9 Hansen Solubility Parameters of Asphalt, Bitumen, and Crude Oils

Per Redelius

ABSTRACT

Hansen solubility parameters (HSP) are shown to be a useful new tool for understanding compatibility relations among bitumens and crude oils. Bitumen and crude oils are complex mixtures of hydrocarbons which are kept in solution mainly by their mutual solubility. They are not colloidal dispersions as previously thought. Although the solubility of the hydrocarbons is mainly determined by the dispersive interactions, it is not possible to make correct estimates of their stability without also taking polar interactions and hydrogen-bonding interactions into consideration. HSP have proven their ability to give a good estimate of the stability of bitumen and/or crude oil having different origins in relation to solvents and polymers. Relations between the HSP of different materials is visualized using 3D plots showing the HSP as ellipsoids. A more precise determination of the extension of the ellipsoids can be found by turbidimetric titrations with three different titrants, each representing a direction in the HSP space, respectively. It is now possible with the help of simple laboratory experiments to predict the consequences of different courses of action, thus eliminating expensive trial and error testing.

SYMBOLS SPECIAL TO CHAPTER 9

C	Amount of bitumen/total amount of solvent and titrant
P	Stability index given by Equation 9.3
FR	Volume of solvent/total volume of solvent plus titrant
p_a	Defined by Equation 9.1
p_o	Defined by Equation 9.2

INTRODUCTION

Even if most of us are not familiar with bitumen, we all know the "black" roads on which we drive every day. The majority of road surfaces are black because the binding agent used to manufacture the surfacing is bitumen, which is mixed with crushed rock aggregate. Road surfaces can also be grey to white in color, in which case an alternative binder has been used: Portland cement concrete.

Bitumen is a semisolid material that can be produced from certain crude oils by distillation. It can also be found in nature as "natural asphalt." It consists of a mixture of hydrocarbons of different molecular sizes containing small amounts of heteroatoms such as sulfur, nitrogen, and oxygen, as well as traces of metals like vanadium and nickel. Bitumen behaves as a viscoelastic thermoplastic solid at ambient temperature and turns into a viscous liquid at high temperature. It presents unique adhesive and waterproofing properties, which make it ideal in the manufacture of asphalt for road

construction and to use in a wide range of industrial application, from waterproofing in construction to sound dampening in the automotive industry.

The term *bitumen* is not completely unambiguous as it has been given different meanings in different parts of our world. In Europe the term is defined as above, whereas in Canada, for example, it is used for heavy crude oils. In the U.S. the term *asphalt* is used instead of *bitumen*. Sometimes bitumen is confused with tar, which is a product of completely different origin. Tar is produced by dry distillation of coal or wood.

The most common process for production of bitumen is by distillation under vacuum of properly selected crude oils. There are however just a limited number of crude oils which permit direct distillation to proper bitumen grades suitable for production of road asphalt. Although the reserves of such crude oils are very large worldwide, they are not primarily produced as they contain too small amounts of fuel, which is the most important and profitable product for refiners.

The functional properties of bitumen are usually related to its use as binder in asphalt for roads. Thus, the most common properties are related to the rheology of bitumen. As the road construction area is very conservative, and bitumen has been used for about 100 years, most tests are empirical and have been used for a long time. Two of the most common tests are penetration at 25°C and softening point Ring&Ball. The penetration gives a measure of the stiffness of the bitumen at most common service temperatures of a road, whereas the Ring&Ball gives the stiffness close to the highest expected temperature in practice. In Europe bitumens are graded according to their penetration at 25°C — for example, 50/70, where the two numbers give the highest and lowest limit for the particular grade. It is also common, particularly in the U.S., to use viscosity gradation based on viscosity at 60°C. Bitumen is, however, a viscoelastic material with a complex rheology and can thus not be completely described by simple penetration testing and softening point. The development of modern and reliable rheometers — for example, the dynamic shear rheometer (DSR) — has made it possible to describe the full rheology of bitumen.

During the last 20 years we have seen an increase in the use of polymer modified bitumen (PMB) with improved properties. The main reason for modification of bitumen is to improve the rheological properties, particularly to make the binder less sensitive to temperatures. It is desired to have a reasonable stiffness of the binder even at the highest surface temperatures a road can reach on a hot summer day, as well as being reasonably flexible at the lowest temperatures on a cold winter day. Another reason for modification with polymers is to increase durability. This will be improved if a proper polymer is selected.

A large number of different polymers have been tested as modifiers for bitumen. In the end, just a few of them have reached larger commercial use. The main restriction for the choice of polymer is the expected improvement of the rheological properties in comparison with the price of the polymer. But even more important is the compatibility or the solubility of the polymer in the bitumen. Until now, there have been very few tools for prediction of compatibility between the polymer and bitumen, so the development of new PMB has to a large extent been done on a "trial and error" basis. The better understanding of the true nature and the solubility properties of bitumen provided by Hansen solubility parameters (HSP) has given a new tool for understanding of polymer compatibility with bitumen as discussed in the following.

MODELS OF BITUMEN

Crude oils have been found in many places around the world. Although the true origin of crude oils is still under discussion, most scientists agree that they have been formed by degradation and transformation of ancient organisms. The properties of crude oil vary depending on age and conditions during formation. Some crude oils are liquids with low viscosity, whereas others are semisolid materials that have a viscosity making them impossible to handle at room temperature. The low viscosity crude oils contain large amounts of fuel but very little bitumen, if any, and the high viscosity crude oils contain very little fuel but large amounts of bitumen.

From a chemical point of view crude oil is an extremely complex mixture of hydrocarbons. Usually small amounts of heteroatom like nitrogen, oxygen, and sulfur, as well as trace amounts of metals like vanadium and nickel, are found, although the content varies depending on type and origin of the crude oil. The smallest molecules are the gaseous methane, ethane, and propane. These are dissolved in the liquid hydrocarbons. The heaviest molecules have molecular weights higher than 1000 and are thus hydrocarbons with 70 carbon atoms or more. The separation of crude oils into different fractions is done in refineries by distillation, with the different fractions being collected based on their boiling points. The low-boiling fractions consist of gasoline and gas oils. The constituents in these fractions have been characterized by modern analytical techniques until almost every single component has been identified. The heavier fractions (heavy gas oil), and particularly the residue after distillation, have escaped such detailed characterization. Most residual oils are further upgraded by different refining processes to fuels. Bitumen may be produced only after a proper distillation process of a selected crude oil using vacuum. Although the residual oil and bitumen have been extensively analyzed with modern equipment, most of the understanding is in terms of averages of different chemical functional groups or structures. From these data tentative structures of the molecules have been suggested.[1] In fact hardly any one single molecule from the complex mixture has been chemically analyzed. There are several reason why this has been a superior challenge:

- The number of different molecules is very large.
- There is no major population of identical molecules.
- The material is black and viscous.
- The range of molecules of different polarities and sizes is continuous.
- The boiling point is higher than approximately 450°C, making the molecules fairly large.

