The Chemistry of Alberta Oil Sands, Bitumens and Heavy Oils

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the oil. Also, it is possible that asphaltene precipitation takes place in the reservoir and that the supernatant oil becomes saturated with asphaltene. In a deep reservoir the temperature and pressure are both high and during the passage of the oil to the surface as the values of these parameters decline, the solubility of the asphaltene will decrease and this may cause further precipitation.

Heavy oils, on the other hand, have experienced as a rule only mild exposure to geothermal heat, their asphaltene's alkyl complement is intact and the high aromatic and resin contents of their maltene fraction makes this maltene an excellent solvent for asphaltene, capable of peptizing large amounts of it.

As the preceding discussions demonstrate, solubility—as are other properties—is determined by molecular composition, structure, size, conformation and colloidal structure. The same parameters determine chemical reactivity as well.

Asphaltene has the least favorable composition of the crude oil fractions: it has the highest NOS, metal and ash contents, the lowest H/C ratios and the highest MW and aggregation state. Also, asphaltene is known to be the most important source of coke during the cracking and refining operations. The residual asphaltenes from these operations, aside from their solubility-based operational definition, may have little in common with their predecessor, the native asphaltene. Their MW is much reduced, alkyl, sulfide and other bridges broken and appendages largely removed, and at the same time their aromaticity increased.

Athabasca oil sand asphaltene is one of the most extensively investigated asphaltenes. Instrumental and, in particular, chemical studies have brought to light many structural features of this material and led to the detection and identification of a host of constituent molecules. Some of the architectural principles of this asphaltene have also been elucidated and the roles of C–C, C–S (and C–O) bridges and side-chain appendages demonstrated.

2.0 Solubility Characteristics and Precipitation of Asphaltenes

The solubility of asphaltene in the maltene of crude oil and the stability of the asphaltene solution with respect to precipitation are of considerable interest to all phases of the petroleum industry—recovery, transportation, storage, refining, upgrading—where asphaltene precipitation can cause troublesome operational difficulties. When conditions under which the asphaltene solution is stable are changed, asphaltene precipitation may take place. Asphaltene solubility may be affected by composition (addition and mode of addition of a miscible solvent, chemical reactions), temperature, pressure, contact with surfactants, metal or hydrogen ions (*pH*), exposure to an electrical potential differential such as that generated by moving charges when the oil flows in a conduit (electrokinetic effect), frictional electricity (triboelectric effect), mechanical shear (shaking, acoustic vibration), *etc.*

Asphaltene precipitation may occur spontaneously in the reservoir as a result of petroleum gas buildup. In a pooled reservoir the precipitated asphaltene may settle to the bottom resulting in an improvement in the quality of the supernatant crude (lower density, viscosity and heteroatom content). Troublesome asphaltene precipitation may take place in the near-wellbore region where asphaltene deposition can block pore throats resulting in a reduction of permeability, changes in wettability and a reduction in the cross-sectional area for flow during the oil recovery operation. The asphaltene particles in the oil have been postulated to carry some positive surface charge

and therefore preferentially deposit on pores containing kaolinite, which is negatively charged. (This could also occur in interfaces with acidic media[10] at *pH* values ≤ 6.5 (*v.i.*).) In the course of thermal processing of the oil or upgrading of the bitumen, asphaltene precipitation leads to coke formation and enhanced coke yields. Another occurrence of asphaltene precipitation is in the laboratory during the analytical determination of the asphaltene content of oil samples.

The separation of asphaltene can be achieved by either digestion of the sample with a precipitant (n-C_5 or n-C_7) or precipitation with a precipitant from a concentrated solution of the sample in a diluent. The quantities and properties of the precipitated asphaltene depend on the temperature, nature and quantities of diluent and precipitant used. (For this reason, in data reporting it is desirable to indicate the precipitant used in the isolation of the asphaltene by a prefix, *e.g.* n-C_5-asphaltene, n-C_7-asphaltene, *etc.*) The solvent power and precipitate-forming efficiency of many hydrocarbon liquids have been investigated and compared. Some results, showing the variation in the percentage amount of precipitate formed from Athabasca bitumen and from an Arabian light atmospheric residue diluted with an equal volume of benzene upon addition of 40 volumes of the specified solvent at room temperature as a function of the carbon number of various types of hydrocarbons,[11,12] are shown in Figure 14.1. The precipitate yield in both cases is highest with the smallest alkane used, propane, and decreases rapidly at first and then more gradually with increasing carbon number in the three most efficient series of precipitating agents, 2-methyl-alkanes, n-alkanes and terminal alkenes. The efficiency of bringing about precipitation for these three series of hydrocarbons follows the order of listing. Cycloalkanes, on the other hand, are relatively good solvents for petroleum asphaltene, although not for coal asphaltene, and therefore are inefficient precipitating agents. The ability of a solvent to solubilize asphaltene or, in general, to dissolve a solid or to form a homogeneous solution with another liquid, may be expressed in terms of solubility parameters.

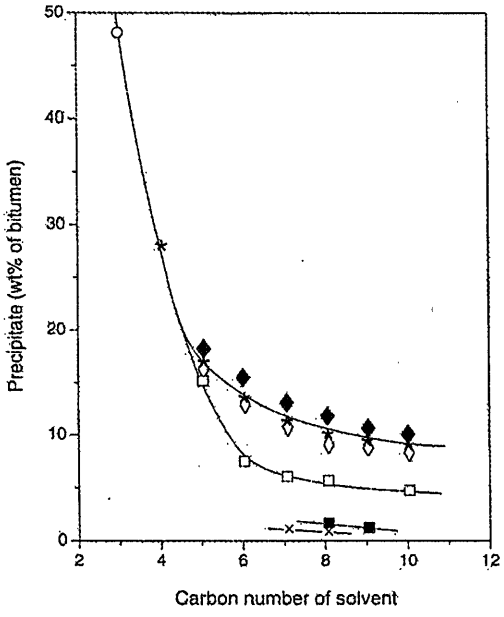

Figure 14.1 Precipitate yield from Athabasca bitumen and Arabian light atmospheric residues as a function of carbon number of the precipitant. Athabasca: ✶, n-alkanes; ♦, 2-methyl paraffins; ◊, 1-alkenes; ×, cycloparaffins; ■, methylcyclo-paraffins. Data from Ref. 11. Arabian: □, n-paraffins. Data from Ref. 12.

2.1 Solubility parameters

Solubility parameters are molecular properties which are defined either in terms of the cohesion energy density or the internal pressure of the solvents, which are assumed to be nonpolar liquids. Thus, Hildebrand[13] defined a solubility parameter which is related to internal pressure as the ratio of the surface tension and the cubic root of the molar volume,

$$\delta_1 = \gamma V^{-1/3} \qquad (1)$$

$$(\text{dyn}\cdot\text{mol}^{1/3}\cdot\text{cm}^{-2} = 0.1\ \text{N}\cdot\text{mol}^{1/3}\cdot\text{mm}^{-2} = 10^5\ \text{J}\cdot\text{mol}^{1/3}\cdot\text{m}^{-3})$$

where δ_1 is the solubility parameter, γ is the surface tension and V is the molar volume.

(hildebrand = $cal^{1/2} \cdot cm^{-3/2}$ = $(MPa^{1/2})/2.04$)

where ΔE_v and ΔH_v are the energy and the enthalpy of vaporization, R is the universal gas constant and T is the temperature (K). The more widely-used parameter, δ_2, is important in the estimation of the heat of mixing for two nonpolar liquids a and b:

$$\Delta H_m \approx \Delta E_m = \phi_a \phi_b (x_a V_a + x_b V_b)(\delta_a - \delta_b)^2 \quad (3)$$

where the ϕ's are the volume fractions of the liquids and the x's are their mole fractions. From the free energy equation

$$\Delta G_m = \Delta H_m - T\Delta S_m, \quad (4)$$

where ΔG_m is the free energy and ΔS_m the entropy of mixing, it is evident that, in order to obtain a negative value for ΔG_m, which is necessary for mixing to occur, ΔH_m must be reduced. This can be achieved if δ_a and δ_b have similar values. The entropy of mixing, ΔS_m, usually has positive values and thus, the important conclusion we have arrived at is that, for mixing of two nonpolar liquids or dissolution of a nonpolar solid in a nonpolar solvent to occur, the components should have similar δ values. Liquids differing by two hildebrands in their δ values are generally incompletely miscible, since the internal pressure (holding a unit volume of liquid together) exerted by the liquid with the higher internal pressure (*i.e.* higher solubility parameter) will "extrude" the molecules of the liquid with the lower internal pressure (lower solubility parameter) out of the solution matrix.

