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Investigation of Physical Chemistry Properties of Asphaltenes Using Solubility Parameters of Asphaltenes and Their Fractions A1 and A2

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The Sphere method developed by Hansen (Hansen, C. M. *Hansen Solubility Parameters: A User's Handbook*; CRC Press: Boca Raton, FL, 1999) to calculate components of solubility parameters (SP), δ_D, δ_P, and δ_H, where D, P, and H stand for dispersion, polar, and hydrogen bonding respectively, have been applied to resins, to asphaltenes, and fractions A1 and A2. Mean values for these compounds in $MPa^{0.5}$ were asphaltenes (19.5 ± 0.1, 4.7 ± 0.2, 4.2 ± 0.1); A2 (19.6 ± 0.1, 5.8 ± 0.1, 4.4 ± 0.2); A1 (20.9 ± 0.2, 5.6 ± 0.3, 6.8 ± 0.2); resins (18.6 ± 0.2, 3.6 ± 0.3, 3.2 ± 0.3). Also, the SP components of the asphaltene sample (AsH-NS), denuded from acidic natural surfactant (NS), were determined affording values equal to A2. These values were obtained after using 57 solvents, and the method is consistent with all known solubility properties of asphaltenes and confirm the expected solubility behavior of A1 and A2, with A1 being the less soluble material in all solvent examined. Excellent affinity between asphaltene with resins was predicted as well as affinity between samples examined. These results are coherent with a colloidal model whereby fraction A1 is in not contact with the solvent, being within a core shielded from the media by a periphery composed by fraction A2 and NS. Flocculation results measured in n-C_7−1-methylnaphthalene mixtures correlate with the above SP showing the following order of flocculation tendency: A1 ≫ A2 > asphaltenes (AsH). We also observed that flocculation points of A2 and AsH-NS were very close, and this strongly supports the colloidal model above. SP were helpful in analyzing other properties such as adsorption, vaporization, affinity, and molecular mass and paraffin's properties.

Introduction

The solubility parameter (SP), generally represented by δ, is a kind of cohesion parameter which describes the interaction between molecules in a condensed phase. The main objective of the application to petroleum materials is to predict mutual solubility or affinity between heavy fraction components and their media.[2−30] As such they have been applied to the study of bitumen, petroleum fractions, and asphaltenes. Xingyi et al. using the activity coefficient equation from Scathard−Hildebrand's regular solution theory and applied SP to several fractions of Athabasca vacuum topped bitumen (VTB). It was found that the solubility parameter of the VTB fraction was not constant, varying from 14 to 16 $MPa^{0.5}$.[2] Johansson et al. claims that intrinsic viscosity and aggregate size both sensitively reflected the state of the asphaltenes in homogeneous solution and used these parameters for determining the SP of the asphaltenes.[5] They found solubility parameters of

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asphaltenes in the range 20.8–22.7 MPa$^{0.5}$ at temperatures in the 293–298 intervals.

Fogler's group used the Hildebrand SP in thermodynamic solubility models to predict asphaltene instability in live crude oils.[9] Gharfeh et al. used a large set of field data related to various facets of asphaltene instability problems at production facilities and proposed a model where SP play a central role.[10]

Correra and Merino-Garcia[11] reported that development of a thermodynamic model to predict the onset of asphaltene precipitation is usually hindered by the complexity of the mixture under consideration. In an attempt to simplify asphaltene modeling, a model related to the Flory–Huggins theory was proposed. The model is based on the fact that asphaltene stability depends upon the quality of the surrounding medium, expressed in terms of the solubility parameter. Other models and methods employing solubility parameters have also been reported.[12–16,23,29] Wiehe et al. analyzed the effect of *n*-paraffin's size on the FP of crude oils and bitumen and concluded that the maximum in volume of *n*-paraffin, as a function of the carbon number of the paraffin at FP (see Symbols Used), is general for crude oil and bitumen.[17] They did so by combining the entropy of mixing of molecules of very different size with the heat of mixing; these heats were calculated with effective blending SP.[17] Zhang et al. reported a combine microcalometry of solution and a DSC method to determine both the enthalpy of solution ΔH_{solu} and mixing ΔH_{mix} of asphaltenes in solvents like quinoline, 1MN (see Symbols Used) and tetraline. According to these authors, the exothermic nature of ΔH_{mix} suggests that asphaltenes are solvophilic for these solvents. These ΔH_{mix} were in the −15.9 to −6.4 J/g range according to the sample.[18] However, they found difficulties to account for asphaltene aggregation and the above negative results. The authors appear to be unaware of the asphaltene composition in terms of A1 and A2 (see the Discussion).

Using a Sphere method, similar to the one used in this article, Redelius reported the following Hansen solubility parameters (MPa$^{0.5}$) for asphaltenes obtained from Venezuelan bitumen: δ_D, δ_P, δ_H = 19.6, 3.4, 4.4; to obtain these values, the author used a set of 48 solvents.[19] Fossen et al. correlated IR and NIR with Hildebrand and Hansen solubility parameters and used them to predict solubility parameters for solvents, crude oils, and SARA fractions.[20] The values of SP prevailing in the medium at the onset of precipitation were estimated by the González group for asphaltenes dissolved in different solvents or for solvent mixtures presenting solubility parameters in the range 18.2–16.5 MPa$^{0.5}$.[22]

Results were reported by Mutelet and co-workers[24] where flocculation threshold experiments and inverse gas chromatography were used to validate the use of the SP approach to asphaltene flocculation phenomena. It was found that values of solubility parameters obtained with both methods are in good agreement. According to these authors, their results confirm the validity of the three-dimensional solubility parameter method proposed by Hansen to deal with petroleum fluids.

Wong and Yen in an electron paramagnetic resonance (EPR) study of the asphaltene macrostructure using vanadyl porphyrines as a probe, noted that a greater amount of mobile vanadyl complexes can be stabilized in a dispersing medium (single-aromatic ring solvent series) with a higher-valued Hansen hydrogen bonding solubility parameter.[26]

To evaluate the interaction forces between asphaltenes and amphiphilic compounds influencing the colloid stability of crude oils during the production, transport, and processing, the cohesion energy parameters according to Hansen were used by Laux et al.[27] They found by calculation of cohesion energy parameters of different homologous series that a stabilizing effect can be expected if the dispersion interactions of amphiphilic compounds correspond with that of asphaltenes and the hydrogen bonds are in the region of 10 MPa$^{0.5}$. The flocculation point determination and thermogravimetric analysis were used to verify this experimentally.

Rogel[30] employed a theoretical procedure which uses a program developed for SP calculations and reported values for Orinoco's asphaltenes in the 21–23 MPa$^{0.5}$ range. Acevedo and co-workers used the *p*-nitrophenol (PNP) method to fractionate asphaltenes in fractions A1 and A2.[31–33] Here A2 has the usual toluene solubility of asphaltenes (between 57 and 100 g L^{-1} depending on the sample; room temperature) whereas solubility of A1 under the same conditions is merely 0.05 g L^{-1}. This unexpected large difference in solubility was not related to differences in ^{13}C NMR aromaticity, heteroatom content,[31,32] or molecular mass.[33] The hypothesis of the authors is that fraction A1 mainly contains molecules with rigid cores with the facility to pack and hence of low solubility, whereas in fraction A2 there are flexible molecules where packing is hindered by internal rotational conformers.

The above review shows how along the years, the solubility parameters have demonstrated their versatility to deal with solubility and other properties of petroleum and fossil solids and liquids, both from the experimental and theoretical points of view. This could be considered a more stringent test for such parameters and provided good grounds for application to related issues such as affinity between asphaltene fractions and of course affinity for solvents and other compounds with reported SP. Once they are determined using reliable methods such as HSP,[1] these SP could be used as another thermodynamic property to predict solubility and thermodynamic interactions with liquids and solids of known SP.

In this article, using the SPHERE method developed by Hansen,[1] we obtain the three components of solubility parameter for asphaltenes and their fractions A1 and A2 as well as the one for resins and AsH-NS. As shown below, the results obtained are consistent with known ideas such as aggregation and dispersion of asphaltenes, asphaltenes colloidal behavior and structure, solubility properties, flocculation, adsorption, vaporization, and molecular weight. As discussed below, being the more cohesive fraction of asphaltenes, A1 should be considered as the main responsible for colloidal behavior and flocculation. Both solubility and important flocculation issues are discussed below in terms of SP and a colloidal model consistent with results presented herein.

Experimental Section

Materials. Hamaca asphaltenes (AsH) were obtained from extra-heavy Hamaca oil (8° API) containing about 14% of asphaltenes, as described earlier.[34] Coprecipitated resins were thoroughly removed with boiling *n*-heptane (*n*-C$_7$) using a Soxhlet apparatus until the emerging *n*-C$_7$ became clear (2–3 days).

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Resins were recovered after evaporation of n-C_7 for further study. Elemental analysis resins: C, 82.8, H, 9.89; N, 0.93; S, 3.73; O, 1.83; H/C, 1.43. Fractionation of asphaltenes with p-nitrophenol (PNP) to obtain fractions A1, A2, and trapped compounds (TC) was carried out using the procedure described elsewhere.[35] Briefly, a cumene (*iso*-propilbenzene) solution of asphaltenes (8 g L^{-1}) saturated with PNP was mechanically stirred and set off for 72 h followed by filtration on a microporous membrane (0.25 μm). The precipitated solid (A1-PNP) was washed with cumene, dissolved in chloroform, and extracted with aqueous sodium hydroxide solution (5%) to remove the PNP. The filtrate (A1-PNP) was diluted with 3 volumes of n-C_7, and the precipitated solid (A2 + PNP) was filtered and treated for removal of PNP as described for A1. The TC fraction was obtained from the filtrate after evaporation of the cumene + n-C_7 solvents, dissolution in chloroform, and extraction of PNP as described above. The yields were 53% for A1, 35% for A2, and 8% for TC; total recovery ~96%.

