Data versus PSM of Repeat Data Set

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