The solubility parameter theory was derived for regular solutions, which are defined as solutions for which the entropy change on mixing, ΔS_m, equals the ideal value and the volume change on mixing, ΔV_m, is zero, but no restriction is imposed on the enthalpy of mixing. These criteria are usually satisfied by solutions of nonpolar solutes in nonpolar solvents where the primary intermolecular forces are London dispersion forces (instantaneous dipole-induced dipole interactions). However, the above criteria are not satisfied when: a) the solute and solvent molecules are polar (in which case dipole-dipole, dipole-induced-dipole, charge transfer and hydrogen bonding interactions may become important); b) specific molecular orientation effects are operative; c) the solvent and solute molecules have rather different sizes; and d) the low density of one of the liquids is near its critical point. Therefore, the solubility parameter theory would not be expected to be applicable for colloidal aggregate solutions of polar, random, polydispersed macromolecules like asphaltenes. Yet, as will be seen from the data available, the correlation between the solubility of asphaltene and solvent solubility parameter is quite good for nonpolar and low-polarity solvents.[15]

Nellensteyn[16] was the first to relate solvent power for asphaltene to physical properties of the solvents. He found that, for simple hydrocarbons, the percentage yield of asphaltene precipitate from bitumen decreases with increasing surface tension of the solvent. The validity of this relationship follows from the relative constancy of the cubic root of the molar volumes of saturated hydrocarbons in the expression for δ_1, Eq. (1). Subsequently, Labout[17] correlated

asphaltene solubility with the δ_1 value of solvents and showed that the percentage amount of precipitate tends to decrease with increasing values of the solubility parameter δ_1 of the solvent and that precipitate formation ceases altogether above a certain value (~4.6 dyn·mol$^{1/3}$·cm^{-2}), Figure 14.2.

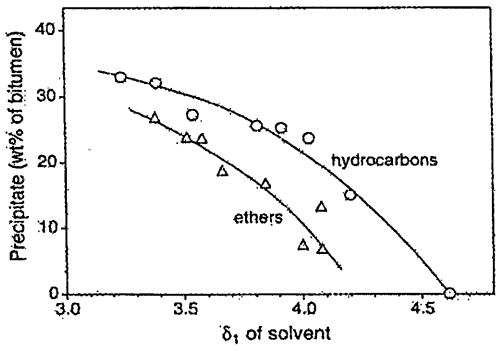

Figure 14.2 Relation of amount precipitated from a Mexican bitumen upon dilution with a 100-fold quantity of precipitant to solubility parameter δ_1. From J.W.A. Labout, Ref. 17. © 1950, Elsevier, Amsterdam.

A more exhaustive study of the correlation between asphaltene solubility and precipitation from bitumen solutions on one hand, and the solubility parameters δ_1 and δ_2 on the other, has been reported[11] on Athabasca bitumen. The yield of precipitate from a concentrated benzene solution of the bitumen upon addition of a 40-fold volume excess of a series of hydrocarbons and other liquids is tabulated in Table 14.1 and plotted as a function of the solubility parameters δ_1 and δ_2 of the precipitant in Figure 14.3, where it is seen that the yield of precipitate increases with decreasing δ_1 or δ_2. Precipitate formation ceases when δ_2 reaches a value of about 17.1 MPa$^{1/2}$ because the asphaltene becomes completely soluble in hydrocarbons with $\delta_2 \geq 17.1$ MPa$^{1/2}$. A δ_2 value can be assigned to asphaltene as well. From the observation that asphaltene becomes completely soluble in solvents with $\delta_2 = 17.1$ MPa$^{1/2}$, and since toluene, benzene, methylene chloride, pyridine and nitrobenzene with δ_2 values of 18.2, 18.9, 20.2, 21.7 and 22.5 MPa$^{1/2}$, respectively, are all excellent solvents for petroleum asphaltene, the value for δ_2 of asphaltene can be established as not less than 19.6 MPa$^{1/2}$. Thus, liquids with $\delta_2 < 17.1$ MPa$^{1/2}$ do not interact sufficiently strongly with asphaltene to break up the bonds between the asphaltene molecules by solvation and therefore would not effect complete solubilization. On the other hand, the solvation energy of the solvents with δ_2 in the 17.1–22.1 MPa$^{1/2}$ range is sufficiently large to overcome the cohesion energy of asphaltene and cause solubilization. From detailed solubility studies a value of 23.0 MPa$^{1/2}$ has been reported for a "purified" asphaltene and a significantly lower value of 20.0 MPa$^{1/2}$ for the same asphaltene in its parent oil.[18] Other values (in MPa$^{1/2}$) reported for a variety of different asphaltenes using different methods of measurement include:

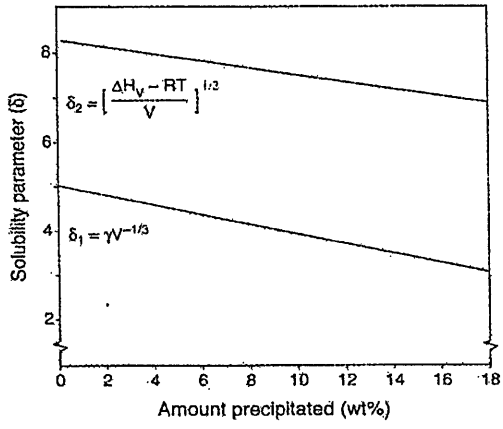

Figure 14.3 Relation of amount precipitated from Athasbasca bitumen to solubility parameters, δ_1 and δ_2, using pure solvents and solvent blends. After D.L. Mitchell and J.G. Speight, Ref. 11. © 1973, Butterworth-Heinemann, Oxford, U.K.

20.5[19]
20.60–20.92 (crude oil)[21]
20.7 (δ_D, δ_P, δ_H: 20.2, 2.0, 4.0)[22]
20[24]
21.9–21.5[20]
21.15–21.90 (n-C_7 asphaltene)[21]
19.50; 20.04 (1–1.07 × 10^{-3}T°C)[23]

Figure 14.3 also features data on binary benzene–n-pentane solvent mixtures, the δ values of which are additive and can be calculated from the molar compositions of solvents a and b:

Table 14.1. Yields of precipitate from Athabasca bitumen using various solvents[a]