Acidic natural surfactants (NS) were extracted from asphaltenes by washing a chloroform solution (20%) with several portions of aqueous sodium hydroxide solution (5%). The aqueous layers were collected and set apart for further treatment (see below). The chloroform layer was washed with water, then with hydrochloric acid (0.01 M) for neutralization, and then with water. After working up, the asphaltenes denuded from the above NS (AsH-NS) was obtained. NS were obtained from the alkaline aqueous layer after neutralization and extraction back in chloroform; after working up, about < 0.7% of NS was recovered.

Solubility test were performed in 57 organic solvents selected for availability, good and bad solvency for asphaltenes, hydrocarbon nature (aliphatic, alicyclic, aromatics), heteroatom content (O, S, and N) and halogen containing organic solvents. Solubility test were carried out in well stoppered flasks using 2 mL of solvent and enough mass of solute to afford 5% or more solute concentration for Good solvents (see below for a definition of Good and Bad solvents). Ultrasound and heating was applied in some cases, in particular with the A1 fraction. All SP reported here correspond to room temperature or 25 °C at atmospheric pressure.

Methods. Elemental analysis (CHNS-O) were performed in a Thermo Scientific model Flash 2000.

SPHERE Program. Details of this program are described in the literature,[1,19] and the more relevant are summarized below.

Basically, solubility trials of sample are performed in as many solvents as possible (57 in this work). The dispersion (δ_D), polar (δ_P), and hydrogen bonding (δ_H) SP components of these solvents are input data; these were collected from Hansen tables.[1] Solvents are categorized by number S, which could be 1 or 0. When $S = 1$, the solvent dissolves the sample and is called "Good", otherwise it is called "Bad" when it fails to dissolve the sample. A Good solvent should dissolve about 5% or more sample. Solvents enter the program with number $S = 1$ for soluble and $S = 0$ for insoluble. The object of the program is to find the radius of the sphere containing the maximum number of Good solvent and the minimum of Bad solvents and outliers (see below). The center of such a sphere would correspond to the HSP of sample under study.

For the same set of data (SP of solvents and their S value), the program could give different results according to the quality and number of solvents used. As the number of both Good and Bad solvents increases, the variance in each of components (δ_D,δ_P,δ_H) would decrease. When the number of Good and Bad solvents is large enough (say 40 or more) and a sufficient number of solvents with RED values (see below for RED definition) very close to one are included, the variance would be minimum and the fitting FIT would approach 1. Such an

endeavor has a component of trial and error. For example, occasionally removal of outliers is required to improve the fitting. In the A1 case, we removed the Good solvent THF (wrong out, see Symbols Used) and the Bad solvent methylene chloride (wrong in) to improve the fitting.

Besides SP, the program output afforded R_0 or the radius of the sphere, the parameter RED the fitting FIT, and the solvents "Wrong in" and "Wrong out"; parameters R_a and RED are defined by eqs 1 and 2.

$$R_a = \sqrt{4(\delta_{D2} - \delta_{D1})^2 + (\delta_{P2} - \delta_{P1})^2 + (\delta_{H2} - \delta_{H1})^2} \quad (1)$$

$$RED = \frac{R_a}{R_0} \quad (2)$$

In these equations, R_a is the distance from the sphere center to points corresponding to each solvent. Note that for $R_a = R_0$, RED = 1; thus, in principle for a Good solvent RED < 1 and for Bad solvents RED > 1; solvents with RED ≈ 1 are very important for finding the correct R_0. Accordingly, RED values are related to solubility: when this parameter approaches 0 the solvent will be increasingly good and vice versa when it approaches or surpass 1. Outliers are solvents that being Bad are inside the sphere (wrong in) or outside the sphere being Good (wrong out); when the number of such outlier decreases to zero, the fitting FIT increases to 1.

For comparison purposes with literature values total solubility parameter were calculated using eq 3.

$$\sqrt{\delta_D^2 + \frac{\delta_P^2 + \delta_H^2}{4}} \quad (3)$$

In this equation, division by four of the polar and hydrogen bonding component normalizes the HSP allowing comparison with others in the literature (see ref 1, Chapter 2, p 30, eq 2.12).

The basic equation for SP definition is given in eq 4:

$$\delta = \sqrt{\frac{-\Delta E}{V}} = \sqrt{\frac{\Delta H_V - RT}{V}} \quad (4)$$

After SP were optimized for each material, RED values for asphaltene pairs (A1 solute in asphaltene; A1 solute in A2; A2 solute in asphaltene) and corresponding resin−asphaltene pairs were calculated with SPHERE instructing the program to proceed with the same optimized SP for the solute. In this way, RED values were obtained for all relevant "solute−solvent" pairs.

Flocculation. Preliminary flocculation tests were carried out using the method reported earlier;[36] briefly the apparatus is equipped with a solvent's mixture pump (a flux meter, a thermostatic mixing cell, a refluxing condenser, a recirculating pump connecting the mixing cell with the measurement chamber). The measurement chamber is provided with a laser source (632 nm) and a pinhole detector both connected to a data station or computer. In this way the experiment was continuously monitored affording curves with acute maxima; n-heptane volume at the maxima was taken as the flocculation point (FP). Samples were dissolved in 10 mL of 1-methylnaphthalene (1MN) or toluene to afford 2 g L^{-1} solutions and flocculated with n-C_7 by adding 0.7 mL/min. FP were detected at the peak of the corresponding flocculation curve. SP of solvent mixtures at FP (δ_f) and corresponding components were obtained by means of eqs 5, 5-1−5-3:

$$\delta_f = \phi_1\delta_{D1} + (1 - \phi_1)\left(\delta_{D2} + \frac{\delta_{P2} + \delta_{H2}}{4}\right) \quad (5)$$

$$\delta_{fD} = \phi_1\delta_{D1} + (1 - \phi_1)\delta_{D2} \quad (5\text{-}1)$$

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Table 1. Total (δ_T), δ Components, and *S* Values of Solvents Used to Calculate RED *a* and SP of Hamaca Asphaltenes

no.	solvent	δ			S	RED*a*	δ_T*b*
		D	P	H			
1	quinoline	19.8	5.6	5.7	1	0.19	20.2
2	ODB*c*	19.2	6.3	3.3	1	0.19	19.5
3	1BN*d*	20.3	3.1	4.1	1	0.32	20.5
4	CH2Cl2*e*	18.2	6.3	6.1	1	0.46	18.7
5	EBZ*f*	17.9	6.2	6	1	0.52	18.4
6	CHA*g*	17.8	6.3	5.1	1	0.52	18.3
7	CHCl3*h*	17.8	3.1	5.7	1	0.53	18.1
8	NB*i*	20	8.6	4.1	1	0.57	20.6
9	2MECHA*j*	17.6	6.3	4.7	1	0.57	18.0
10	1MN*k*	20.6	0.8	4.7	1	0.6	20.7
11	DCB*l*	18.3	7.7	2.8	1	0.6	18.8
12	pyridine	19	8.8	5.9	1	0.61	19.7
13	DBE*m*	18.5	8.4	8.8	1	0.68	18.7
14	PNT*n*	20.1	9.6	3.9	1	0.71	20.8
15	toluene	18	1.4	2	1	0.72	18.0
16	xylene	17.6	1	3.1	1	0.76	17.7
17	cumene	18.1	1.2	1.2	1	0.78	18.1
18	benzene	18.4	0	2	1	0.8	18.4
19	THF*o*	16.8	5.7	8	1	0.87	17.5
20	CS2*p*	20.5	0	0.6	1	0.9	20.5
21	DCE*q*	16.5	7.8	3	1	0.96	17.0
22	TBE*r*	22.6	5.1	8.2	1	0.97	23.1
23	CTC*s*	17.8	0	0.6	1	0.97	17.8
24	BRB*t*	16.3	7.7	4.4	1	0.98*ss*	16.9
25	TCAA*u*	18.3	5.8	11.4	1	0.98*ss*	19.4
26	1CB*v*	16.2	5.5	2	1	0.99*ss*	16.5
27	DEC*w*	18	0	0	0	1.00*ss*	18.0
28	OA*x*	16	2.8	6.2	0	1.01*ss*	16.4
29	NBA*y*	15.8	3.7	6.3	0	1.04*ss*	16.2
30	EA*z*	15.8	5.3	7.2	0	1.07*ss*	16.4
31	MEK*aa*	16	9	5.1	0	1.13	16.8
32	Cy5*bb*	16.4	0	1.8	0	1.14	16.4
33	Cy6*cc*	16.8	0	0.2	0	1.16	16.8
34	NMP*dd*	18	12.3	7.2	0	1.18	19.4
35	NTD*ee*	16.2	0	0	0	1.29	16.2
36	CyOL*ff*	17.4	4.1	13.5	0	1.33	18.8
37	C7Ol*gg*	16	5.3	11.7	0	1.35	17.2
38	decane	15.7	0	0	0	1.39	15.7
39	acetone	15.5	10.4	7	0	1.39	16.7
40	EOE*hh*	14.5	2.9	5.1	0	1.39	14.8
41	1-hexeno	14.7	1.1	3	0	1.42	14.8
42	octane	15.5	0	0	0	1.43	15.5
43	phenol	18	5.9	14.9	0	1.46	19.7
44	heptane	15.3	0	0	0	1.47	15.3
45	AA*ii*	16	11.7	10.2	0	1.55	17.8
46	hexane	14.9	0	0	0	1.56	14.9
47	pentane	14.5	0	0	0	1.65	14.5
48	PA*jj*	14.7	5.3	12.4	0	1.68	16.2
49	DMSO*kk*	18.4	16.4	10.2	0	1.8	20.8
50	AcA*ll*	14.5	8	13.5	0	1.88	16.5
51	1POL*mm*	16	6.8	17.4	0	2	18.5
52	ACN*nn*	15.3	18	6.1	0	2.17	18.0
53	ethanol	15.8	8.8	19.4	0	2.32	19.1
54	MeA*oo*	13	7.3	17.3	0	2.52	16.0
55	PNP*pp*	20.4	20.9	15.1	0	2.65	24.1
56	methanol	15.1	12.3	22.3	0	2.88	19.8
57	glycerol	17.4	12.1	29.3	0	3.56	23.5
	A1	20.8	5.7	6.9		0.48	21.3
	A2	19.7	5.8	4.4		0.18	20.0
	HR*qq*	18.6	3.6	3.2		0.36	18.8
	FMC7-1MN*rr*	16.7	0.2	1.22		1.09	16.7