The most common approach for chemical characterization of bitumen involves a separation into generic fractions based on chromatographic principles. The most common separation procedure is called *SARA analysis* (saturates, aromatics, resins, and asphaltenes). It consists of two principally different steps: first, creation and precipitation of a solid fraction by dilution of the bitumen with *n*-heptane, and then a separation of the soluble fraction with respect to polarity. The precipitated fraction is called *asphaltenes* and is defined as the fraction of bitumen that is insoluble in *n*-heptane. The *n*-heptane soluble fraction is named *maltenes* and is further separated by polarity into three more fractions. These fractions have been given names like "resins," "aromatics," and "saturates." The most common and widespread hypothesis about the structure of bitumen, which is found in most books and papers on bitumen chemistry, teaches that bitumen is a colloidal dispersion of asphaltenes in maltenes. The dispersion is assumed to be stabilized by the resins. The first one to introduce this concept was Nelensteyn (1924).[2] The model was later refined by Pfeiffer and Saal.[3] Although the model might be attractive for mechanical engineering, it is more difficult to accept for an organic chemist, particularly since colloidal dispersions of hydrocarbons in other hydrocarbons are rare, except in the case of polymers. A number of questions are immediately raised: "Do the asphaltenes have enough different chemistry to permit dispersion rather than dissolution?" and "If it is a colloidal dispersion, what is the mechanism for its stabilization?"

Other models that question the existence of micelles have also been proposed. Examples of models are the continuous thermodynamic model by Park and Mansoori[4] and Buduszynski et al.,[5] and the micro structural model as a result from the SHRP development program in the U.S.[6] Recent research has shown that the asphaltenes do not form micelles but are soluble in the maltenes, and thus no micelles can exist in the bitumen.[7,8] These models describe bitumen as a solution of organic material of different polarity and different molecular weight having a kind of mutual solubility in each other. When a solvent such as *n*-heptane is added to the system, the balance is disturbed. Part of the system precipitates. The precipitation behavior of asphaltenes is what could be predicted from regular solution theory and could be described as *flocculation*. In spite of the solubility model

being a more precise description of the true nature of bitumen, it has received surprisingly low acceptance in the research on bitumen and crude oils.

ASPHALTENES

During production, transport, and refining of certain crude oils there are sometimes problems with the formation of precipitates and deposits. The deposits have been claimed to be asphaltenes, and therefore there is considerable interest in them and money spent to save, if the formation of precipitates could be controlled. Thus, extensive research has been performed to investigate the chemistry of asphaltenes[9,10] as well as mechanisms of formation of the precipitates. There is a clear definition of the term *asphaltenes*[11,12] as the material that precipitates on dilution of bitumen or crude oil with *n*-heptane. Most of the characterization work has been conducted on precipitated asphaltenes, and very little attention has been given to asphaltenes in their natural environment in the bitumen. Much confusion has come from the misuse of the term *asphaltenes* to mean all kinds of precipitates from bitumen, suggesting that the insolubles in *n*-heptane could represent precipitates in general. This assumption might have been correct if the asphaltenes were a colloidal fraction in bitumen, but this it is not the case. As will be proven later in this chapter the cause of formation of precipitates is more related to general solubility rather than just solubility in *n*-heptane. The mechanism of precipitate formation is certainly not only an academic matter but is of major importance for the whole oil industry as precipitates may cause blocking and fouling of equipment used in crude oil production as well as in transport and refining. It is worth discussing some of the more common statements about the chemistry of asphaltenes and to compare them with experimental facts.

MOLECULAR WEIGHT

A general statement about the molecular weight of asphaltenes would be that they are high molecular weight material. The true molecular weight of asphaltenes has been under discussion for many years. Investigations using vapor phase osmometry (VPO) on precipitated asphaltenes dissolved in different solvents have shown molecular weights from 1000 up to 10000, depending on the source of asphaltenes. The apparent molecular weight is strongly dependent on the solvent. This indicates that the asphaltenes associate in solution.[1] Other attempts to determine molecular weight using field ionization mass spectrometry (FIMS) reveal an apparent molecular weight of 700–1000. These results also vary depending on crude oil source.[5] It is obvious that the VPO overestimates the true molecular weight due to interactions between the molecules, and FIMS likely gives a more correct value, although there might be a risk that some degradation has taken place in the ion source. Recent studies with fluorescence depolarization techniques have confirmed the FIMS results.[13] It may be speculated that large size molecules are less soluble in *n*-heptane, and thus asphaltenes should consist mainly of high molecular weight material. A high dependency of molecular weights on solubility is well known from polymers. There are, however, several hydrocarbons of lower molecular weight that are not soluble in *n*-heptane (for example, coronene or dibenz(a,h)anthracene, where the very high aromatic content leads to very high dispersion parameters compared with the relatively low dispersion parameter for *n*-heptane in the HSP concept), and similar molecules may be part of the asphaltenes fraction. It is thus reasonable to assume that the lowest molecular weight in the asphaltenes is equal to the smallest molecule with a boiling point at the cut-point of the bitumen. This varies with different crude oils but may be estimated as being 500°C. This roughly corresponds to hydrocarbons with 35 carbon atom, less for polycyclic aromatics and more for *n*-alkanes. The conclusion is that the asphaltenes fraction likely consists of a range of molecules of different molecular weight, which might range from as low as 300 up to more than 1000.

POLARITY

Asphaltenes are claimed to be a "highly polar" fraction in bitumen, in contrast to the more nonpolar oils (maltenes). This statement is based on the fact that asphaltenes are insoluble in *n*-heptane, a nonpolar solvent. The asphaltenes are, however, easily soluble in relatively nonpolar solvents like benzene, toluene, and dichloromethane, whereas they are insoluble in polar solvents like water, glycerine, and methanol. It is thus more correct to state that the asphaltenes are not polar in a chemical sense, but they might be considered as more polar than the other hydrocarbons in bitumen and crude oil. As nitrogen and oxygen are the only atoms in asphaltenes that could contribute significantly to a permanent polarity, an estimation of the relative polarity can be made by considering the amounts of nitrogen and oxygen atoms compared to the amount of carbon atoms. Elemental analyses have revealed that the total amount of oxygen and nitrogen in the asphaltenes is usually lower than 4%.[14] This is not more than about one to three nitrogen and oxygen atoms per asphaltene molecule assuming a molecular weight of about 1000. This is not enough to make them particularly polar. The apparent polarity might, however, be increased by the content of polyaromatic compounds in some asphaltenes. These are polarizable and thus may act as polar molecules in contact with other polar molecules. In spite of this, the asphaltenes remain mainly nonpolar, and the claims that they are highly polar have without any doubts been misleading in the attempts to understand the role of the asphaltenes in bitumen and crude oils.