Solvent	Solubility parameter, δ			Precipitate
	$gV^{-1/3}$ (dyn·mol$^{1/3}$·cm^{-2})	$[(\Delta H_v - RT)/V]^{1/2}$ (cal$^{1/2}$·cm$^{-3/2}$)	MPa$^{1/2}$	wt% bitumen[b]
normal hydrocarbons				
pentane	3.2	7.0	14.4	16.9
hexane	3.5	7.3	14.9	13.5
heptane	3.8	7.5	15.3	11.4
octane	3.9	7.6	15.4	9.8
nonane	4.0	7.7	15.6	9.4
decane	4.1	7.7	15.8	9.0
2-methyl hydrocarbons				
*iso*pentane	3.1	6.8	13.8	17.6
*iso*hexane	3.4	7.1	14.4	15.3
*iso*heptane	3.7	7.2	14.8	12.8
*iso*octane	3.8	7.4	15.0	11.5
*iso*nonane	3.9	7.5	15.4	10.0
*iso*decane	3.9	7.6	15.5	9.8
terminal alkenes				
pentene	3.4	7.1	14.6	16.2
hexene	3.6	7.3	15.0	13.0
heptene	3.8	7.5	15.4	10.9
octene	4.0	7.6	15.6	9.0
nonene	4.1	7.7	15.8	8.6
decene	4.1	7.8	16.0	8.5
cycloparaffins				
cyclopentane	5.0	8.2	16.8	1.0
methylcyclopentane	4.6	7.9	16.2	1.4
ethylcyclopentane	4.6	9.0	18.5 (?)	1.9
cyclohexane	5.3	8.2	16.8	0.7
methylcyclohexane	4.7	7.9	16.2	1.0
ethylcyclohexane	4.9	8.1	16.6	1.4
decalin	5.5	8.6	17.6	0
aromatics				
benzene	6.5	9.2	18.9	0
toluene	6.0	8.9	18.2	0
o-xylene	6.1	9.0	18.5	0
m-xylene	5.8	8.8	18.0	0
p-xylene	5.7	8.8	18.0	0
ethylbenzene	5.9	8.8	18.0	0
n-propylbenzene	5.6	8.7	17.8	0
n-butylbenzene	5.4	8.6	17.6	0
miscellaneous hydrocarbons				
2,2,4-trimethylpentane				
*iso*octane	3.4	6.9	14.1	15.8
*neo*pentane	2.4	6.2	12.7	21.5
*neo*hexane	3.2	6.7	13.7	17.9
cyclohexene	6.0	8.5	17.4	0
other solvents				
pyridine	8.6	10.6	21.7	0
nitrobenzene	9.3	10.8	22.1	0
chloroform	6.3	9.2	18.9	0
carbon tetrachloride	5.8	8.6	17.6	0
methylene chloride	7.1	9.8	20.1	0

[a] After D.L. Mitchell and J.G. Speight, Ref. 11. © 1973, Butterworth-Heinemann; used in the construction of plots in Figure 14.3. [b] Bitumen was diluted with an equal volume of benzene before precipitation with a 40-fold volume of *n*-pentane.

$$\delta_{ab} = \frac{x_a V_a \delta_a + x_b V_b \delta_b}{x_a V_a + x_b V_b} \quad (5)$$

where xs and Vs are the mole fractions and molar volumes.

The observed variation in the quantities of precipitate formed as a function of the δ_1 values of the solvents in Table 14.1 and Figure 14.3 is closely similar to that using δ_2 values.[11] From the limiting δ_1 values at which precipitation ceases, for example, with cyclohexane having $\delta_1 = 5.3$ dynes·mol$^{1/3}$·cm^{-2} and a precipitate yield of only 0.7%, the maximum value of the surface tension of the solvent at which precipitation still takes place can be estimated. Thus, taking the molar volume of cyclohexane, 108.7 cm^3·mol^{-1}, and multiplying its cubic root, 4.8 cm·mol$^{-1/3}$, by $\delta_1 = 5.3$ dynes·mol$^{1/3}$·cm^{-2}, we obtain for γ, the surface tension of the liquid at which precipitation still occurs, 25.4 dynes·cm^{-1}. All good solvents for asphaltene, such as benzene, for which $\gamma = 29.3$ dynes·cm^{-1}, have surface tensions greater than 25 dynes·cm^{-1} and poor solvents causing precipitation of asphaltene from its solution have surface tensions lower than 25 dynes·cm^{-1}, *e.g.* *n*-pentane, $\gamma = 15.7$ dynes·cm^{-1}.

More advanced theoretical treatments of solubility parameters have led to the extension of the range of their applicability to include polar molecules. In one such treatment the effective solubility parameter is the sum of three independent components:

$$\delta = \sqrt{\delta_D^2 + \delta_P^2 + \delta_H^2} \quad (6)$$

δ_D is included to take into consideration the dispersion forces which nearly correspond to the δ_2 values listed in Table 14.1, δ_P to take into consideration the polar, and δ_H, the hydrogen bonding interactions. This so-called three-dimensional solubility parameter theory is capable of giving satisfactory accounts of the solubility behavior of many weakly polar molecules and may explain, Table 14.2, why pyridine, quinoline and nitrobenzene, for example, are better solvents for asphaltene than carbon disulfide. In the latter molecule only dispersion forces are operative, but in the former solvents, moderate-strength polarization and hydrogen bonding interactions are also operative in addition to strong dispersion forces. Nonetheless, the intermolecular force dominating the solubility of asphaltene is the dispersion force and the interaction energy arising from this force is proportional to the product of the polarizabilities of the asphaltene and the solvent (*v.i.*). The polarizabilities of aromatic compounds are, in general, higher than those of paraffinic compounds and this explains their higher solvent power.

The closest match of the δ_D, δ_P and δ_H values with Athabasca asphaltene occurs for the case of naphthalene (Table 14.2), α-methylnaphthalene, (anthracene, phenanthrene), *o*-dichlorobenzene and methylene chloride; these compounds are probably the best pure solvents for asphaltene.

There are several treatments of the solubility of polymers reported in the literature. By applying thermodynamic, statistical, statistical thermodynamic and statistical mechanical models as well as fractal aggregation kinetics and, more recently, molecular mechanics calculations, various theories have been developed for homogeneous and heterogeneous polymers and asphaltenes. For asphaltene solubility and precipitation point calculations, the most notable treatment is in terms of the simple solution thermodynamic model-based equation[23] which relates the solubility of asphaltene to a combination of the solubility parameter with the Flory–Huggins entropy of mixing for polymer solutions.

In order to understand this we need to consider the equation for the energy of mixing for one mole of solution, given by the Hildebrand-Scatchard (H–S) equation

Table 14.2 Three-dimensional solubility parameters of various liquids at 25 °C[a]

Solvent	Molar volume V	Parameters ($MPa^{1/2}$)			
		δ_D	δ_P	δ_H	δ(total)
benzene	89.4	18.4	0	2.0	18.5
methyl chloride	55.4	15.3	6.1	3.9	16.9
methylene chloride	63.9	13.4	11.7	9.6	20.2
chloroform	80.7	17.8	3.1	5.7	19.0
carbon tetrachloride	97.1	17.8	0	0.6	17.8
tetrahydrofuran	81.7	16.8	5.7	8.0	19.5
diethyl ether	104.8	14.5	2.9	5.1	15.6
acetone	74.0	15.5	10.4	6.9	19.9
acetophenone	117.4	19.6	8.6	3.7	21.7
methyl *iso*butyl ketone	125.8	15.3	6.1	4.1	17.0
methyl *iso*amyl ketone	142.8	15.9	5.7	4.1	17.4
nitrobenzene	102.7	17.6	14.0	0.0	22.5
pyridine	80.9	19.0	8.8	5.9	21.8
aniline	91.5	19.4	5.1	10.2	22.5
quinoline	118.0	19.4	6.9	8.9	22.4
carbon disulfide	60.0	20.4	0	0.6	20.4
dimethyl sulfoxide	71.3	18.4	16.3	10.2	26.6
dimethyl sulfone	75.0	19.0	19.4	12.2	29.8
benzyl alcohol	103.6	18.4	6.3	13.7	23.8
cyclohexanol	106.0	17.4	4.1	13.5	22.4
o-dichlorobenzene	112.8	18.0	9.8	0.0	20.5
water[b]	18.0	15.5	15.9	42.2	47.7
asphaltene[c]		20.2	2.0	4.0	20.7
asphaltene					20.3
naphthalene		19.2	2.0	3.9	19.7
α-methylnaphthalene		20.6	0.8	4.7	21.2
phenanthrene					20.0
anthracene					20.3
pentene–1		13.9	4.1	–	14.5
hexene–1		14.4	3.9	–	15.0
heptene–1		14.6	3.6	2.7	15.3
octene–1		15.0	3.5	2.3	15.5
none–1		15.4	3.4	–	15.8
decene–1		15.7	3.3	1.3	16.0
cyclopentene		15.3	5.8	4.1	16.9
methylcyclopentane		15.7	3.5	0.0	16.0
ethylcyclopentane		15.9	3.3	0.0	16.2
ethylcyclohexane		16.1	2.6	0.0	16.3
undecane		16.0	0.0	0.0	16.0
dodecane		16.2	0.0	0.0	16.2

[a] Solid, treated as supercooled liquid. [b] Values uncertain. [c] Athabasca asphaltene with a molar mass 3, 920 g·mol^{-1} (from Ref. 22).

$$\Delta_m U_v = (x_L V_L + x_A V_A)(\delta_L - \delta_A)^2 \phi_L \phi_A,$$

where $m = V_A/V_L$, $\phi_L = x_L/(mx_A + x_L)$, $\phi_A = m x_A/(mx_A + x_L)$, is the molar volume and x is the mole fraction.