a Calculated using SPHERE; average of seven determinations and arranged in decreasing solubility order. *b* In MPa$^{0.5}$; calculated using eq 3. *c* o-Dichloro benzene. *d* 1-Bromo naphthalene. *e* Dichloro methane. *f* Ethyl benzoate. *g* Cyclohexanone. *h* Chloroform. *i* Nitrobenzene. *j* 2-Methylcyclo hexanone. *k* 1-Methyl naphthalene. *l* 1,4-Dibromobutane. *m* 1,1-Dibromoethane. *n* p-nitro toluene. *o* Tetrahydrofurane. *p* Carbon disulfide. *q* 1,2 Dichloro ethane. *r* 1,1,2,2-Tetrabromo ethane. *s* Carbon tetrachloride. *t* 2-Bromo butane. *u* Trichloro acetic acid. *v* 1-Chloro-butane. *w* Decaline. *x* Oleic acid. *y* n-Butyl acetate. *z* Ethyl acetate. *aa* Methyl

ethyl ketone. *bb* Cyclopentane. *cc* Cyclohexane. *dd* N-methyl-2-pyroolidi-none. *ee* n-tetradecane. *ff* Cyclohexanol. *gg* 1-Heptanol. *hh* Diethylether. *ii* Acetic anhydride. *jj* Propionic acid. *kk* Dimethyl sulfoxide. *ll* Acetic acid. *mm* 1-Propanol. *nn* Acetonitrile. *oo* Methyl amine. *pp* p-Nitrophenol. *qq* Hamaca resins. *rr* Flocculation mixture composed of n-C$_7$ and 1-methyl naphthalene. *ss* Border line solvents.

$$\delta_\text{fP} = \frac{(1 - \phi_1)\delta_\text{P2}}{4} \quad (5\text{-}2)$$

$$\delta_\text{fH} = \frac{(1 - \phi_1)\delta_\text{H2}}{4} \quad (5\text{-}3)$$

In these equations, all SP are in MPa$^{0.5}$, ϕ_1 is the n-C$_7$ volume fraction at FP, δ_D1 is the SP dispersion component of n-C$_7$ (15.3, the other two are equal to zero), and $\delta_\text{D2}, \delta_\text{P2}$, and δ_H2 are the corresponding component of either toluene or 1MN. Once the FP is determined, ϕ_1 is determined which allows calculation of δ_f and the corresponding D, P, and H components of the mixture at FP (eqs 5 and 5-1–5-3). According to description above, the solvent mixture at FP should give a RED value close to 1.

Estimation of SP for AsH. SP of AsH was estimated using their A1, A2 and TC composition employing an approach similar to the one described in the above section; in this case and for the components, the same set of equations were employed but considering three instead of two mixture components: that is:

$$\delta_\text{D}^\text{AsH} = \phi_1\delta_\text{D1} + \phi_2\delta_\text{D2} + \phi_3\delta_\text{D3} \quad (6\text{-}1)$$

$$\delta_\text{P}^\text{AsH} = \phi_1\delta_\text{P1} + \phi_2\delta_\text{P2} + \phi_3\delta_\text{P3} \quad (6\text{-}2)$$

$$\delta_\text{H}^\text{AsH} = \phi_1\delta_\text{H1} + \phi_2\delta_\text{H2} + \phi_3\delta_\text{H3} \quad (6\text{-}3)$$

We use the A1, A2, and TC composition described in the Experimental Section, and for of volume fraction ϕ calculation, we use asphaltenes density = 1.17 g cm^{-3}.[39a] For resins, a value of 1 g cm^{-3} [39b] was used. The total SP for AsH was obtained from the above components using eq 3.

Enthalpy of Vaporization. With the use of the basic definition of δ, given in eq 4, the enthalpy of vaporization at STP for any sample ($\Delta H_\text{V}°$) could be obtained provided both δ and the molar volume V are known. The procedure is helpful to obtain unknown $\Delta H_\text{V}°$.

Relative Response Factor Parameter f_R. Response factor f_R to volatilization energy from a source and relative to resins was estimated for A1 using eq 7:

$$f_\text{R} = \frac{(\Delta H_\text{v}°)_\text{R}}{(\Delta H_\text{v}°)_\text{A}} \quad (7)$$

After substitution of enthalpies using eq 4 and using molecular mass instead of volumes, we obtained eq 8:

$$f_\text{R} = \frac{\rho_1(\delta_3{}^2 M_3 + RT\rho_3)}{\rho_3(\delta_1{}^2 M_1 + RT\rho_1)} \quad (8)$$

Here M_1, M_3 and ρ_1, ρ_3 are the molecular mass and densities of asphaltene samples and resins, respectively. Equation 8 evaluates the vaporization of sample compared to the resins; note that this equation has no units.

Results

Solubility Parameters. The list of solvents and corresponding SP for one asphaltene calculation is shown in Table 1; SP for all samples studied here are presented in Table 2. Values of SP components D, P, and H are solvent properties, as well as δ_T calculated using eq3 (see Table 1). *S* is a solvent−solute property, RED values are solvent−solute properties, and R_0 is solute property (see Table 2). Asphaltenes were soluble in

<p align="center">**Table 2. Solubility Parameters[a] for Asphaltenes, Fractions A1 and A2, and Resins**</p>

samples	SP[b]			$\delta_T{}^c$	$R_0{}^d$	FIT	G/B[g]
	D	P	H				
AsH	19.5 ± 0.1	4.7 ± 0.2	4.9 ± 0.1	19.8 ± 0.15	7.3 ± 0.1	1.000	28/29
As-NS[e]	19.6 ± 0.1	5.8 ± 0.1	4.4 ± 0.1	20 ± 0.2	7.9 ± 0.1	1.000	29/28
A2	19.6 ± 0.1	5.8 ± 0.1	4.4 ± 0.2	20 ± 0.2	7.9 ± 0.1	1.000	29/28
A1[f]	20.9 ± 0.2	5.6 ± 0.3	6.8 ± 0.2	21.3 ± 0.3	7.8 ± 0.6	0.98	16/40
resins	18.6 ± 0.2	3.6 ± 0.3	3.2 ± 0.3	18.7 ± 0.5	9.7	1.000	42/15
AsH[h]	20 ± 1	5.4 ± 0.5	5.5 ± 0.5	$20 \pm 1{}^i$			

[a] In MPa[0.5]; using the SPHERE program with a total of 57 solvents. [b] Average of 12 calculations. [c] Calculated using eq 3. [d] Sphere radii. [e] Note that SP of this sample are equal to the one determined for A2. [f] Outliers, 2; THF was not included in this calculation. [g] Good and Bad solvents. [h] Estimated from asphaltenes composition (see Methods, eqs 6-1−6-3 and text). [i] Calculated using eq 3.

solvents classified as $S = 1$ and insoluble in solvents where $S = 0$. In Table 1, values were arranged in increasing RED order, equivalent to decreasing solubility; thus quinoline was the best and glycerol the worst. Errors in RED values were very small ($\leq \pm 0.03$) for all samples and the fitting (FIT) was equal to 1; somewhat larger errors were found for sample A1 where FIT = 0.98. As can be seen in Table 1, RED values are consistent with all known solubility properties of asphaltenes. To begin with the method is consistent with solubility in aromatic hydrocarbon solvents such as benzene, toluene, ethyl benzene, cumene, and 1-methyl naphthalene (1MN); also high solubility (low RED values) are correctly found for *o*-dichlorobenzene (ODB) and nitrobenzene as well as quinoline and pyridine. Solubility in aliphatic organic chlorides is also consistent with RED < 1. The method also gives RED > 1 for both aliphatic and alicyclic solvents such as hexane, pentane, octane, cyclopentane, decaline, etc. A known Bad solvent nature of alcohols such as ethanol, methanol, 1-propanol, 1-heptanol, and glycerol is also coherent with RED ≫ 1. As was the case for asphaltenes, solubility properties of resins such as solubility in alkanes, cycloalkanes, aromatics, etc. were consistent with RED values. Some RED values for selected solvents are shown in Table 3; the complete list is shown in Table 1. The most interesting solubility property of resins, being affinity for asphaltenes, is correctly predicted by the method affording a low RED (0.37) close to the one found for nitrobenzene (see Table 3), a known very Good solvent for asphaltenes. Once the method proved excellent agreement for both asphaltenes and resins, it was applied to the A1, A2, and AsH-NS samples. Results for A2 and AsH-NS were almost identical, and explicit results for AsH-NS were omitted except in relevant cases. The list of solvents for A1 and A2 was the same as for AsH and are not shown in this paper. An example of the Sphere calculation is shown in Figure 1.

The comparison of RED values for AsH, A1, and A2 is shown in Figure 2 for 20 selected solvents. For asphaltenes, RED values were arranged in increasing order. The main features of this figure are that for all solvents, A1 has the highest RED and hence the lower solubility; AsH and A2 afforded close RED values for all solvents; these findings are coherent with corresponding SP (see Table 2 below). Figure 2 cover the RED range in full from lowest and best solvent (0.19, quinoline) to the highest and worst (3.59, glycerol). CS_2 was a Good solvent for all samples; however, when the "normal" set of SP of CS_2 was used (where $\delta_P = 0$; see Table 1) only asphaltenes and A2 afforded RED < 1. Thus, all samples were calculated with the alternative set (D, 19.9; P, 5.8; H, 0.6), where $\delta_P \neq 0$, (also found in Hansen tables[1]) to obtain the correct result for all samples (RED < 1).