SOLUBILITY PARAMETERS OF BITUMEN

The first attempts to determine the solubility parameters of bitumens were made using the Hildebrand solubility parameter concept.[15–20] The focus in these investigations was to study the onset of precipitation of asphaltenes and their solubility properties. In these investigations traditional systems using ratios between a good solvent and a poor solvent are used. The choice of good solvent was usually toluene and the poor solvent was usually *n*-heptane, but sometimes other *n*-alkanes were used. This approach gives reasonably good results, as long as it is in accordance with the definition of asphaltenes. As bitumen and crude oil mainly consist of hydrocarbons, the simple Hildebrand solubility parameters were believed to give a good prediction of solubility properties. When the solubility properties of bitumen are extended to more varied types of solvents than aromatic and aliphatic hydrocarbons, the good agreement with the Hildebrand solubility parameter is to some extent lost.[21] The authors of Reference 22, for example, found that all good solvents for bitumen fall between = 15 MPa$^{1/2}$ and = 23 MPa$^{1/2}$, but not all solvents in this range were good solvents. This shows that the Hildebrand solubility parameters are not appropriate for bitumen, probably because there are other interactions between the molecules that are not taken into consideration. The authors of this paper and others[23] found that using two-dimensional solubility parameters gives a better description of the solubility properties, but the best estimation was given by the Hansen three- dimensional solubility parameter.[24,25] There are still some deviations. This indicates that the prediction could be slightly improved if more than three types of interactions are used, but this will make the model unnecessarily complicated.

Determination of solubility parameters of bitumen and crude oil is rather complicated as these consist of a very complex mixture of hydrocarbons. In fact, it is not completely evident that solubility parameters should be applicable for such mixtures, and particularly not if the assumed colloidal model would be correct. Use of common methods based on physical and chemical parameters, which easily can estimate the solubility parameter of pure compounds, cannot be applied to such complicated mixtures as bitumen. The best approach is probably to make solubility tests of the material in a large number of solvents with known solubility parameters and then try to find the best average of the good solvents. Even this seemingly simple approach is rather complicated, however, when applied to bitumen. The first complication comes from the fact that bitumen is very black, and it is rather difficult to see with the eye whether the solution is clear or not. Another complication is that several solvents

may partly dissolve the bitumen, leaving a small precipitate or residue. The third complication is that one has to take the mutual solubility between the bitumen molecules into consideration. The effect of the mutual solubility is that a higher concentration of bitumen results in better solubility, which is contradictory to normal solubility theory that teaches that a saturation level for the solute is reached. In this case solubility becomes better for higher concentrations.

TESTING OF BITUMEN SOLUBILITY

Solubility testing may be used for calculation of the solubility parameters of bitumen by the method given in the following. In the testing of the solubility we find that most solvents give a kind of partial solubility with more or less residue. As bitumen is very black, it is sometimes difficult to notice small traces of precipitate. In uncertain cases a drop of the solution can be placed on a filter paper. If a black dot appears at the spot of the drop, the solution contains precipitate, but if the staining of the filter paper is a uniform darkish brown, it does not contain any precipitate. As it is so difficult to estimate true solubility, it is sometimes better to give a grading of the solubility in several steps, although the final calculation requires only "soluble" or "not soluble." In an experiment using 15 different bitumens, the solubility was determined in 6 different grading levels, ranging from completely soluble to completely insoluble.[26] Each level of solubility was designated as a solubility grade according to the following rules:

1. Totally dissolved: no residue by filter paper test.
2. Almost totally dissolved: light residue was noticed by filter paper test.
3. Partly dissolved: large residue was noticed in dark brown liquid.
4. Slightly dissolved: large residue was noticed in red-brown liquid.
5. Very slightly dissolved: mainly residue in brownish liquid.
6. Not dissolved: colorless or almost colorless liquid.

The bitumens were selected to cover a wide variation of different properties. Some samples were taken from the market, and some were made experimentally for this purpose.

It is known that the solubility of bitumen is concentration dependent. Thus, a fixed concentration was used in all experiments to get comparable data. In all experiments, 0.5 g bitumen was dissolved in 5 ml solvent. In most cases the samples were left to dissolve for at least 24 h and sometimes for up to 48 h.

HILDEBRAND SOLUBILITY PARAMETERS

Solubility data for 15 different bitumens are given in Table 9.1. All solvents with no visible residue (grade 1) were considered as "good solvents," and all others were considered "poor solvents." A bar diagram of the solvents for bitumen No. 1 in relation to the Hildebrand solubility parameter is given in Figure 9.1. It is evident that the majority of the "good solvents" can be found in a range between = 17.8 MPa$^{1/2}$ and = 25.8 MPa$^{1/2}$, but it is also obvious that several "poor solvents" are found in the same range. The range of solubility parameters is slightly higher than claimed in Reference 21, which is probably due to a slightly different selection of solvents and bitumen types. The results confirm the earlier findings that the Hildebrand solubility parameter is of little or no value to predict solubility properties or compatibility between solvents or other materials with bitumen. One may speculate that the reason could be the presence of other kinds of interactions in bitumen such as, for example, polar interactions, hydrogen bonding, or π-interactions between the molecules. If these interactions are of significant importance, it explains the poor correlation with the Hildebrand solubility parameter, and also indicates that a better correlation may be achieved when more interactions are taken into consideration.