The most important derived molar property from the H–S equation is the activity coefficient, f_A

$$RT\ln(f_A) = RT\ln(a_A/x_A) = V_A \phi_A^2 (\delta_L - \delta_A)^2$$

where "a" is the activity. The infinitely dilute solution where $V_A x_A << V_L x_L$, $RT\ln(a_A/x_A) = V_A(V_L x_L/V_A x_A + V_L x_L)^2 (\delta_L - \delta_A)^2 = V_A(\delta_L - \delta_A)^2$. These equations are valid for the binary mixtures of species A and L where n, the molecular sizes, are not too different. If this condition is not met the inclusion of a correction term, the Flory-Huggins size effect term is necessary. This involves replacing $-R\ln x_A$ in the entropy of mixing with $-R[\ln x_A + \phi_L(1 - V_L/V_A)]$. Various modifications of the resulting equation led to different results as illustrated by Eqs. (7–9):

$$f_{VA} = \exp\left\{\frac{V_A}{V_L}\left[1 - \frac{V_L}{V_A} - \frac{V_L}{RT}\left(\delta_A - \delta_L\right)^2\right]\right\} \tag{7}$$

Here, f_{VA} is the volume fraction of asphaltene soluble in the crude oil (liquid), V_A and V_L are the molar volumes of asphaltene and crude oil (liquid) and δ_A and δ_L are the respective solubility parameters.

The Flory-Huggins term appended activity coefficient function has been used with various modifications with lesser or greater success for "molecularly dispersed" asphaltene solutions in pure solvents or solvent mixtures and in deasphaltened crude oil. Another example[22,25] of this is Eq. (8)

$$K_i = \exp\left\{1 - \frac{V_i^L}{V_m} + \ln\left(\frac{V_i^L}{V_m}\right) + \frac{V_i^L}{RT}\left(\delta_i - \delta_m\right)^2\right\} \tag{8}$$

and its three-dimensional variant, Eq. (9)

$$K_i = \exp\left\{1 - \frac{V_i^L}{V_m} + \ln\left(\frac{V_i^L}{V_m}\right) + \frac{V_i^L}{RT}\left[\left(\delta_{Di} - \delta_{Dm}\right)^2 + b\left[\left(\delta_{Pi} - \delta_{Pm}\right)^2 + \left(\delta_{Hi} - \delta_{Hm}\right)^2\right]\right]\right\} \tag{9}$$

where K_i is the equilibrium ratio x_i^s/x_i^l (x_i^s and x_i^l are the solid- and liquid-phase mole fractions of component i), V_i^L and V_m are the liquid-phase molar volumes of component i and the solvent, and the variable b is a weighting factor. The expression containing the squared differences of the solubility parameters in Eq. (9) is the distance between the solvent solubility "sphere" and the solubility sphere of asphaltene component i. The closer the two spheres, the more likely the asphaltene to be dissolved.

Eq. (7) gave good results for precipitation point predictions when nonassociated asphaltenes were treated as homogeneous substances, but predictions for the amount of precipitated asphaltene were less satisfactory. In recent studies on Athabasca asphaltene, the molar mass distribution was determined experimentally and correlations were developed for the physical properties required for the solubility calculations: molar volume and the solubility parameter. Solubility curves calculated this way for Eqs. (8) and (9) in comparison with experimental measurements are shown in Figures 14.4 and 14.5. It is seen that both the one-dimensional and the three-dimensional solubility parameter models correctly predict the solubility of asphaltene in nonpolar and slightly polar solvents including *normal* and branched alkanes, aromatics, dichloromethane, 1-hexene and decalin. In slightly more polar media the three-dimensional model gives better results for the solubility of asphaltene than the one-dimensional

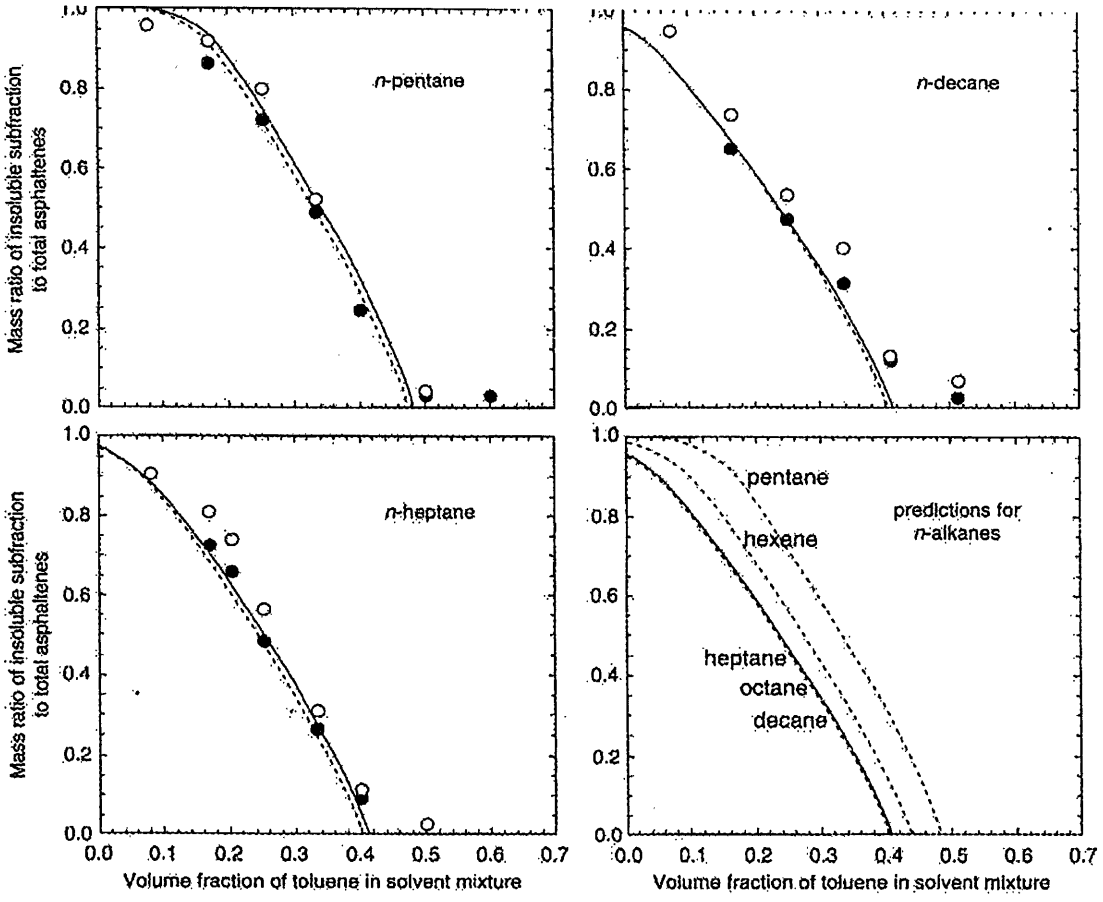

Figure 14.4 Solubility of asphaltenes in solutions of toluene/*n*-alkanes. ●, precipitation method, O, solubility method; —, one-dimensional model, Eq. (8), - - -, three-dimensional model, Eq. (9). From K.D. Mannistu, *et al.*, Ref. 22. © 1997, American Chemical Society.