Mean values of SP and Ro for samples studied here, as well as FIT and number of Good and Bad solvents are shown in

Table 2; some mean values of RED for solvents are shown in Table 3 where AsH, A1, A2, and resins are compared. In all calculations, at least four solvents have RED values very close to 1 and this is important for setting R_0 (see Methods). In this particular case (Table 1), there were eight such solvents both for AsH and A1 and four for A2. These solvents are very helpful in finding the correct sphere radius R_0 and therefore their center which corresponds to SP of the sample (see Methods). For resins, these borderline solvents are shown at the bottom of Table 3. It is interesting that pentane is within this list; this is coherent with the quantity of material precipitated from crude oil which is higher with pentane when compared to other larger *n*-paraffin ($n > 5$).[37]

For AsH, resins, A2, and AsH-NS samples, fitting were equal to 1. In all cases, errors in SP and R_0 were very small, given credit to the method used. As mentioned in the Methods section, these errors come from the nature of the program calculation and are not experimental. A total of 57 solvents were employed for getting sample's SP. Solvents methylene chloride (wrong in) and THF (wrong out) were excluded in A1 calculations to improve the fitting; PNP was included for reason to be discussed below. Note that SP of A2 and sample AsH-NS are identical (see Table 2). This equality is very interesting and will be discussed below.

Solubility in NMP (see Symbols Used; solvent part) was the only solubility difference we found between the asphaltene, A2, and AsH-NS samples; A2, AsH-NS, and resins were found soluble in this solvent, and this led to the small difference in SP found between asphaltenes, A2, and AsH-NS (see Table 2). Prediction of the solubility of asphaltenes and the other samples by SP values is possible because they are thermodynamic properties of these mixtures. As such, they can be compared with others, subtracted or added conveniently, and used to predict unknown interactions.

Figure 3 is a plot of δ_T for solvent used as a function of RED to show that in general these parameters do not correlate; this is expected because in general, contrary to RED, δ_T of the solvent is not related to any solute property. This is underlined in Figure 3 by the parabolic fitting, showing that both good and bad solvents could have the same δ_T. In Figure 4, a similar δ_T−RED plot was carried out using hydrocarbon solvents only. The shown line is a linear fitting to *n*-paraffins, affording good linear correlation; other hydrocarbons were included in the plot (see Figure 4). Good fitting to paraffins, in the range shown in Figure 3, is expected because in this case δ_D of the solvent is the only contributor to δ_T. However, fair correlations could be found either with a family of compounds, such as *n*-alcohols or with

(37) Corbet, L. W.; Petrossi, U. *Ind. Eng. Chem., Prod. Res. Dev.* **1978,** *14,* 342.

Table 3. Comparison of RED[a] (Affinities) for Several Materials

materials[b]	solvents[c]	RED
AsH		0.19
A1		0.33
A2	quinoline	0.16
RH		0.42
AsH		0.19
A1		0.7
A2	ODB	0.17
RH		0.314
AsH		0.36
A1		0.64
A2	nitrobenzene	0.37
RH		0.59
AsH		0.456
A1		0.71
A2	pyridine	0.46
RH		0.615
AsH		0.522
A1		0.865
A2	cyclohexanone	0.48
RH		0.37
AsH		0.60
A1		0.84
A2	1MN	0.69
RH		0.51
AsH		0.72
A1		1.27
A2	toluene	0.76
RH		0.3
AsH		0.81
A1		1.34
A2	cumene	0.81
RH		0.35
AsH		0.87
A1		rejected[d]
A2	THF	1.01
RH		0.64
AsH		0.98
A1		1.74
A2	CTC	0.99
RH		0.5
AsH		1.12
A1		1.56
A2	MEK	1.01
RH		0.8
AsH		1.02
A1		1.56
A2	oleic acid	1.03
RH		0.63
AsH		1.17
A1		1.71
A2	cyclohexane	1.16
RH		0.63
AsH		1.47
A1		2.11
A2	heptane	1.44
RH		0.86
AsH		1.01
A1		1.53
A2	decaline	1.01
RH		0.53
AsH		1.15
A1		1.23
A2	NMP	0.995
RH		0.97
AsH		0.98
A1		1.01
A2	TCAA	0.96
RH		0.82
AsH		1.37
A1		1.68
A2	acetone	1.24
RH		1.02
AsH		1.56
A1		1.783
A2	DMSO	1.56
RH		1.45

Table 3. Continued

materials[b]	solvents[c]	RED
AsH		2.33
A1		2.39
A2	ethanol	2.18
RH		1.77
AsH		2.65
A1		2.36
A2	PNP	2.51
RH		3.02
AsH		0.37
A2		0.41
A1	resins	0.9
A1	As[e]	0.6
A1	As[e]	0.6
A1	A2[e]	0.5
A2	As[e]	0.2
AsH		1.15
A2		1.14
A1	paraffine 40 C[g]	1.7
HR[f]		0.6
RH[f]	pentane	0.99
	TBE	0.99
	acetone	1.02
	cyclohexanol	1.07

[a] Calculated using Sphere method with errors ≤6%. [b]:Properties of sample AsH-NS (not included) are the same as these for A2. [c] For acronymic see Symbols Used. [d] Wrong out. [e] Considering the material in the first row as solute. [f] Hamaca resins. [g] 40 carbon atom paraffin; see text and Supporting Information for SP paraffin's calculation.
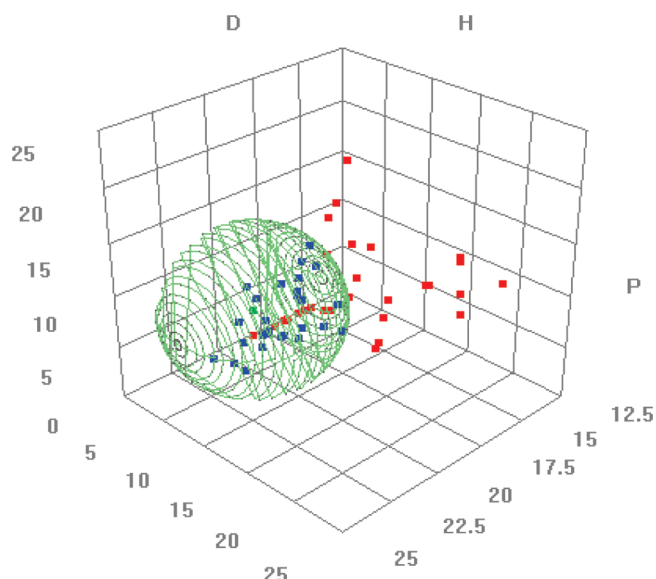

Figure 1. A graphical result in 3D (D, P, H) showing the sphere obtained in one asphaltene calculation. Here the blue points correspond to Good solvents (26) placed inside the sphere and red points corresponds to BAD solvents (31) placed outside the sphere. In this particular calculation, the center of the sphere is placed at the following (D, P, H) point: 19.51, 4.9, and 4.9 with R_0 (radius) = 7.4, all in $MPa^{0.5}$. The center corresponds to SP of asphaltenes. Within the SPHERE scheme, R_a is the distance from the center to the points (see eq 1) and the RED ratio R_a/R_0 is a measure of the solubility of sample in the particular solvent characterized by R_a.

solvent bearing a common characteristic with the solute, such as is the case of asphaltenes with hydrocarbons.

Comparison of δ components of asphaltenes in Table 2 with the one reported:[19] D, 19.6; P, 3.4; H, 4.4 is very good considering differences in the sample and differences in the set of solvents used. In fact, the δ_T calculated (see eq3) using the reported values was also 19.8, equal to the one in Table 2 within the calculation error. According to results in Table 2,
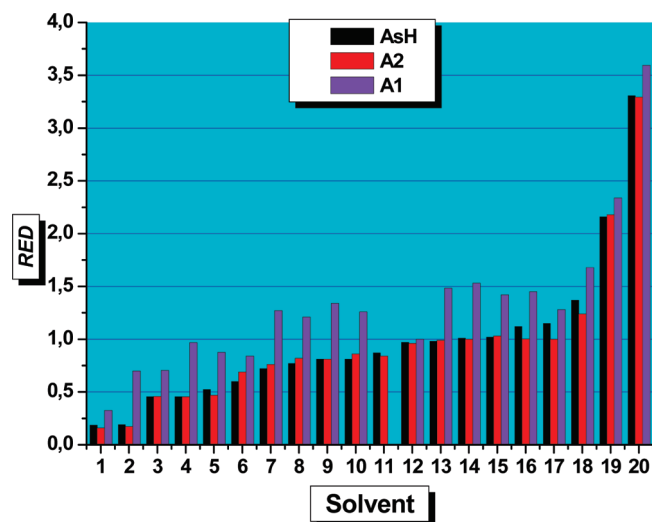
Figure 2. Comparison of RED values for samples AsH, A2, and A1 arranged from AsH's low to high RED values or in order of decreasing solubility in 20 selected solvents which cover the entire RED range studied. Solvents below RED = 1 are Good or else they are Bad; note that for each solvent A1 has the higher RED value in agreement with its lower solubility and higher SP (see Table 2). Note also that for AsH and A2, RED values are similar in all cases because theirs SP are very similar (see Table 2). The same trend was observed in all solvents studied. Legend for solvent number is as follows: (1) quinoline, (2) ODB, (3) pyridine, (4) CS$_2$, (5) cyclohexanone, (6) 1MN, (7) toluene, (8) xylene, (9) cumene, (10) benzene, (11) THF (this solvent was excluded in A1 calculations), (12) TCAA, (13) CTC, (14) decaline, (15) oleic acid, (16) MEK; (17) NMP; (18) acetone; (19) ethanol; (20) glycerol. For abbreviations, see Symbols Used.
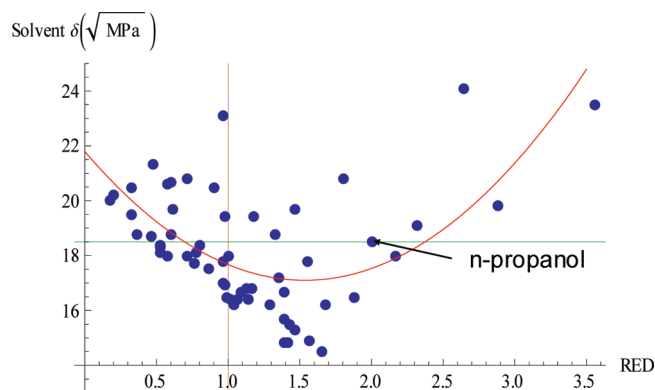
Figure 3. Plot of δ_T as a function of RED: points are from Table 1; vertical line corresponds to RED = 1, and the horizontal line corresponds to AsH δ_T = 18.5 MPa$^{0.5}$. Good solvents are to the left of RED = 1 and Bad to the right. Parabolic curve is an illustrative fitting to underline that δ_T alone is not enough for solubility criteria. Note that the closeness between δ_T of the solvent and solute is not a general criterion for good solvency. For instance, solvent *n*-propanol is on the horizontal line and hence has the same δ_T as AsH; however, it is a BAD solvent with RED = 2. The lack of correlation is because δ_T contains no information about the solute.