TABLE 9.1
Solubility Test of 15 Different Bitumens in 42 Different Solvents

Solvent	Bitumen Sample – Code No.														
HSP No. and Name	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
	Solubility Grade														
7 – Acetone	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4
11 – Acetophenone	1	2	2	3	3	1	1	1	2	2	2	2	2	1	2
46 – Aniline	4	4	4	4	4	4	4	5	4	4	4	4	4	5	4
52 – Benzene	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
92 – 1-Butanol	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
102 – n-Butyrolactone	2	2	3	2	2	2	2	3	3	2	2	2	2	2	2
115 – y-Butyrolactone	5	5	5	5	5	6	5	5	5	5	5	5	5	5	5
122 – Carbon tetrachioride	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
148 – Chloro benzene	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
182 – Cyciohexanol	3	4	5	3	3	3	3	4	3	3	3	3	3	5	5
209 – Diacetone alcohol	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
234 – Dichlorobenzene	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
255 – Diethylether	3	3	3	3	3	2	2	3	3	2	2	2	2	3	3
263 – Diethylene glycol	6	6	5	6	6	6	6	6	6	6	6	6	6	6	6
297 – Dimethylformamide	5	4	4	4	5	4	4	5	4	4	4	4	4	4	4
303 – Dimethylsulfoxide	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
306 – 1,4-Dioxan	3	3	3	3	3	3	2	3	3	3	3	3	3	3	3
325 – Ethanol	5	6	5	5	6	6	6	6	6	6	6	5	6	6	6
326 – Ethanolamine	6	6	5	5	6	6	6	6	6	6	6	5	6	6	6
328 – Ethyl acetate	4	4	4	4	4	3	3	3	4	4	4	4	3	4	4
367 – 1,2-Dichloroethane	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
368 – Ethylene glycol	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6
375 – Ethylene glycol butyl ether	3	3	4	3	3	3	3	3	3	3	3	3	3	3	3
376 – Ethylene glycol ethyl ether	5	5	5	5	5	5	5	5	5	5	5	4	5	5	5
380 – Ethylene glycol methyl ether	5	5	5	5	5	5	5	5	5	5	5	5	5	6	5
397 – Formamide	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6
417 – n-Hexane	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3
438 – Isophorone	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
456 – Methanol	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6
481 – Methylethyl ketone	3	3	4	3	3	3	3	3	3	3	3	3	3	3	3
491 – Methylisobutyl ketone	2	1	3	2	2	2	2	3	2	2	2	2	2	2	3
521 – N-Methyl-2-pyrrolidone	3	3	3	3	3	3	3	4	3	3	3	3	3	3	3
524 – Methylene chloride	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
532 – Nitroethane	5	4	4	4	5	5	4	5	4	5	4	4	4	4	5
534 – Nitromethane	5	5	5	5	5	5	5	5	5	5	5	4	5	5	5
536 – 2-Nitropropane	4	4	4	4	4	5	4	4	4	4	4	3	4	4	4
584 – Propylene carbonate	6	5	6	5	6	6	6	6	6	6	6	5	5	6	6
585 – Propylene glycol	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6
617 – Tetrahydrofuran	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
637 – Toluene	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
649 – Trichloroethylene	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
698 – Xylene	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1

Note: The solubility is graded from 1 (completely soluble) to 6 (completely insoluble).
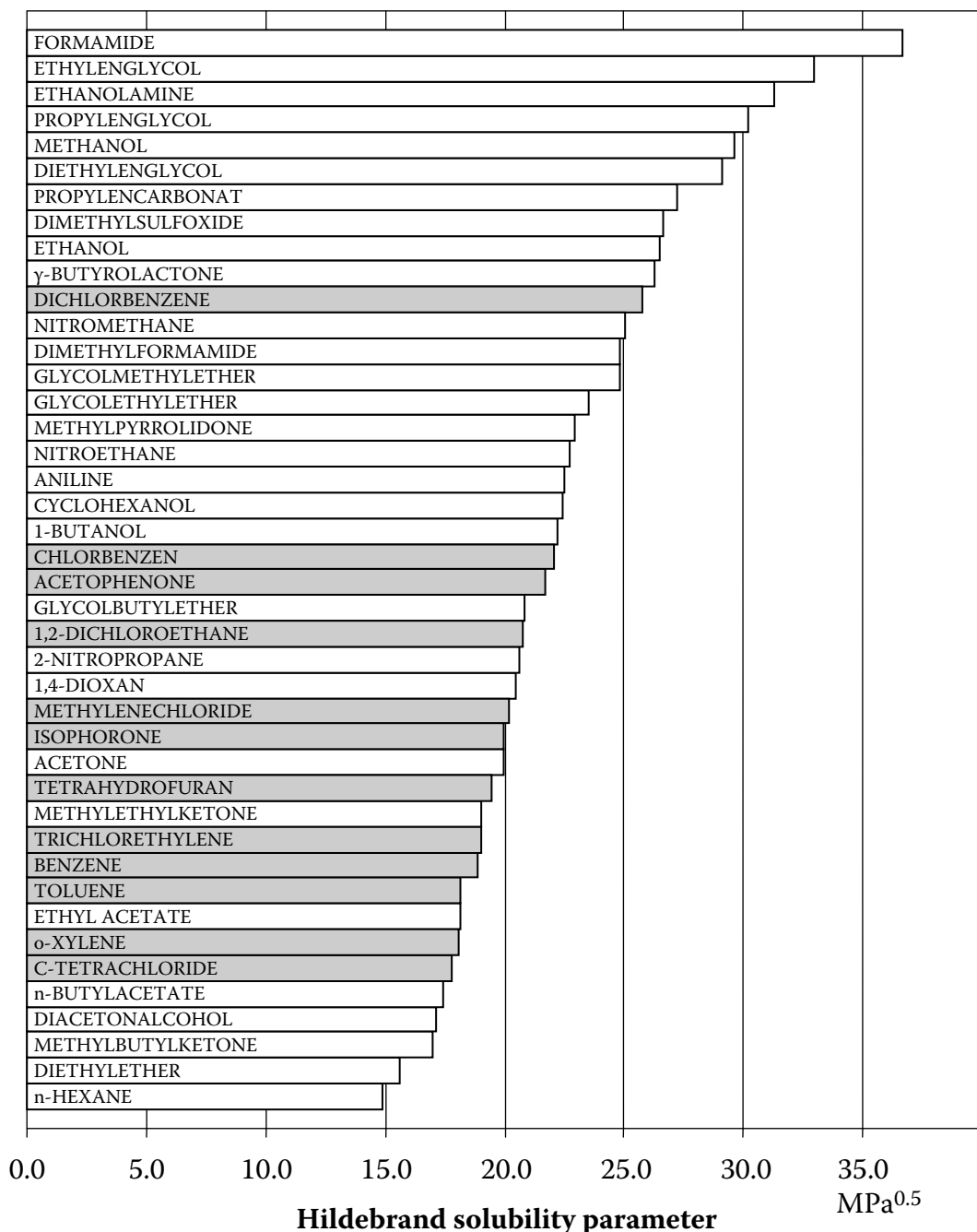
FIGURE 9.1 Solubility of bitumen No 1 (Table 9.1) in different solvents of known Hildebrand solubility parameter. White bars = poor solvents, gray bars = good solvents.

HANSEN SOLUBILITY PARAMETERS (HSP)

The data set for bitumen No.1 in Table 9.1 was used for testing whether HSP gives a better model for bitumen solubility than Hildebrand solubility parameters. HSP consists of three components, each giving a quantitative value for the dispersion (D), polar (P), and hydrogen bonding (H)
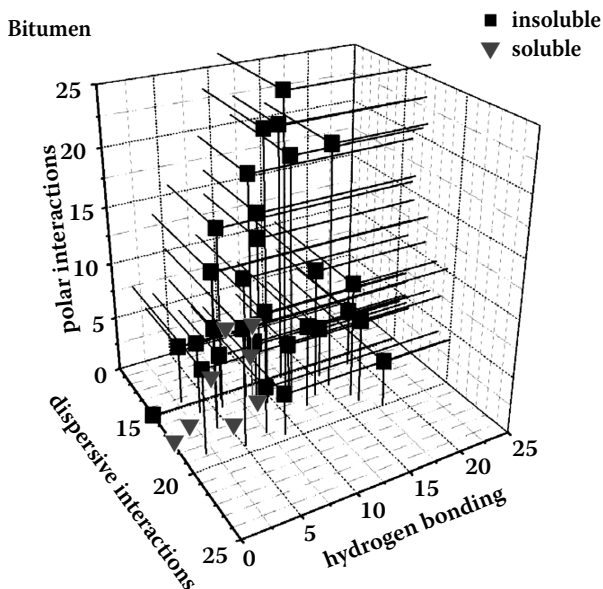
FIGURE 9.2 Plot of the solvents in Table 9.1, bitumen No.1, in a 3D, x-y-z plot, where each axis is one of the Hansen solubility parameters.

interactions, respectively. The suitability of HSP may be illustrated by using a three-dimensional (3D) diagram where each axis constitutes one of the interactions. All solvents with a solubility grade 1 were considered as "good solvents" and all other grades as "poor solvents."