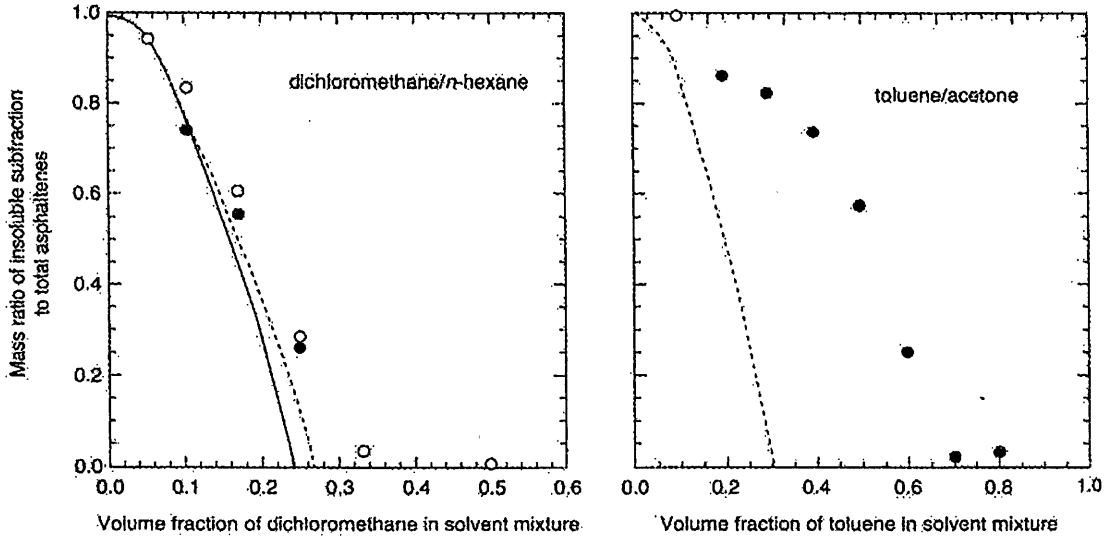

Figure 14.5 Solubility of asphaltenes in solutions of dichloromethane/*n*-hexane and toluene/acetone. ●, precipitation method, O, solubility method; —, one-dimensional model, Eq. (8), - - -, three-dimensional model, Eq. (9). From K.D. Mannistu *et al.*, Ref. 22. © 1997, American Chemical Society.

model. For highly polar solvents the one-dimensional model fails, while the three-dimensional model gives results of limited validity.*

It has also been observed[22,25,26] that the amount of asphaltene precipitate is greater when the asphaltene is dissolved from a solid form than when it is precipitated from solution. This behavior is not consistent with the solubility model for asphaltene considered thus far, and the reasons for the observed "hysteresis" will be discussed later in this chapter.

None of the solubility models discussed above takes into consideration the presence of electrical charges or free spins on asphaltene (or the stream electrical charges in a flow of oil through a pipe).

A diagrammatic approach to the solubility of asphaltene employs a two-dimensional solubility parameter field in which a closed area representing the complete solubility domain of a petroleum fraction is mapped out. The two solubility parameters used are the complexing solubility parameter δ_C and the field force solubility parameter δ_{FF}. The former is considered to be the measure of the "interaction energy that requires a specific orientation between an atom of one molecule and a second atom of a different molecule" (essentially the vectorial sum of δ_P and δ_H, *i.e.* $\delta_C = \sqrt{\delta_P^2 + \delta_H^2}$) and the latter to be the measure of "the interaction energy of the liquid that is not destroyed by changes in the orientation of the molecules". Hydrogen bonding and donor–acceptor interactions are part of the complexing solubility parameter component and van der Waals and dipole interactions are part of the field force solubility parameter component. The solvent power of each liquid is represented by a vector from the origin to a point on these diagrams, Figure 14.6, with the magnitude of the vector being the overall solubility parameter $\delta_O = \sqrt{\delta_C^2 + \delta_{FF}^2}$.

In the plots of Figure 14.6[27] the residue fractions are divided according to whether they are completely soluble, partially soluble or insoluble. This defines solubility polygon areas based on the fact that mixtures of solvents are solvents. Even nonsolvents on one side of the solubility domain can be mixed with nonsolvents on the other side to form solvents. Examples are seen in Figure 14.6D for 50–50% by volume of methyl ethyl ketone and *n*-hexane and tetrahydroquinoline with cyclohexane and with decalin.

This method, aside from its simplicity, offers the advantage that solubility is not defined by a single point—a single solubility parameter value—but instead by a visual image of a closed domain in a solubility parameter field. In the example provided by the Cold Lake residue fractions it is seen that the saturate fraction has low solubility, even in moderately-complexing liquids. The large solubility area of the aromatics is attributed to the low molecular mass of this fraction, the lowest among the fractions. Asphaltene, as seen, requires high δ_{FF} and low δ_C values for maximum solubility. It is noted that solvents for coke represent a subset of solvents for asphaltene, asphaltene for resins, resins for aromatics meaning that solvents for asphaltene are solvents for resins, *etc.* and neither these fractions can be solvent extracted but can readily be precipitated.

* It is interesting to note the linear relationship in Figure 14.3 between measured asphaltene solubility and the solubility parameter ($q = \alpha(\delta - 8.5)$, where q is the amount of precipitate formed and α is a proportionality factor) in contrast to the exponential character of Eqs. (7–9) as well as that of the equation $\ln x_a = -M_a / RT\rho_a [(\delta_s - \delta_a)^2]$ (where x_a is the mole fraction solubility of the asphaltene, δ_s and δ_a are the solubility parameters of the solvent and the asphaltene, M_a is the molecular weight and ρ_a is the density of asphaltene) derived from the activity coefficient function without the Flory-Huggins correction term. J.G. Speight, The Chemistry and Technology of Petroleum, Third Edition, 1999, Marcel Dekker, N.Y. p. 452.