the SP range in asphaltenes goes from 19.5 to 21 MPa$^{0.5}$; this range is smaller than the one above-reported by Johansson.[5] Comparison with theoretical values reported by Rogel (quite a while ago[30]) is interesting because they correspond to Orinoco's Basin, the same place as Hamaca's. The range reported (20–23.1 MPa$^{0.5}$) is however significantly higher that the one in Table 2 (19.5–20.9, including A1); the values are in excellent agreement
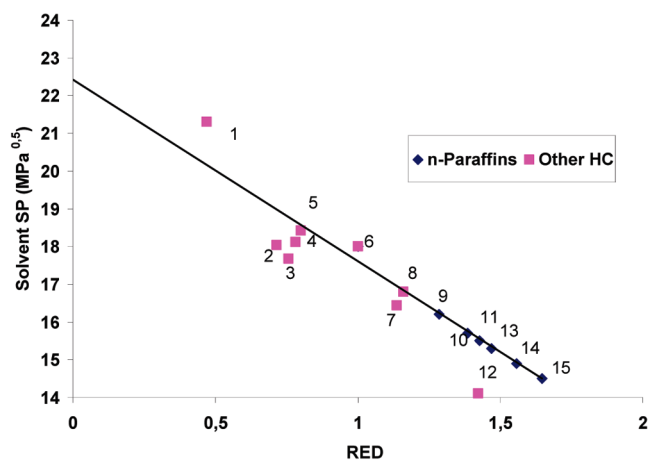

Figure 4. Correlation SP-RED for AsH using hydrocarbon solvents; shown line is a fitting to *n*-paraffins values: (1) 1MN, (2) toluene, (3) xylene, (4) cumene, (5) benzene, (6) decaline, (7) cyclopentane, (8) cyclohexane, (9) *n*-tetradecane, (10) decane, (11) octane, (12) 1-hexene, (13) heptane, (14) hexane, (15) pentane.

with the experimental, close to 20 MPa$^{0.5}$, and were found for A1TMs using a simple molecular mechanics method.[32]

SP for AsH estimated from their composition are shown in the last row of Table 2. These were calculated using eq 3 for δ_T and eqs 6-1–6-3 as described (see Methods). Errors were calculated by routine derivative methods, and although most probably the values are above the experimental, the calculated and observed SP for AsH are within the calculated errors.

Table 3 compares RED values for samples in several solvents; they were grouped in four rows sets for each solvent. Note that for all sets, the RED value is the highest for A1. Note also that RED values predict good solubility or affinity among the three materials; as expected affinity for resins was lowest in the A1 case. Good affinity between As, A1, and A2 should be expected because they are mixtures of similar materials; this is correctly predicted by the low RED values found (Table 3).

RED values predicts negligible affinity between the samples and PNP. However, according to literature data, "solubility" of PNP in A1 is about 10% which is the PNP/A1 mass ratio in the precipitated A1–PNP complex.[31] However, SP are not expected to hold when there is a reaction between the pair as is the case in complex formation (see below)

Vaporization Enthalpy. With the use of the procedure outlined above (see Methods and eqs 4, 7, and 8), values for $\Delta H_V°$ were obtained for samples shown in Table 4. These calculations were performed using $\bar{M}$ = 1000 g mol^{-1} for asphaltenes and 600 g mol^{-1} for resins. The values of asphaltene M_n close to 1000 were reported recently,[38] and the value for resins was assumed close to others reported;[34] the density for asphaltenes was assumed close to others reported by Tanaka et al.,[39a] and the density of resins was assumed equal to 1 g cm^{-3}.[39b] It should be mentioned that relevant arguments regarding this point do not depend on particular $\bar{M}$ or density values chosen. For comparison purposes, the values for benzene were included; the method used was "calibrated" using benzene where the $\Delta H_V°$ calculated was

(38) Acevedo, S.; Guzmán, K.; Ocanto, O. *Energy Fuels* **2010**, *24*, 1809–1812.

(39) (a) Zhang, Y.; Takanohashi, T.; Sato, S.; Saito, I.; Tanaka, R. *Energy Fuels* **2004**, *18*, 283–284. (b) Chambart, D.; Cormerais, F. X.; Laborde, M. *Process for deasphalting a heavy hydrocarbon feedstock*. U.S. Patent: 4,810,367, March 7, 1987 (available at http://www.docstoc.com/docs/39581432.

Table 4. Standard Enthalpy of Vaporization $\Delta H_V^{\circ a}$ and Other Sample Parameters

sample[b]	$V(cm^3)^c$	$\delta_T{}^f$	$\Delta H_V°$ (kJ mol^{-1})	$f_R{}^i$	ΔHr^j
AsH	855[c]	19.8	338	0.615	10
A2	855[c]	20	344	0.603	10
A1	855[c]	21.3	390	0.532	12
resins	667[d]	18.6	233	1.00	7
benzene	89.4[e]	18.5[g]	33[h]	6.35	1

^{a} Calculated using eq 4. ^{b} Sample AsH-NS afforded the same results as A2. ^{c} Calculated using M average = 1000 g mol^{-1} and density = 1.17 g cm^{-3} (see text). ^{d} Calculated using M average = 600 g mol^{-1} and density = 1 g cm^{-3}. ^{e} Handbook value. ^{f} Values from Table 2 unless stated otherwise. ^{g} Calculated from SP data (see Table 1). ^{h} Handbook value = 33.8 kJ mol^{-1}. ^{i} $\Delta H_V°$ ratio between resins and sample (see text). ^{j} $\Delta H_V°$ ratio between sample and benzene.
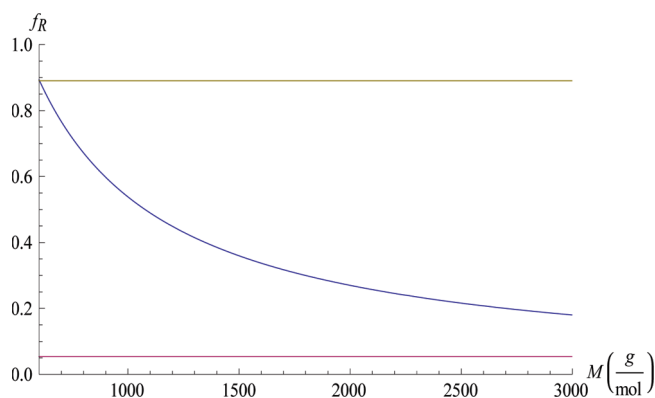
Figure 5. Change of ratio f_R with the molecular mass of A1 calculated using eq 8; pink line corresponds to f_R = 0.054 for MM = 10 000 g mol^{-1} and intercept line (0.89) corresponds to A1 sample having the same M as resins (600 g mol^{-1}). The calculation presumes that resins are the more volatile of the compounds compared.

practically equal to the experimental (see Table 4). Even so, these calculated for samples have only a relative value enough for purposes of this work; these relative values are represented here with parameter f_R defined in eqs 7 and 8, equal to the ratio of $(\Delta H_V°)_R/\Delta H_A°$, where $(\Delta H_V°)_R$ is the value corresponding to the resins and $(\Delta H_V°)_A$ corresponds to the sample. This shows that $f_R \leq 1$ for all samples with $\bar{M} > 600$ g mol^{-1}. It is evident that this factor will affect any method depending on vaporization of samples, such as MALDI and similar techniques. Thus, on this basis, the less volatile of all is sample A1, the one with the highest δ_T in Table 4. Figure 5 shows how f_R would change with molecular mass M for a material such as A1. As could easily be verified, $f_R \propto M_S^{-1}$ and drops rapidly to about 0.06 as M increases in the range from 600 to 10 000 g mol^{-1} (see Figure 5).

Flocculation. Flocculation results of asphaltenes, A1, and A2 are shown in Tables 5 and 6 and Figures 6 and 7; these were obtained using 2 g L^{-1} of sample in 10 mL of 1MN or toluene. Of all solvents tried, 1MN was the only hydrocarbon solvent which dissolves A1 as well as asphaltenes and A2. In these tables, values for sample AsH-NS were included. Total SP for solution mixtures at the flocculation point δ_{fT} were obtained from eq 5 and the corresponding SP of the components calculated using eqs 5-1 and 5-3 (see Methods); the components were then placed as input as another solvent in SPHERE and corresponding RED values obtained with the same optimized SP for samples (see the bottom of Table 1 for one example). Because at $V_h = 0$, the system contains

Table 5. RED and Other Parameters for Sample Solutions in 1MN or Toluene^a at the Flocculation Point^b

solutions	V_h(mL)^c	$\phi_h{}^d$	$\delta_{fT}{}^e$	$\delta_T{}^f$	RED^g
AsH−toluene	13.2	0.57	16.8 ± 0.2	19.7	1.14
A2−toluene	7.1	0.42	17.3 ± 0.2	20	1.06
AsH−1MN	28.5	0.74	17 ± 0.2	19.7	1.1
(AsH-NS)−1MN	20.6	0.67	17.5 ± 0.2	20	1.01
A1−1MN	7.5	0.43	19.2 ± 0.3	21.3	1.2
A2−1MN	21.1	0.68	17.4 ± 0.1	20	1

^{a} 10 cm^3 of toluene or 1MN; sample concentration, 2 g L^{-1}. ^{b} n-Heptane as flocculant. ^{c} n-Heptane volume at the flocculation point (FP). ^{d} n-Heptane volume fraction at FP. ^{e} SP (MPa$^{0.5}$) of mixture at FP, calculated using eq 5 (see Methods and Table 6); average of two determinations. ^{f} From Table 2. ^{g} Average obtained after 10 calculations with the Sphere program.