The result is illustrated in Figure 9.2 where all "good solvents" are falling within a certain region separated from the "poor solvents." This confirms that the solubility properties of bitumen can be reasonably well predicted by HSP. Although the "good solvents" are found in a region of relatively high dispersion interaction and relatively low polar and hydrogen bonding interaction, it seems like the latter two types of interactions are still of fundamental importance for understanding the properties of bitumen. Even if we cannot completely rule out the possibility that there exist other types of interactions, we may, however, conclude that the HSP estimate is good enough, and particularly for understanding the true nature of bitumen. It can be assumed that the same situation is valid also for crude oils, which indicates that the use of HSP would be a valuable tool, also, for crude oil production, transport, and processing.

THE SOLUBILITY SPHERE

Chapter 1 includes a discussion of a computer program called SPHERE for calculation of the best estimated HSP as well as the radius of the best fitted pseudo sphere, which includes the "good solvents" and excludes the "poor solvents," based on a set of solubility data. The program was applied on the data in Table 9.1 for calculation of the best estimate for HSP for 15 bitumens. The program permits only two levels of solubility, "good solvents" and "poor solvents," however, whereas the solubility in Table 9.1 was determined in 6 grades. For comparison, the HSP were calculated using two different criteria for "good solvents." In the first calculation only the best solvents (grade 1) were selected as "good solvents" and then in a second calculation the two best grades (1 and 2) were taken as "good solvents." All other solvents were considered as "poor solvents." The results are listed in Table 9.2. It is obvious that the calculated HSP for the different bitumens become slightly different, depending on the choice of solubility grade for the "good solvents." Although the different bitumens are selected to represent a range of products produced

TABLE 9.2
Calculated HSP for 15 Bitumens Using Two Levels of Solubility as the "Good Solvents"

	Grade 1 = "Good Solvents"				Grades 1 and 2 = "Good Solvents"			
Bitumen	D	P	H	RAD	D	P	H	RAD
1	18.0	4.8	3.2	5.5	17.9	5.1	3.1	5.8
2	17.6	5.0	2.8	5.5	17.9	5.1	3.1	5.8
3	17.9	4.5	3.3	5.3	18.0	4.8	3.2	5.5
4	17.9	4.5	3.3	5.3	17.5	4.7	2.7	5.7
5	17.9	4.5	3.3	5.3	17.5	4.7	2.7	5.7
6	18.0	4.8	3.2	5.5	17.4	4.0	2.0	6.6
7	18.0	4.8	3.2	5.5	17.9	3.3	2.5	7.3
8	18.0	4.8	3.2	5.5	18.0	4.8	3.2	5.5
9	17.9	4.5	3.3	5.5	18.1	5.5	2.9	6.0
10	17.9	4.5	3.3	5.5	17.4	4.0	2.0	6.6
11	17.9	4.5	3.3	5.5	17.4	4.0	2.0	6.6
12	17.9	4.5	3.3	5.5	17.4	4.0	2.0	6.6
13	17.9	4.5	3.3	5.5	17.4	4.0	2.0	6.6
14	18.0	4.8	3.2	5.5	17.9	5.1	3.1	5.8
15	17.9	4.5	3.3	5.5	18.1	5.3	3.1	5.9
Average	17.91	4.63	3.23	5.46	17.72	4.56	2.64	6.13

from different crude oils as well as different process conditions, the difference in HSP is surprisingly small. The average HSP for bitumen based on calculations using "grade 1" as "good solvents" are D = 17.9 MPa$^{0.5}$, P = 4.6 MPa$^{0.5}$, and H = 3.2 MPa$^{0.5}$. The "sphere" radius (RAD) is 5.5 in the same units.

The small variation in HSP between the different bitumens is a result of the small variation in solubility as seen in the data from Table 9.1, with only a few solvents giving different solubility for different types of bitumen. If solvents giving a small residue (solubility grade 2) are accepted as "good solvents," one still gets a very similar average HSP, but the variation between the different binders becomes more evident. The main general trend is a small shift toward lower hydrogen-bonding interactions and a larger radius of the solubility sphere. The larger radius is an expected consequence when more solvents are accepted as "good solvents." The decrease in hydrogen bonding is more difficult to explain, but it might indicate that the "sphere" is not completely symmetrical.

In applications where bitumen is used — for example road building and water proofing — it is well known that bitumen produced by different methods and from different crude oils have different performance. Although the 15 bitumens listed in Table 9.1 are primarily intended for use in the water-proofing industry, they are selected and manufactured to cover a wide variety of crude sources as well as different types of manufacturing processes. Laboratory experiments, and field experience for some of the samples, show that there is a large variation in performance of the bitumens. One example is the compatibility with polymers, such as styrene/butadiene/styrene (SBS), which varies to a large extent. It is expected that some of these differences should be reflected in the different chemical compositions of the bitumens and that these same differences should also be reflected in the HSP. The results given in Table 9.2 show, however, that there are only very small differences, particularly when calculated with only the best solvents as "good solvents." If "grade 2" is also accepted as "good solvent," the variation between the binders becomes more evident, but a comparison with known composition and performance still does not allow a simple correlation.