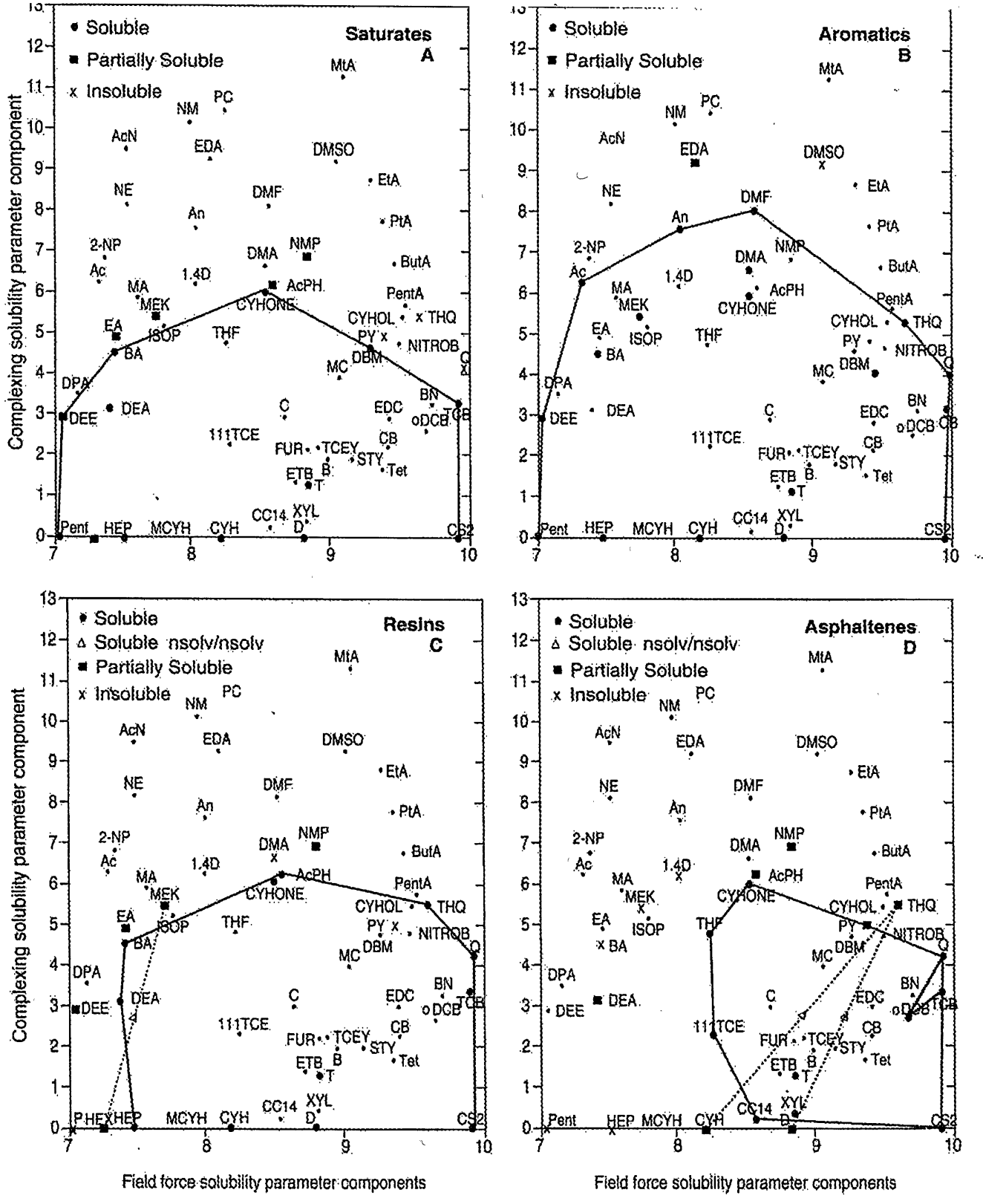

Figure 14.6 Two-dimensional solubility parameter diagrams for Cold Lake saturates, aromatics, resins and asphaltenes at concentrations 0.1 g/25 mL. The dark triangle in the asphaltenes diagram represents coke. From I.A. Wiehe and S.K. Liang, Ref. 27. © 1996, Elsevier.

The method is clearly an empirical one and the diagrams in Figure 14.6 would have to be determined for each asphaltene (fraction) sample over the entire solubility range.

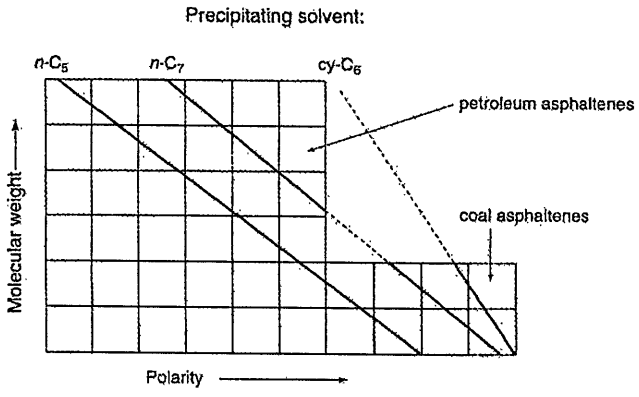

Figure 14.7 Comparison of petroleum and coal asphaltenes precipitation. Adapted from R.B. Long, Ref. 28. © 1981, American Chemical Society.

A simple schematic approach to the solubility of asphaltene[28] is based on a phase diagram representation in terms of polarity and MW. In the schematic MW *versus* polarity plot shown in Figure 14.7 the diagonal line for *n*-heptane indicates the phase distribution between precipitated asphaltene, above and to the right of the diagonal line, and the *n*-heptane solution of the asphaltene below and to the left of the line. As seen from the diagram, less-polar materials of higher MW and more-polar materials of lower MW both precipitate as asphaltene. With *n*-pentane as the precipitating agent the diagonal line shifts to the left including both less-polar and lower-MW materials in the precipitate and therefore increasing the total amount of precipitate.

The extension at the lower right of the diagram depicts the phase distribution for coal liquids. Coal asphaltenes have lower MWs and, on account of their high phenolic oxygen content, a higher polarity than petroleum asphaltenes. In the diagram, both *n*-heptane and *n*-pentane are shown to cause asphaltene precipitation from either petroleum residua or coal liquid solutions, but cyclohexane does not cross through the polarity–MW field of the petroleum asphaltene, only that of coal liquids. This representation illustrates the fact that coal asphaltenes are not soluble in cyclohexane while petroleum asphaltenes are.

Thus, even if such a diagrammatic representation does not advance the theory of asphaltene solubility, it may serve as a simple educational aid.

A measure of the solvent-solute interaction is the enthalpy of solution, but only a few measurements of enthalpies of solution have been reported for asphaltene. These include the heats of solution of Athabasca asphaltene[29] in toluene and xylene to form 1.0% solutions at 25°C:

Substance dissolved	Solvent	ΔH/J (g substance dissolved)$^{-1}$
bitumen	toluene	18.39
asphaltene	toluene	−6.94
maltene	toluene	8.87
bitumen	xylene	13.20
asphaltene	xylene	−8.88
maltene	xylene	5.14
bitumen	methylene chloride	18.2

From these data and the asphaltene content of the bitumen, 17%, it can be calculated that upon dissolution of 1.0-g asphaltene in 4.98-g maltene the heat of dissolution will be −73.2 J, which is an order of magnitude larger than the heat of solution in toluene or xylene. Further dilution

with the maltene to give 1.0% solution of the asphaltene would be accompanied by even more heat evolution. The exothermicity of these processes is a manifestation of solvent strengths, indicating that the order of solvent strength for asphaltene in toluene ~ xylene << maltene, in agreement with the values of the solubility parameters from direct measurements, Tables 14.1, 14.3 and 14.4. Also the high exothermicity explains the good solubility of Athabasca asphaltene in the maltene fraction of its bitumen.

Table 14.3 Cot θ and δ_2 solubility parameters[30a]

Solubility parameter	Cot θ_v	Cot θ	δ_2, $MPa^{1/2}$ (literature)
Pure hydrocarbons			
n-heptane	–1.00	–1.00	15.3
1-heptene	–0.35	–	–
cyclohexane	+0.48	+0.35	16.8
1,2-dimethylcyclohexane	+0.38	–	–
xylene	+2.14	+1.73	18.0
benzene	+2.38	+1.38	18.8
decalin	+1.79	–	–
tetralin	+2.14	+1.96	19.4
Hydrocarbon mixtures			
deodorized varsol	–0.21	–	–
coker gas oil	+0.18	–	–
virgin gas oil	+0.18	–	–
Athabasca coker gas oil	+0.82	–	–
hydrotreated A.C.G.O.	+0.91	–	–
Athabasca natural gas oil	+0.99	–	–
steam cracked gas oil	+1.12	–	–
cracked gas oil	+1.28	–	–
Solvesso + 150	+2.37	+2.41	17.3
heavy aromatic naphtha	+2.75	–	–
Other pure solvents			
*iso*butylheptylketone	+1.41	+0.80	15.9
pyridine	+2.41	+1.30	21.8
tetrahydrofuran	+2.41	–	19.5
carbon tetrachloride	+1.94	+1.19	17.7
trichloroethylene	+2.41	+1.46	19.0
o-dichlorobenzene	+4.13	+2.90	20.8

Table 14.4 Solubility parameter and compositional data for Athabasca bitumen compound class fractions[30a]

Oil fraction	Solubility parameter Cot θ_v	H/C ratio	Wt%	
			sulfur	nitrogen
Saturates	1.1	1.65	1.9	<0.02
Aromatics	3.2	1.38	5.9	0.2
Resin 1	4.0	1.53	5.4	0.7
Resin 2*	4.5	1.46	5.1	0.9
Asphaltene	–	1.23	8.2	1.2
Maltene	2.4	–	–	–

* More polar.

The endothermicity of the dissolution in maltene is due in part to the low affinity of the aromatic solvents for the saturate fraction of the maltene and in part to the much higher cohesion energy density of the resin fraction of the maltene compared to that of the aromatic solvents (*v.i.* and Tables 14.3 and 14.4).