Table 6. Solubility Parameters and RED Values for Several Mixtures at Flocculation Point

solutions	$\phi_h{}^b$	SP^a				RED^c
		$\delta_{fT}{}^c$	$\delta_D{}^d$	$\delta_P{}^d$	$\delta_H{}^d$	
AsH−toluene	0.57	16.8	16.5	0.6	0.9	1.14
A2−toluene	0.42	17.3	16.9	0.8	1.2	1.06
AsH−1MN	0.74	17	16.7	0.2	1.2	1.1
AsH-NS−1MN	0.67	17.5	17.1	0.3	1.6	1.01
A2−1MN	0.68	17.4	17	0.3	1.5	1.03
A1−1MN	0.43	19.2	18.4	0.5	2.7	1.2

^{a} In MPa$^{0.5}$. ^{b} n-C$_7$ volume fraction. ^{c} From Table 5. ^{d} Calculated using eqs 5-1−5-3.

1MN and a minute quantity of asphaltenes and the intercept in Figure 6 should correspond to δ_T of 1MN.

As expected, A1 solution required much less n-C$_7$ to flocculate than the other three samples (see paragraph below). Comparison with toluene shows that 1MN shifts V_h to significantly higher values because 1MN is a better solvent than toluene (see corresponding RED values in Tables 1 and 4).

Figure 6 compares V_h with both δ_{fT} for solution and δ_T for samples. The flocculation point is, no doubt, dependent on both the solute and solvent mixture; thus, in this case, δ_{fT} correlates with an associated parameter such as V_h and SP of samples from which δ_{fT} was calculated (see eq 5). Hence the lower V_h, the higher both δ_T and δ_{fT} should be. Hence, in this case the lowest V_h found for A1 is expected in view of his higher δ_T (see Figure 6).

Comparison between AsH and AsH-NS when 1MN is the solvent shows a significant decrease of about 28% in V_h resulting in a value very close to the one found for A2 (see Figure 6 and Table 5, column 2). As described above (see Experimental Section), the very small amount of NS removed from asphaltenes (< 0.7%) is the difference between these two samples.

Table 7 and Figure 7 shows a linear correlation between RED values corresponding to sample−1MN pairs (see Table 3) and V_h in the particular RED range covered. The linear correlation is likely to be due to the few points used to obtain it; correlation between RED and V_h could be expected because both are parameters depending on the solute.

Discussion

SP are properties of materials, and the results above shows that the known solubility of asphaltenes in common solvents could be expressed on this basis by RED values. Lower solubility of A1 is predicted; this was the case in 57 solvents
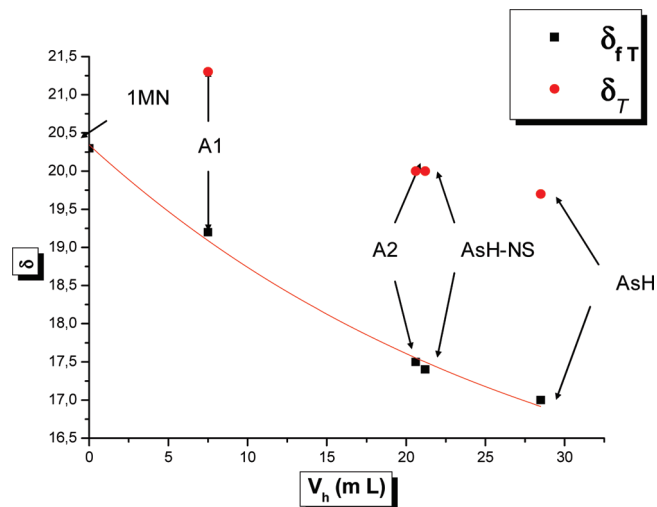
Figure 6. Plot of SP of samples (δ_T) and flocculation mixtures ($\delta_{f\,T}$) against n-C_7 flocculation's volume (V_h). Sample As-NS corresponds to asphaltenes without NS. The fitting is to show tendency, and the intercept was taken equal to δ_T of 1MN (20.3 MPa$^{0.5}$).
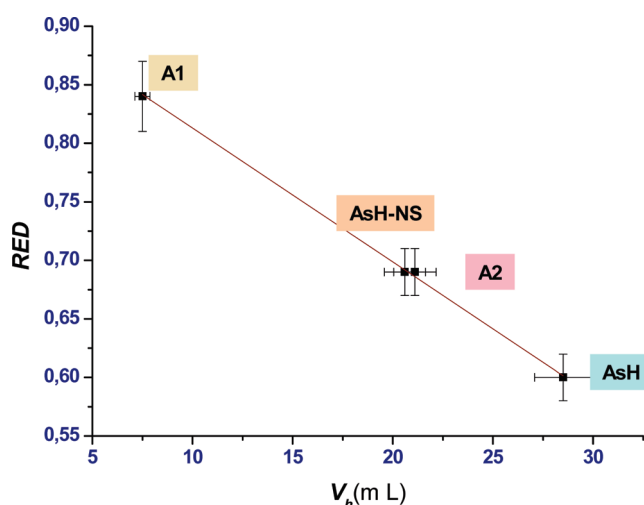

Figure 7. Linear correlation between RED and V_h for samples shown. RED values in this case correspond to sample−1MN pairs taken from Table 3; since flocculation depends on both solute and solvent (such as RED), correlation between these parameters could be expected (see the text).

(THF and dichloromethane were exceptions for A1; see Figure 2), thus this lower solubility is reasonably independent of solvent and must be associated with a property of A1 when compared to AsH and A2, in particular for aromatic solvents where both AsH and A2 dissolved and A1 did not. Of these tried, 1MN was the only aromatic solvent where A1 could be dissolved. The very low solubility in toluene strongly suggest that A1TM would be the first to aggregate in this solvent at the very low asphaltene concentration reported for this phenomenon.[40−42] At some stage during aggregation, A2TM would form part of the aggregate allowing for solubilization of the A1 fraction.

(40) Acevedo, S.; Ranaudo, M. A.; Pereira, J. C.; Castillo, J.; Fernández, A.; Pérez, P.; Caetano, M. *Fuel* **1999**, *78*, 997–1003.

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Table 7. Flocculation $V_h{}^a$ and RED Values Corresponding to Sample−1 MN^b Pairs

sample	V_h (mL)	RED
AsH	28.5	0.6
AsH-NS	20.6	0.69
A1	7.5	0.84
A2	21.1	0.69

^{a} From Table 5. ^{b} From Table 3.

Good solubility prediction by the RED parameter is not generally followed by δ_T of solvent as can be clearly appreciated in Figure 3. This is expected because whereas RED is related to both SP of solute and solvent, δ_T relates only to the solvent's SP. As described above (see Results), only for the n-paraffin's case a good linear correlation was found (see Figure 4). From these results we conclude that in general neither δ_T nor the closeness of solute−solvent SP could be used as good solubility criteria; in this regard, only RED values could be reasonably used as such. This was demonstrated in the many examples shown in Tables 1 and 3 and Figure 2 described in the Results section, in particular, the results concerning affinity among the samples studied. The affinity of asphaltenes by resins and vice versa is well-known,[43−47] and this is coherent with values shown in Table 3, where high affinity for both AsH and A2 was found and an expected lower affinity (RED = 0.9), close to the solubility limit, was found for A1; this fraction was always less soluble than the others regardless of solvent used and should be related to structural differences with A2. This point is further discussed below.

SP around 17 MPa$^{0.5}$ for a C_{40} normal paraffin was calculated using the group contribution method[1] described in the Supporting Information. This was used as another solvent to obtain the paraffin's RED values shown in Table 3. This size paraffin's were detected earlier coprecipitated with asphaltenes and resins.[35] As shown in Table 3, the affinity with resins is very significant; as expected affinity with the asphaltenes samples is poor affording RED > 1 in all cases.

Before discussing the results any further, we would like to remind the reader that neither A1 nor A2 contains any NS extractable by aqueous sodium hydroxide and the method use here to extract NS from AsH (see the Experimental Section). This is so because this same method is used during workup to extract PNP before isolation of fractions A1 and A2.[31−33,35]

Many results in this work could be conveniently discussed using Figure 8 as reference; this is a crude model depicting colloidal structure under conditions studied here. Important features are: asphaltene colloids are represented by three concentric layers: one exterior layer of NS, an intermediate layer constituted mainly by A2, and a medullar layer formed by A1. When NS are removed, the AsH-NS colloid is obtained. For an observer placed in the solvent, both AsH-NS and A2 colloids would look the same and this would conduce to identical δ_T values as found (see Table 2); moreover,

(43) Bouts, M. N.; Wiersma, R. J.; Muijs, H. M.; Samuel, A. J. *J. Pet. Technol.* **1995**, *47*, 782–787.

(44) Chatergoon, L.; Whiting, R.; Grierson, L.; Peters, T.; Smith, C. *Fuel* **1995**, *74*, 301–304.

(45) Bardon, C.; Barre, I.; Espinat, D.; Guille, V.; Li, M. H.; Lambard, J.; Ravey, J. C.; Rosemberg, F.; Zembi, T. *Fuel Sci. Technol. Int.* **1996**, *14* (1 and 2), 203–242.