This lack of correlation is without any doubt disappointing. We may however speculate that it is mainly due to a lack of precision. The solvents in Table 9.1 are selected to cover a large area in the 3D solubility space, whereas most bitumens are mixtures of hydrocarbons where the differences in chemical properties are relatively small. Obviously it is necessary to have much better precision than the solubility testing as shown in Table 9.2. The better precision may be achieved in two ways. The first improvement is to use a better selection of solvents for the solubility testing. Solvents that have HSP close to the border of solubility are preferred to better define the border. Another approach is to perform turbidimetric titrations to estimate the exact HSP at the precipitation point calculated from the ratio of a "good solvent" and a "poor solvent" at precipitation. This approach is further discussed as BISOM titrations below. An improved selection of solvents should focus on solvents with RED values around 1, as these are close to the boundary. The RED (relative energy difference) concept is discussed in Chapter 1. As much variation as possible with respect to the dispersion, polar, and hydrogen bonding interactions is desired. This requires, of course, that an approximate HSP of the material is already available. And finally, nontoxic and inexpensive solvents are preferred. A suggested set of solvents, optimized for determination of HSP of bitumens and similar materials is presented in Table 9.3. These solvents have RED between 0 and 2 related to the estimated HSP of bitumen as presented above. When using this set of solvents for a Venezuelan binder, the HSP is D = 18.6 MPa$^{0.5}$, P = 3.0 MPa$^{0.5}$, H = 3.4 MPa$^{0.5}$, and the radius of the sphere is 6.3 in the same units. This set of numbers is different from the previously estimated values in Table 9.2. A comparison can be made with binder No. 9 (D = 17.9 MPa$^{0.5}$, P = 4.5 MPa$^{0.5}$, H = 3.3 MPa$^{0.5}$, and a radius of 5.5 MPa$^{0.5}$), which is similar to the binder used to obtain the data reported in Table 9.3. If the HSP of other types of materials than bitumen are going to be measured, also in the petroleum area, it is suggested that other sets of solvents may be needed to get the best precision. Examples are light crude oils, distillates, base oils, petroleum waxes, etc.

COMPUTER PROGRAM FOR CALCULATION AND PLOTTING OF THE HANSEN 3D PSEUDOSPHERE

The SPHERE program described in Chapter 1 has given very good approximations of the HSP as well as the diameter of the (solubility) sphere for a large number of materials. In the SPHERE program, a factor 4 is used as a multiplier for the difference in the dispersion interactions of the species concerned. This means that the "sphere," with the three different types of interactions as coordinates, is in fact an ellipsoid (spheroid). A disadvantage with the SPHERE program is the lack of a tool for plotting the ellipsoid in a diagram that would be beneficial for illustration purposes. Thus, an improved program which permits 3D plotting of the ellipsoid was developed. During the development it was discussed that although the factor 4 has been proven to be a good approximation for most materials there might be complex mixtures which could give a better fit with experimental data if other factors were used. The new program has the following features:

- Permits plotting of the HSP solubility ellipsoid in a 3D diagram.
- Permits plotting of up to three ellipsoids representing different materials in the same 3D diagram.
- The input data should be based on "poor solvents," "good solvents," and "borderline solvents."
- There should be an option to make other types of fitting than the SPHERE program to the available data.
- Negative values of HSP interaction coefficients are not taken into consideration.

TABLE 9.3
Solvents Used for Determination of the Solubility of Bitumen with Their HSP in MPa$^{0.5}$

HSP No.	Solvent	D	P	H	Solubility
56	Benzophenone	19.6	8.6	5.7	1
93	2-Butanol	15.8	5.7	14.5	0
717	2-Butyl octanol	16.1	3.6	9.3	0
1060	Butyraldehyde	15.6	10.1	6.2	0
118	Caprolactone (epsilon)	19.7	15.0	7.4	0
955	1-Chloro pentane	16.0	6.9	1.9	1
156	Chloroform	17.8	3.1	5.7	1
182	Cyclohexanol	17.4	4.1	13.5	0
183	Cyclohexanone	17.8	6.3	5.1	1
184	Cyclohexylamine	17.2	3.1	6.5	1
188	Cyclopentanone	17.9	11.9	5.2	0
194	*cis*-Decahydronaphthalene	18.8	0	0	1
1019	1.4-Dichlorobutane	18.3	7.7	2.8	1
791	1.1-Diethoxy ethanol (acetal)	15.2	5.4	5.3	0
269	Ethylene glycol monoethyl ether acetate	16.2	5.1	9.2	0
1084	Diisopropylamine	14.8	1.7	3.5	0
889	1.2-Dimethoxybenzene	19.2	4.4	9.4	0
328	Ethyl acetate	15.8	5.3	7.2	0
333	Ethyl benzene	17.8	0.6	1.4	1
353	Ethyl lactate	16.0	7.6	12.5	0
345	2-Ethyl-hexanol	15.9	3.3	11.8	0
758	Ethylene glycol dibutyl ether	15.7	4.5	4.2	0
412	Hexadecane	16.3	0	0	0
419	Hexyl acetate	15.8	2.9	5.9	1
440	Isopropyl acetate	14.9	4.5	8.2	0
1063	Laurylalcohol	17.2	3.8	9.3	0
450	Mesityl oxide	16.4	6.1	6.1	0
464	Methyl acetate	15.5	7.2	7.6	0
472	Methyl benzoate	17.0	8.2	4.7	1
481	Methyl ethyl ketone	16.0	9.0	5.1	0
500	1-Methyl naphthalene	20.6	0.8	4.7	1
502	Methyl oleate	14.5	3.9	3.7	0
1029	3-Methyl-2-butanol	15.6	5.2	13.4	0
524	Methylene dichloride	18.2	6.3	6.1	1
531	Nitrobenzene	20.0	8.6	4,1	0
546	Oleyl alcohol	14.3	2.6	8.0	0
1051	Pyrrolidine	17.9	6.5	7.4	1
704	Salicylaldehyde	19.4	10.7	14.7	0
617	Tetrahydrofuran	16.8	5.7	8.0	1
618	Tetrahydronaphthalene	19.6	2.0	2.9	1
885	1.2.3.5-Tetramethylbenzene	18.6	0.5	0.5	1
637	Toluene	18.0	1.4	2.0	1
953	2-Toluidine	19.4	5.8	9.4	0

TABLE 9.3 (CONTINUED)
Solvents Used for Determination of the Solubility of Bitumen with Their HSP in MPa$^{0.5}$

HSP No.	Solvent	D	P	H	Solubility
648	1.1.2-Trichloroethane	18.2	5.3	6.8	1
653	Tricresyl phosphate	19.0	12.3	4.5	0
667	1.2.4-Trimethylbenzene	18.0	1.0	1.0	1
670	2.2.4-Trimethylpentane	14.1	0	0	0
698	*o*-Xylene	17.8	1.0	3.1	1

Note: Good solvents are indicated with a "1" and poor solvents are indicated with a "0." This set of solvents better defines the boundary region as discussed in the text.

The computer program hsp3D was developed on a MATLAB platform.[27] The program permits 6 different kinds of fit to create a 3D body, based on a large set of solubility data. In each case all good solvents are included and all poor solvents are excluded.