As has been discussed above, in solubility parameter theory, solubility—that is, the maximum amount of solute that a given quantity of solvent under a given condition is capable of keeping in solution—is related to the total cohesion energy or internal pressure, *i.e.*, solubility parameters of the solvent and solute. Solubility parameters can be calculated from a variety of different physical properties of a substance; however, direct measurement of solubility yields the most reliable data. For this reason, other empirical methods for solubility parameter measurements and comparisons have been proposed. The one employed at the Imperial Oil research department in Sarnia[30a] in the late 1950s–early 1960s is based on incompatibility arising from the insolubility of the least-soluble asphaltene components of the oil.[30] This critical solubility point—precipitation point or flocculation threshold— of asphaltenes was determined by titrating oil in solution with different solvents against a reference titrant, such as *n*-heptane, using microscopic observations of the precipitation end point.

The method is illustrated schematically in Figure 14.8. The volumes of solvent per weight of oil are plotted as a function of the volume of titrant per weight of oil. Good solvents give positive slopes, Figure 14.8A. If the line is vertical, Figure 14.8B, the asphaltenes are critically soluble in the solvent. If the line has a negative slope, Figures 14.8C and D, it represents a poor solvent. When the solvent and titrant are the same the slope of the line is –45° with the *x*-axis. The smaller the positive slope the better the solvent, Figure 14.8E. Thus, the slope of the line described for a given solvent-titrant system is a measure of the solvent power of the solvent and cot θ, Figure 14.8F, is a practical measure of the solvent power for hydrocarbon mixtures. The experimental procedure is relatively quick and gives reproducible results which are transposable from one solvent system to the other. Some examples of the results are shown in Figures 14.9 and 14.10 where the characteristic nature of the *x*-axis intercept for a particular precipitant is illustrated for pure and industrial hydrocarbons, and the characteristic nature of the y-axis intercept for a particular solvent.

Values of cot θ_v (volume) and cot θ (molar) solubility parameters relative to *n*-heptane are given in Table 14.3 along with their δ_2 values. The higher the solvent power, the larger the positive value cot θ will acquire. A poor solvent

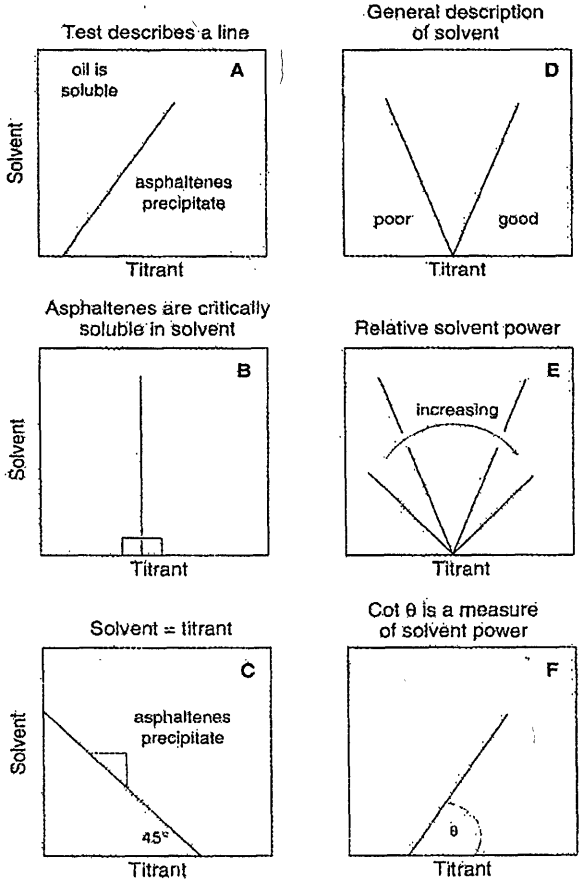

Figure 14.8 Interpretation of the cot θ solubility parameter. From Ref. 30a.

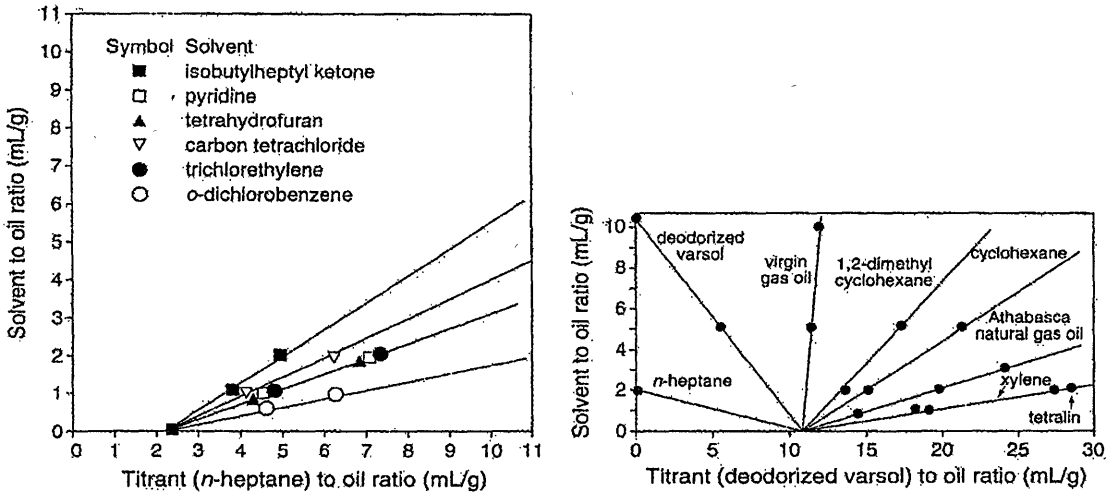

Figure 14.9 Experimental titration plots for the cot θ solubility parameter. From Ref. 30(a).

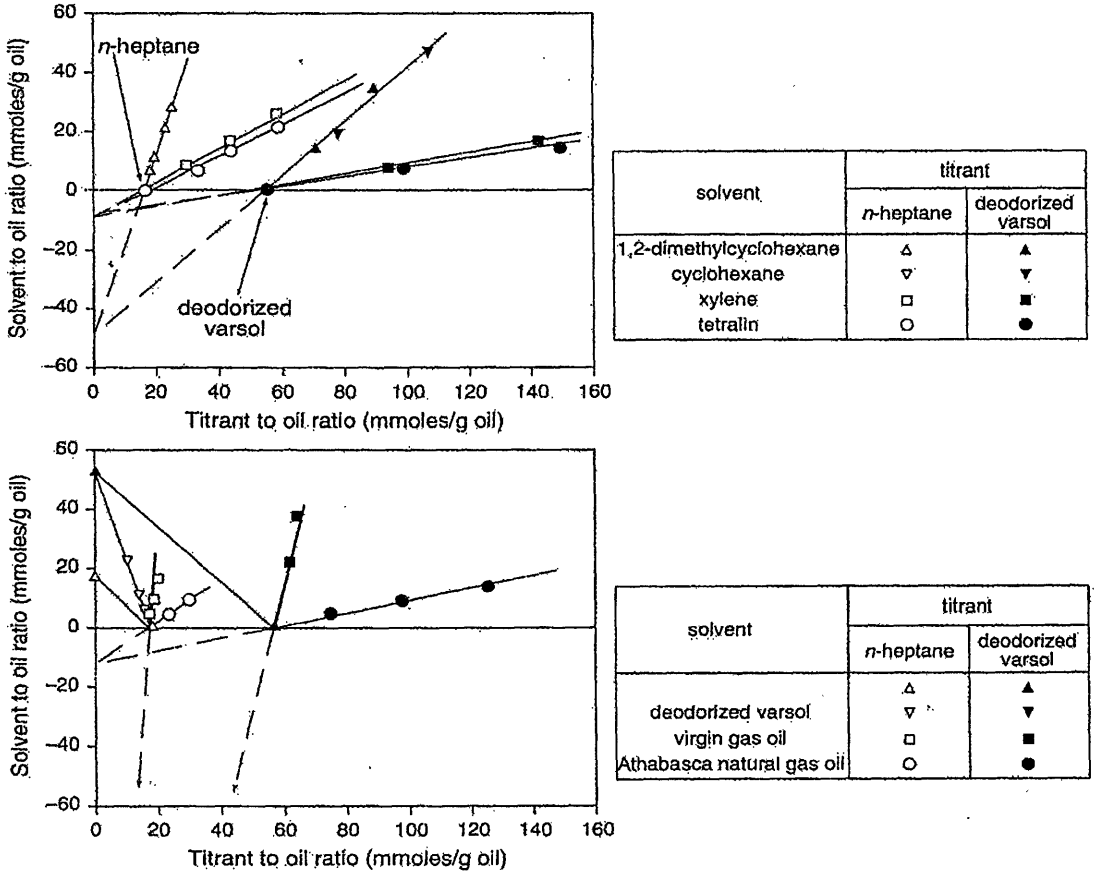

Figure 14.10 Experimental titration plots for the cot θ solubility parameter for pure and industrial hydrocarbon solvents showing *y*-axis intercepts. From Ref. 30(a).