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(47) Leon, O.; Contreras, E.; Rogel, E.; Dambakli, G.; Acevedo, S. *Langmiur* **2002**, *18*, 5106–5112.

$$\delta_T = 20\ MPa^{0.5}$$

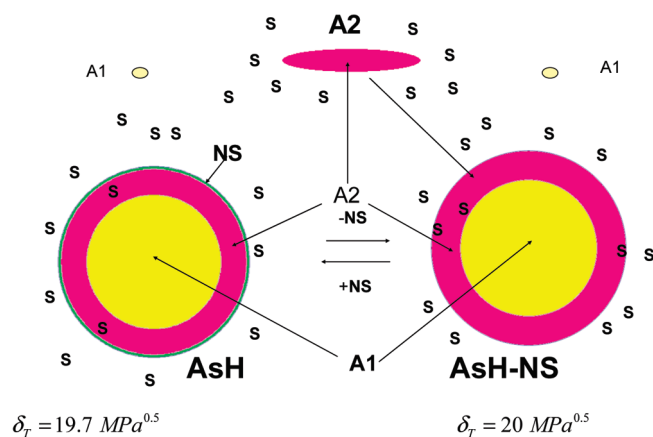$$\delta_T = 19.7\ MPa^{0.5} \qquad \delta_T = 20\ MPa^{0.5}$$

Figure 8. Model depicting the following features: colloidal structures for AsH and AsH-NS; NS layer in AsH periphery; A2 layer in both AsH and AsH-NS peripheries; A2 (molecules or aggregates) in solution (big ellipsis); the tiny quantities of A1 in solution (small ellipsis); removal of NS from colloidal AsH to afford AsH-NS colloids. Removal of NS from asphaltenes leads to AsH-NS with a corresponding increase in δ_T. In spite of NS being in small quantities, such a change is significant because of its peripheral position and functionality (carboxylic acids). As shown, removal of NS exposes the A2 layer of AsH to the solvent (represented by S) leading to a material of the same δ_T as A2; as a consequence $\delta_{T(AsH-NS)} = \delta_{T\ A2}$.

because NS are present in small amounts (see the Experimental Section), this would lead to a small difference in δ_T similar to the one found between AsH and A2, suggesting that solvents penetrate the periphery of AsH colloids being in contact with both NS and A2 layers.

However, because colloid flocculation depends strongly on material placed in the colloid periphery, a significant shift in the flocculation point, such as the one found (see Tables 5 and 6 and Figure 6), should be observed. The results show that removal of NS shifts V_h from 28 mL in AsH to 20 mL in AsH-NS or 28%. This is a very significant V_h shift which underlines the importance of NS in flocculation. Such a shift could come either from blocking of potential flocculating functional groups by NS and/or from osmotic (steric) stabilization factors.

As any model, Figure 8 is a crude representation of asphaltene colloids; for instance, boundaries between components would not be sharp but diffuse and domains of one fraction would contain quantities of the other; as shown above, predicted affinity between A1 and A2 is high ($R = 0.5$) and no interface should be expected between them; besides these fractions (A1, A2, and NS) are complex mixtures rather than single compounds. Regarding solvent S, it could be anywhere asphaltenes dissolve forming aggregates driven by dispersion forces, as is probably the case for aromatic solvents.[60]

When the system is below but close to flocculation, it would be similar to a saturated solution, and hence RED values for solvent mixtures should be close to 1 and this is indeed the case (see Table 5). This represents a very demanding test of the method which is accomplished in a very satisfactory manner considering that flocculation is not a thermodynamic property. Moreover, according to results shown in Table 7 and Figure 7, RED for sample−1MN pairs (see Table 3) correlates with V_h. Although at this time we have limited results and

cannot reach any solid conclusion, it appears that RED values and flocculation points found as above are related. This seems to be the consequence of similitude among all asphaltenes samples examined. In any case we conclude that flocculation and solubility problems associated to asphaltenes are related to fraction A1; knowing how far A1 flocculation is from asphaltene flocculation could suggest how efficient the periphery in stabilizing the asphaltene is. In the present case, measurement in terms of V_h periphery appears to be very efficient.

With the combination of solubility (see Table 2 and Figure 2) and flocculation results, there is no doubt that compared to A2, fraction A1 is less soluble and corresponding A1 colloids would be less porous to solvents, in particular for Bad ones. For Good hydrocarbon solvents such as 1MN, a partial solution of A1 molecules could be expected, allowing penetration of A1 periphery leading to colloidal solutions.

When resins are present in asphaltene colloidal solutions, they would be part of colloidal periphery as long as affinity for A2 is higher than affinity for the media. Since affinity for A2 is very high (low RED, about 0.4; see Table 3) this, in general, is bound to be the case; if so colloidal periphery would have a SP low enough to keep asphaltenes in solution provided the SP of media is not far below about 18 MPa$^{0.5}$ (compare with $\delta_{f\ T}$ values in Table 5). Moreover, as described above and shown in Table 3, resins are capable of "trapping" high M paraffins as reported earlier.[17] The low RED for resins-C$_{40}$ shown in Table 3 seems to be an important factor in this trapping. It is reasonable to assume that part of these and other paraffinic compounds would be part of the colloidal periphery in crude oils leading to a system of very low interfacial tension and hence thermodynamically stable. A good example of this is the extra-heavy Cerro Negro crude oil; when examined under the electron microscopy, it looks like a completely flocculated system with colloidal particles around 9 nm diameters;[46] however, this is very stable crude with any flocculation tendency.

As shown in Table 2, dispersion and hydrogen bonding SP components are the main contributors to A1 and A2 SP differences. Dispersion forces promotes piling up or cofacial aggregation whereas hydrogen bonding promotes side by side bonding either with itself or with other media molecules allowing either aggregate formation or colloidal dispersion. The presence of colloidal nanoparticles in crude oil and benzene[48,49] and pyridine solutions[50] is well-known as well as a hypothesis suggesting that A1 occupies the colloidal core and solvent and A2 are placed at the periphery.[31−33] The above results are coherent both with data and with this hypothesis.

Relatively high SP of A1 and low V_h are consistent with continental type structures; at the time of this writing we speculate that by being the continental type and solvent repelling, A1 molecules in cumene would facilitate PNP coordination and packing into a precipitation solid. On the other hand, the relatively low SP of A2 makes it less solvent repelling and this, combined with flexibility, would preclude complex formation. Figure 9 shows models of continental and archipelago type asphaltenes taken from the literature.[51]

Archipelago type molecules would have internal rotational degrees of freedom in excess of these for the continental type.

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(49) Sheu, E.; Acevedo, S. *Energy Fuels* **2001,** *15,* 702–707.

(50) Sheu, E.; Storm, D. A. In *Asphaltenes: Fundamentals and Applications*; Sheu, E. Y., Mullins, O. C., Eds.; Plenum Press: New York, 1995; Chapter I.
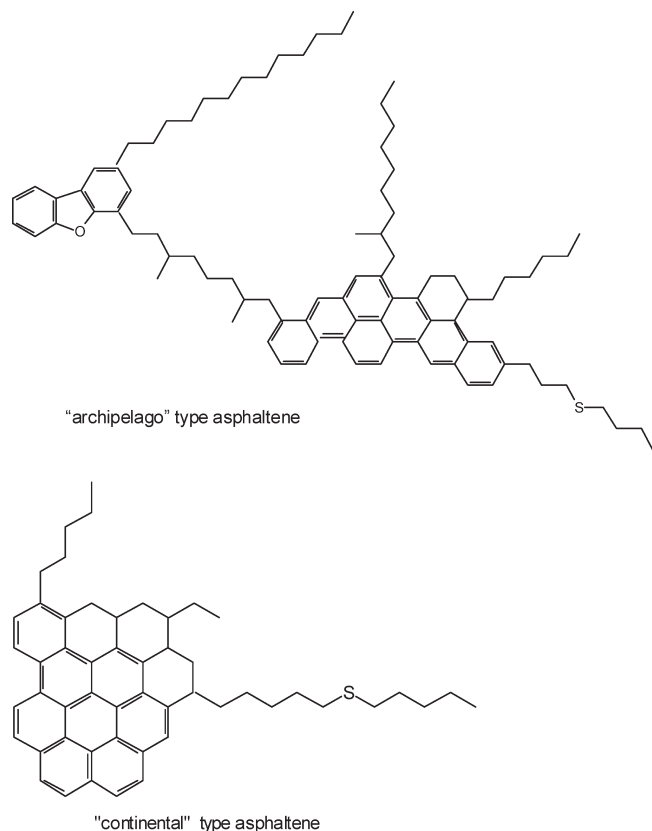
"archipelago" type asphaltene

"continental" type asphaltene

Figure 9. (Top) Archipelago type model $C_{89}H_{118}$; H/C, 1.32; MM, 1235 g mol^{-1}. (Bottom) Continental asphaltene model $C_{50}H_{52}$; H/C, 1.04; MM, 685 g mol^{-1}, from ref 51.

These contribute to the so-called molar conformational entropy $\Delta \overline{S}_C$, a factor very well-known in the biological sciences and related to changes in conformation, suffered by proteins during the folding and unfolding processes.[52−55] In our case, A2TM could fold and unfold according to surrounding media. In very good solvents they would unfold because of good mutual solute−solvent affinity or else they would fold thus avoiding phase separation. Obviously, for A1TM, conformational entropy is limited to aliphatic type chains located at the periphery leading to lower solubility.

High affinity between A1 and A2 (see Table 3) is coherent with adsorption data where asphaltene solubility in toluene is drastically reduced.[56] Asphaltenes adsorption in a multilayer at the silica−toluene interface is a well-known phenomenon.[33,56−58] According to the above ideas, A1 is expected to be adsorbed as colloids and because above mutual affinity A2 would also be adsorbed. A1−A2 interaction though would limit conformational movement as it would not be avoided but slowed down accounting for slowness of adsorption. Moreover, A2 is likely to be adsorbed in one of the many folded conformations and

would unfold slowly promoted by affinity for neighbor A1 molecules at the surface. This would lead to almost irreversible adsorption of asphaltenes at the toluene−silica interface.[56]

Separation of asphaltenes in fractions A1 and A2 have been effective in all asphaltenes samples treated by our research group; besides Hamaca, we have treated the following asphaltenes: Furrial, Cerro Negro, DM-153, and Boscan, which come from crude oils of different characteristics.[31] Moreover, with the use of ^{1}H DOSY NMR, Quoineaud and co-workers detected continental and archipelago type asphaltenes in Maya, Buzurgan, and Athabasca asphaltenes.[59] As commented on earlier[32] and confirmed latter,[59] asphaltenes in general are a mixture of continental or A1TM and archipelago or A2TM molecules.