1. ***Convex hull*** fit which could be described as the points for the good solvents being wrapped with a flexible membrane. This fit makes use of only the good solvents.
2. The ***Hansen fit*** is the same type of fit as in the SPHERE program using Equation 1.9. The search algorithm is however slightly different, so the results compared to the SPHERE program might be slightly different.
3. ***Axis-aligned ellipsoid*** fit, which is similar to the Hansen fit above, but with variable coefficients for the three axes (the three types of interactions). In the normal ***Hansen fit*** a factor 4 is used for transformation of the dispersion interactions, in the axis-aligned fit this factor as well as the factors for the other two axes are adjusted to optimize the fit.
4. ***Rotated ellipsoid*** fit, which is similar to the Axis-aligned ellipsoid above but allows the body to rotate and tilt to obtain a better fit. In all of the fits above it is assumed that the axis of the ellipsoid is aligned along the three axes. In the rotated ellipsoid the program can tilt the axes to improve the fitting, and at the same time also optimize the transformation factors for the axes.
5. ***Rotated ellipsoid with convex hull center and volume***. The body for this fit has the same center coordinates and volume as the convex hull but attempts to align with the "good solvents" to minimize distance to its surface.
6. ***Minimum enclosing ellipsoid*** is the body with the smallest volume that encloses all the "good solvents."

The features of the improved computer program hsp3D were further examined using the solubility data from Table 9.3. The results from the different available fits were compared in 3D diagrams with three different fits in each (Figure 9.3 and Figure 9.4). From Figure 9.3 it is evident that there is a very small difference between the resulting ellipsoids using different fitting algorithms. Transformation or tilting of the axis did not give any major improvement compared to the SPHERE data. This indicates that the factor 4 in Equation 1.9 seems also to be valid for such complicated mixtures as bitumen. In Figure 9.4 we see a comparison between the convex hulls, which probably is the best figure to describe the solubility properties, as it is the truest body constructed without approximations. This might be the first choice if different materials are going to be compared. Another way of comparing the quality of the fit using the different algorithms is to compare some indicators like volume, number of outliers, and fitting coefficient.
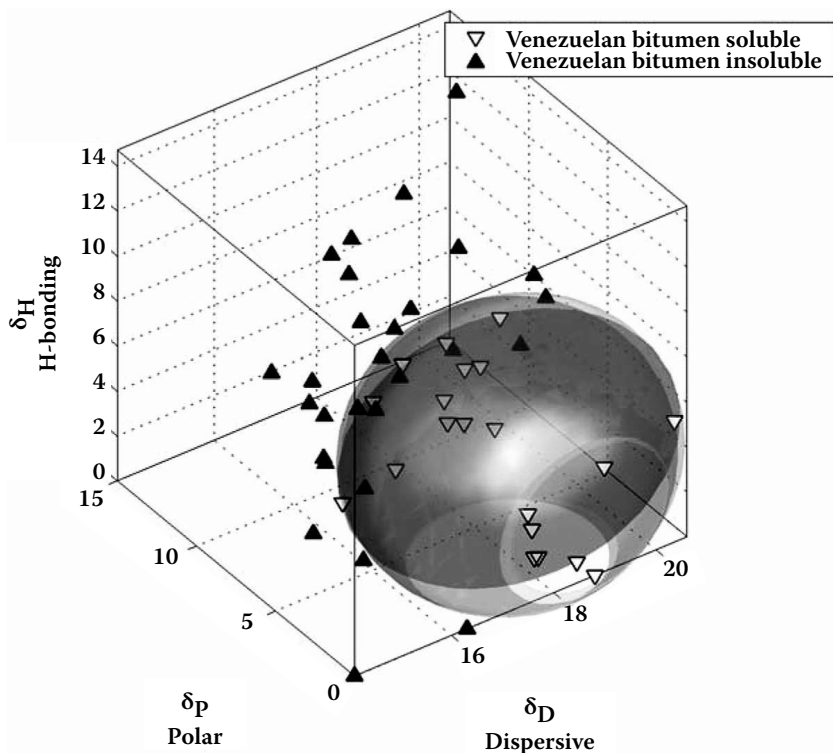
FIGURE 9.3 3D solubility body of bitumen using computer program hsp3D. The ellipsoids according to Hansen fit, axis-aligned ellipsoid, and rotated ellipsoid are compared.

It can be seen in Table 9.4 that the HSP for the particular Venezuelan bitumen, and most likely also for other bitumens, is more or less independent of the fitting method. This shows that the approximation with an ellipsoid is rather robust. The best solubility body is the one having the smallest volume, the least number of outliers, and the highest fitting coefficient. The Hansen sphere and the axis aligned ellipsoid give almost the same results. The rotated ellipsoid gives a smaller volume but at the expense of more outliers and less good fitting. The most extreme case is the ellipsoid with the same center point (HSP) and the same volume as the convex hull, which gives the smallest volume, most outliers, and less good fitting. This is, of course, a result of the algorithm. If a body with multiple corners is transferred to an ellipsoid with the same volume, most of the corners mathematically will fall outside the ellipsoid. The fact that the coordinates are different indicates that the convex hull is skewing for this material compared to the Hansen Sphere. This might, however, also be due to an uneven selection of solvents rather than properties in the material.

COMPONENTS OF BITUMEN

Bitumen is a very complex mixture of different hydrocarbons but yet with very similar properties. It is almost impossible to isolate chemically uniform fractions; instead, bitumen is usually divided into fractions that are defined by the selection of the separation method. Perhaps the most common separation of bitumen is the precipitation of asphaltenes from the maltenes. As stated above, the definition of asphaltenes is the material that precipitates upon dilution of bitumen (or oil) with *n*-heptane.[11,12] The fractionation could also be considered as an extraction of *n*-heptane soluble molecules from the bitumen, leaving a residue named "asphaltenes." The asphaltene-free fraction from bitumen is called "maltenes." In almost all of the literature about bitumen and asphalt it is
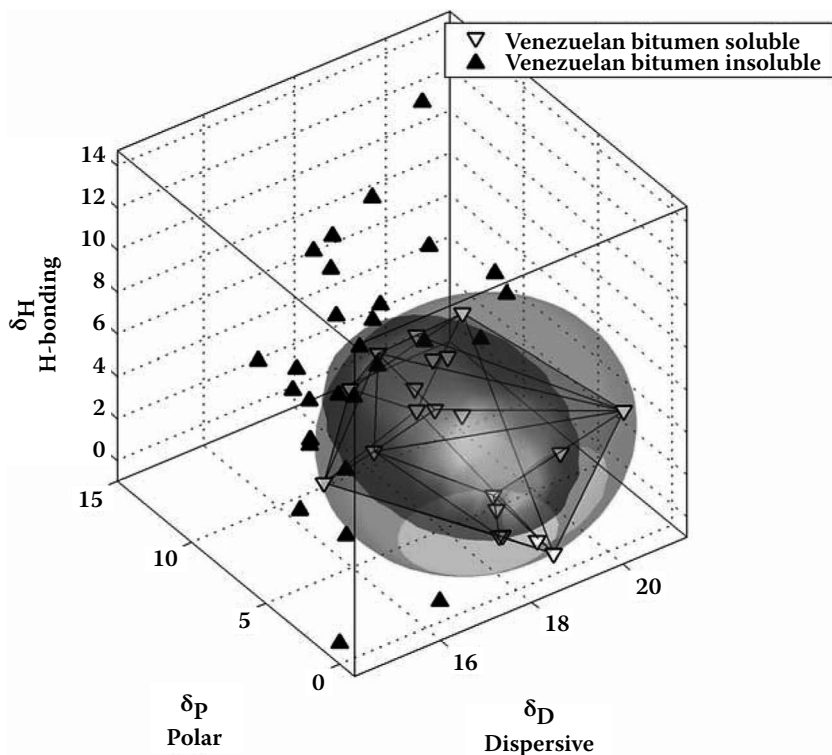
FIGURE 9.4 Plots of fit of bitumen solubility data using hsp3D showing the Convex hull model, the ellipsoid with the same center and volume, and also the minimum enclosing ellipsoid.