has a negative value and the titrant has a value of −1.0. Solvents with values below −1 are poorer solvents than the titrant and solvents in which asphaltenes are just critically soluble have a cot θ value of zero.*

Cot θ solubility parameters for the low-hydrogen-bonding hydrocarbons with $\delta_2 \leq 19.4$ $MPa^{1/2}$ correlate well with δ_2 but polar solvents like pyridine and ketones do not.

At the critical solubility point the interfacial tension between the immiscible phases changes from zero to a positive value. Also, cot θ is zero at the critical solubility point and hence

$$\sum_{x=1}^{x=n} \cot\theta \; m_x = 0, \tag{10}$$

where m is the mole fraction of the solvent component x. From this equation cot θ values can be calculated for a single component of solvent mixtures. If the solubility parameter of the titrant is known the solubility parameter of the solvent can be calculated and *vise versa*.

Cot θ values for the silica gel separated class fractions of a bitumen, along with some compositional data, are presented in Table 14.4. The data predict increasing solvent powers for asphaltene in the order saturates < aromatics < resin 1 < resin 2. Moreover, the resins 2 ($\cot\theta_v = 4.5$) are far superior solvents to any pure solvent ($\cot\theta_v$ (max) ≈ 4.13).

Following these earlier studies, since the early 1980s various other methods for the determination of the flocculation threshold have been developed (or reported as being under development) and employed in the oil industry. These incorporate more advanced detection techniques, overcoming the drawbacks of visible light/visual microscopic detection systems. They include, among others, the following:

i) infrared laser light/variable length fiber optics/photodetector;
ii) capillary viscometry;
iii) electrical conductivity measurements;
iv) optical fluorescence spectroscopy/cross-polarization microscopy;
v) differential scanning calorimetry;
vi) refractive index measurement. This method is based on the correlation between the Hildebrand solubility parameter and the cohesion parameter "a" in the van der Waals equation of state (which is a different measure of the internal pressure):

$$\delta_2 \approx \frac{a^{1/2}}{V} \tag{11}$$

The correlation can be shown,[31] with some assumptions, to lead to the following expression for δ_2 in terms of the refractive index n:

$$\delta_2 = \left(\frac{\sqrt{3}\pi h\upsilon}{384\,\sigma^3}\right)^{1/2} \frac{\sigma^3}{V/N} \cdot \frac{n^2-1}{(n^2+2)^{3/4}} \tag{12}$$

where σ is the hard sphere diameter of the molecule, h is Planck's constant, υ is the UV absorption frequency and N is Avogadro's number;

vii) laser photon correlation spectroscopy;
viii) particle size analysis;
ix) heat transfer analysis, *etc.*

* θ is characteristic for the solvent relative to the titrant; the x-axis intercept is a characteristic of the oil and it is a measure of the stability of the asphaltene solution in the oil; the y-axis intercept is a characteristic of the solvent, independent of the titrant used and is a measure of solvent power.

Employing a flocculation threshold point apparatus, the design of which was based on technique "i", a "precipitation potential" scale has been established[32] for a set of solvents/precipitants. On this scale, Figure 14.11, precipitants have positive precipitation potentials and solvents negative precipitation potentials. The rankings (according to solvent power) reported correlate well with the cot θ values.

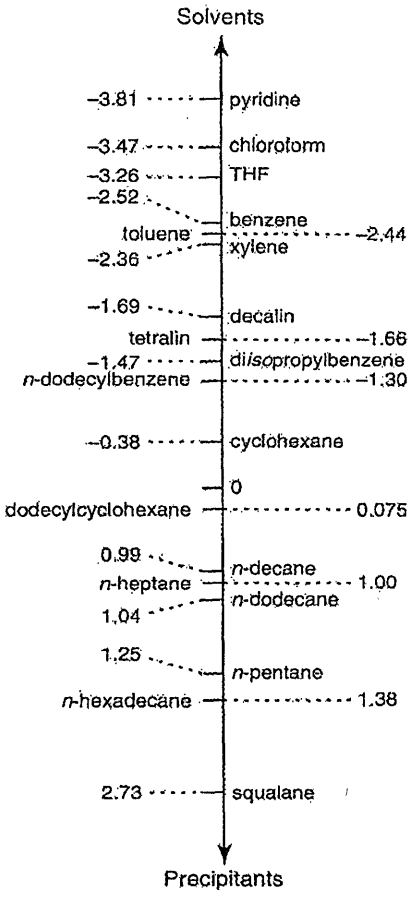

Figure 14.11 Precipitation potential scale. From G. Hotier and M. Robin, Ref. 32. © 1983, Inst. Franc. Petr.

Returning to Figure 14.1, we note that the difference in yields between the *n*-heptane and the *n*-decane precipitate is quite small, but the *n*-pentane precipitate yield is about 1.5–2.5 times greater than the *n*-heptane precipitate yield. The higher alkanes precipitate only the least-soluble portions of the asphaltene which, in general, have a different composition and MW from the lower-alkane-precipitated asphaltenes. The yield of the material corresponding to the difference between *n*-pentane and propane precipitation is quite large and this material was defined in the early days of petroleum chemistry as the resin fraction of the oil.

The material corresponding to the difference between the *n*-pentane and *n*-heptane precipitates represents low-MW asphaltene fragments and maltene molecules adsorbed to the asphaltene. These materials are analogous to what used to be called the "difference asphaltene", the material which is removable from *n*-C_5-asphaltene by ether extraction. The quantities of the "difference asphaltenes" for a number of Athabasca oil sand and conventional crude oil asphaltenes have been reported to comprise 30–35% of the *n*-C_5-asphaltene. Sequential extraction of Athabasca *n*-C_5-asphaltene[33] having an initial number average (VPO) molecular weight of 3350 g·mol^{-1} with *n*-pentane, ethanol, acetone and ethyl acetate removed 37% of the asphaltene and the molecular weight of the residual asphaltene increased to 6320 g·mol^{-1}. The color of the isolated asphaltene varies with the mode of separation. Thus the native, Athabasca *n*-C_5-asphaltene has a dark brown color. After acetone extraction, which removes 21–22% material, the extract has a deep reddish-brown color and the extracted asphaltene is black.

The shapes of the curves in Figure 14.1 are probably representative of most native bitumens and petroleum vacuum residua but conventional crude oils may show considerable departure from these curves. Examples of such departures are provided by the Rengiu, Zhongyuan and Shengly crudes from China[34] with 10–15% *n*-C_5-asphaltene and less than 0.2% *n*-C_7-asphaltene contents. Thus, some 98% of these *n*-C_5-asphaltenes should be considered to be resins.

2.1.1 General solvency and chemistry

It has been known for some time that the intermolecular forces between hydrocarbons and nonpolar, non-hydrogen-bonded molecules are, in general, dominated by London dispersion forces. The interaction energy, ε, generated between molecule A and molecule B by dispersion forces is given by the equation