In a recent report,[38] it was found that, when measured in several solvents, the number average molecular mass (M_n) for A1 were consistently higher than A2; moreover, when measured in ODB, A2 afforded $M_n \approx 1000$ g mol^{-1}, whereas $M_n > 2600$ g mol^{-1} was found for A1. As described above, ODB was the next best solvent for asphaltenes, A1, and A2, and on the basis of the results in Table 3 one would expect that aggregation should be negligible or small for the A2−ODB pair. This, of course, is coherent with the relatively low M_n above found for A2. Affinity for the pair A1−ODB is far below RED solubility limits, and of course A1 dissolves easily in ODB; however, according to the high M_n, above it does so by forming nanoaggregates in solution. It is clear then that even in very good solvents, SP alone cannot tell whether the solute dissolves as molecules or aggregates.

As described in the Introduction, Zhang et al. reported negative ΔH_{mix} for some solvent−asphaltene pairs[18] and found difficulties to justify asphaltene aggregation in some of these Good solvents. On light of the above results, it seems clear that although A2 and other asphaltene components, such as NS and TC, may be dissolved with heat evolution, A1 remains aggregated to a significant extent. Within the SP scheme, negative ΔH_{mix} should lead to very low RED values, as is the case for quinoline and pyridine, two of the solvents used by these authors (see Tables 1 and 3).

Conclusions

RED values, calculated with the sphere method, were found consistent with known solubility (Good and Bad) of asphaltenes, and the SP calculated for asphaltenes are in good agreement with those in the literature. Solubility and SP results for A1 and A2 were coherent with the role these fractions should play in solubility and in both colloidal formation and stabilization. Results above are consistent with low solubility of A1 in general and with insignificant solubility in monoaromatic hydrocarbon solvents in particular. SP are thermodynamic parameters and as such allows prediction of solubility behavior of the materials studied here. High affinity between asphaltenes and resins is predicted by the method, which affords RED values close to those of very good solvents. This of course is consistent with the well-known affinity of asphaltenes by resins.[43−47] According to the low RED value for the AsH−resin pair (0.37, Table 3), one could expect that a large part of asphaltenes should be dissolved rather than dispersed by resins. Also affinity between A1 and A2 (0.5, Table 3) is high enough to suggest miscibility between them.

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(52) Spolar, R. M.; Record, T., Jr. *Sci., New Ser.* **1994,** *263,* 777–784.
(53) DAquino, J. A.; Gomez, J.; Hilser, V. J.; Lee, K. H.; Amzel, L. M.; Freire, E. *Proteins: Struct., Funct., Bioinf.* **1998,** *25,* 143–156.
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(59) Durand, E.; Clemancey, M.; Lancelin, J. M.; Verstraete, J.; Espinat, D.; Quoineaud, A. A. *Energy Fuels* **2010,** *24,* 1051–1062.
(60) Rogel, E. *Energy Fuels* **2000,** *14,* 566–574.

Both solubility and flocculation results are coherent with a colloidal model where A1 prevails in the core or medullar part and both A2 and NS prevails at the periphery. Solubility of AsH in solvents where A1 is practically insoluble strongly suggest solubilization of A1 by A2. Flocculation results were consistent with the important role of NS in stabilizing the AsH's colloid and underlined the roles played by them, by A1, and by A2 in colloidal physical chemical behavior where A1 promotes flocculation and NS, A2, and resins promote stabilization. After adsorption onto A1, stabilization by A2 is provided by avoiding A1−media contact. Stabilization by resins could be expected in media with SP close to these shown for flocculation mixtures (Table 6, RED > 1). SP and parameters derived from them, such as vaporization enthalpies, proved to be helpful in discussing MM methods such as VPO and MALDI MS.

Previously proposed colloidal model where A1 prevails at the core and A2 prevails in the periphery[31−33] was extended to include NS, resins, and other compounds such as paraffins. From the SP point of view, the asphaltene colloid is a body with a SP range from about 21 to 17 MPa$^{0.5}$ inside out. This leads to nanometer sized and thermodynamic stable colloidal systems similar to microemulsions in this regard.

With the combination of solubility (see Table 2 and Figure 2) and flocculation results, there is no doubt that compared to A2 fraction A1 is less soluble and corresponding A1 colloids would be less porous to solvents, in particular for Bad ones. For Good hydrocarbon solvents such as 1MN, partial solution of A1 molecules could be expected, allowing penetration of A1 periphery leading to colloidal solutions.

Because A1 is the main flocculation's promoting fraction, knowing how far A1s FP is from asphaltenes FP could suggest how efficient the periphery in stabilizing the asphaltene is; in the present case, measured in terms of V_h periphery (A2 + NS) appears to be very efficient.

Previously, SP for both A1TM and A2TM were performed using molecular mechanics methods.[32] A1 SP results in Table 2 agree very well with the theoretical value reported (21.5 MPa$^{0.5}$). This good agreement is being further analyzed in our research group. The advantage of SP, of being a collective property, allows solubility and related studies of complex mixtures such as asphaltenes and their fractions A1 and A2.

Results in Tables 2 and 3 strongly suggest that these complex mixtures behave as a family of compounds of similar composition and structure because otherwise the shown regularities in RED values would not be observed. Thus, with no exception, RED values for A1 were the highest and corresponding values for A2 and AsH were close to each other. Finally SP could be used as unifying view to analyze many physicochemical properties of asphaltenes such as solubility, vaporization, colloidal properties, adsorption at surfaces, flocculation, molecular mass, molecular structure, and more.

Supporting Information Available: Calculation of SP for *n*-paraffins and plot of RED−SP for resin−*n*-paraffin pairs. This material is available free of charge via the Internet at http://pubs.acs.org.

Symbols Used

A1 = fraction of asphaltenes (Hamaca in the present case) obtained alter treating the sample (8 g/L) in a cumene saturated with PNP. This leads to formation of solid complex A1·PNF which after working up affords A1

A2 = asphaltene fraction soluble in the above mixture obtained after working-up

AsH = Hamaca asphaltenes

AsH-NS = Hamaca asphaltenes sample denuded from NS (see NS below)

API = as used here, American Petroleum Institute gravity or density

A1TM = molecules present in fraction A1 and characterized by a rigid polycyclic core with alkyl-type substitutions connected to periphery atoms, also called continental type (see Figure 9 for an example)

A2TM = molecules present in fraction A2 and characterized by polycyclic moieties connected between them by alkyl-type chains, also called archipelago type (see Figure 9 for an example)

Bad = referred to solvents which do not dissolves the sample; bad solvents have RED ≥ 1

border line = solvents with RED ≈ 1; important to find accurate SP

D = dispersion component of SP

DOSY = ^{1}H, NMR two dimension diffusion technique where *x*-axis is the regular NMR spectrum and *y*-axis affords diffusion values of sample being studied

EOS = equation of state

DSC = differential scanning calorimetric method

FP = flocculation point

Good = referred to solvents which dissolves the sample; good solvents have RED ≤ 1

H = hydrogen bonding component of SP

$\Delta H_V°$ = enthalpy of vaporization at STP

HSP = Hansen SP

P = polar component of SP

SP = solubility parameter

THF = tetrahydrofurane solvent

ODB = *o*-dichloro benzene

TCAA = trichloroacetic acid

CS2 = carbon disulfide

CTC = carbon tetrachloride

M = molecular mass

1MN = 1-methyl naphthalene

NMP = *N*-methyl-2-pyrrolidinone

MEK = methyl, ethyl ketone

MALDI-MS = matrix assisted laser desorption ionization mass spectrometry

OA = oleic acid

SARA = acronym for saturate, aromatic, resins, and asphaltenes referring to chromatographic methods to separate them

PNP = *p*-nitrophenol

NS = acidic natural surfactants extracted with aqueous sodium hydroxide from asphaltenes−chloroform solution

δ = general representation of SP

δ_T = total SP

δ_{fT} = SP of toluene−*n*-C$_7$ or 1MN- *n*-C$_7$ mixtures at the flocculation point

$\delta_D, \delta_P, \delta_H$ = dispersion, polar, and hydrogen bonding components of SP, respectively

FIT = SPHERE parameter expressing fitting

SPHERE = program employed to obtain SP of samples

R = gas constant equal to 8.306 J K^{-1} mol^{-1}

R_a = parameter defined in eq 1 and measuring "distance" (in SP terms) from center of sphere to any $(\delta_D,\delta_P,\delta_H)$ points within and outside the calculated sphere

RED = parameter of SPHERE program, define by eq 2 and associated to solubility: the lower RED < 1, the higher the solubility of sample; samples insolubles affords RED > 1

R_0 = radius of sphere

S = SPHERE parameter; values used in this work were 0 for nonsoluble and 1 for soluble in a particular solvent; solubility referred to sample and STP conditions

$\overline{V}$ = molar volume

T = Kelvin temperature

TC = n-C$_7$ soluble, nonasphaltenic compounds trapped within the A1−A2 network; TC are recovered after PNP treatment

Abbreviations for Solvents Used

TCAA = trichloro acetic acid

TBE = 1,1,2,2-tetrabromo ethane

CTC = carbon tetrachloride

EBZ = ethyl benzoate

CHA = cyclohexanone

2MCHA = 2-methylcyclohexanone

NB = nitrobenzene

DCB = 1,4-dichlorobutane

DBE = 1,1-dibromoethane

PNT = p-nitro toluene

CS2 = carbon disulfide

DCE = 1,2 dichloro ethane

BRB = 2-bromo butane

1CB = 1-chloro butane

Cy5 = cyclopentane

Cy6 = cyclohexane

NBA = n-butyl acetate

EA = ethyl acetate

NTD = n-tetradecane

CyOL = cyclohexanol

C7OL = heptanol

EOE = diethyl eter

AA = acetic anhydride

PA = propionic acid

DMSO = dimethyl sulfoxide

AcA = acetic acid

1POL = 1-propanol

DBE = 1,2-dibromo ethane

ACN = acetonitrile

HR = Hamaca resins

FMC7 1MN = flocculation mixture n-C$_7$, 1MN

DEC = decaline

MeA = methyl amine