TABLE 9.4
Precision Indicators for Fitting the Data in Table 9.3 to Ellipsoids

Type of Fitting	D	P	H	Volume	Outliers	Fit Coeficient
Hansen Sphere	18.4	3.9	3.6	399	3	0.980
Axis aligned ellipsoid	18.3	3.9	3.5	399	3	0.987
Rotated ellipsoid	18.4	4.1	3.6	242	5	0.939
Ellipsoid: convex hull c and v	18.0	4.4	4.1	99	10	0.798
Minimum enclosing ellipsoid	18.4	4.1	3.7	371	6	0.983

Note: Outliers = number of "good solvents" with RED > 1 + number of "poor solvents" with RED < 1.

erroneously claimed that the asphaltenes are dispersed in the maltenes as a colloidal dispersion. That this is not correct can easily be proven by solubility testing and plotting of the solubility ellipsoids using the hsp3D program. Asphaltenes isolated by the standard method ASTM D6560[12] have been tested for solubility in the set of solvents listed in Table 9.3. The isolated maltene fraction is also tested for solubility in the same set of solvents. The solubility ellipsoids for the two materials are plotted using the hsp3D program (Figure 9.5).

Figure 9.5 confirms that there is no overlap of the HSP for *n*-heptane and the ellipsoid for asphaltene, and it can be considered that they are so far apart that the asphaltenes are not soluble in *n*-heptane. This agrees with the definition of asphaltenes. It is also evident that the HSP of the
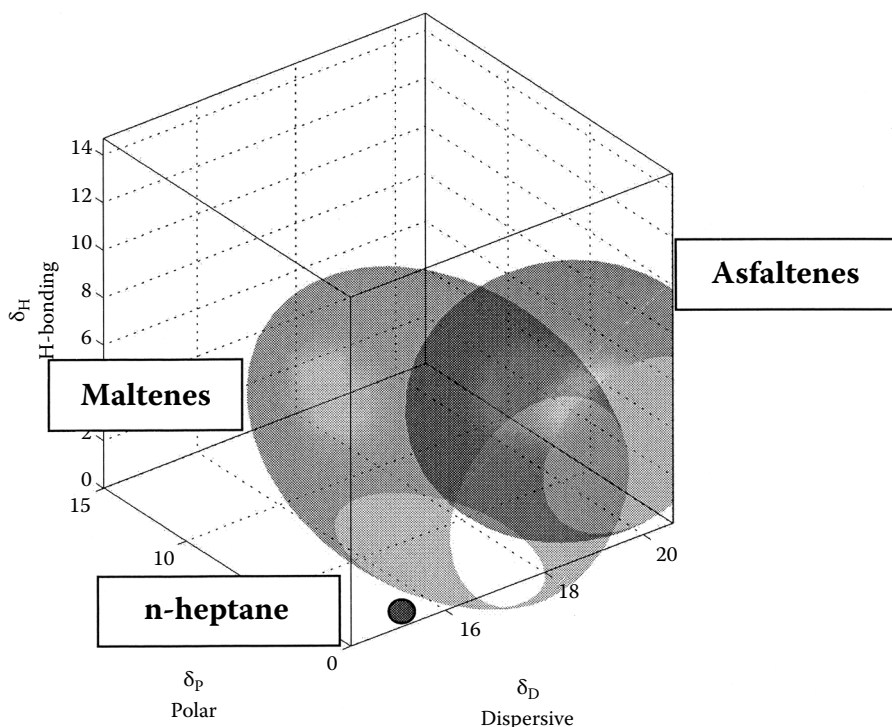
FIGURE 9.5 Solubility ellipsoids for asphaltenes and maltenes compared with *n*-heptane.

maltenes is different from the HSP of *n*-heptane. Thus, there is no reason to believe that the asphaltenes will appear in the same state in maltenes as in *n*-heptane. The fact that they are insoluble in *n*-heptane is no evidence that they are insoluble in the maltenes. In fact, there is such a large overlap between the solubility ellipsoids of the maltenes and the asphaltenes that they are quite likely to be soluble in each other. This strongly suggests that the asphaltenes are not dispersed in the maltenes as a colloidal dispersion but are more likely dissolved. It might be argued that some of the asphaltenes molecules with extreme HSP might not be soluble in the maltenes, and thus could still be dispersed rather than dissolved. This is, however, less likely as long as the continuum in the asphaltenes and the maltenes is kept intact. In some experiments the asphaltenes have been further fractionated into "soluble" asphaltenes and "insoluble" asphaltenes.[28] If a fraction of the "insoluble" asphaltenes is mixed with the maltenes they might be insoluble. The reason is that the continuum has been broken and would probably not reflect the conditions in the original sample. In fact, removal of fractions from either the maltenes or the asphaltenes will create a risk for phase separation. This is also the reason why one should be very careful in making any claims or predictions of bitumen properties based on the properties of fractions.

BITUMEN AND POLYMERS

It is a very common practice to improve bitumen properties by adding different additives. The reason is to improve the low temperature properties by making the bitumen softer at very low temperatures (<20°C) and at the same time make the bitumen more stiff at higher temperatures (+60°C). The temperatures are representative of the highest and lowest temperatures on the surface of an asphalt road during winter and summer, although in reality the maximum and minimum temperatures vary considerably with geographical location. The most common and well known modification is the addition of different types of polymers to bitumen. Probably all possible types

of polymers have been tested in bitumen — for example, plastomers, elastomers, two component curing systems, and even recycled rubber and plastics. The requirements on such products are, however, very strict, so in practice very few polymers have found a wider use as modifiers for bitumen. One of the most important requirements is the "compatibility" between the bitumen and the polymer. In this case, the meaning of "compatibility" is the stability against phase separation. Another important factor is the cost efficiency, which means that a good improvement of the bitumen properties is achieved with fairly small levels of polymeric additives. In the road building industry where the volumes are large and the price constraints are strong, the maximum level of modification is typically below 5%. In the roofing industry higher levels are generally accepted as product quality is more important than price.

The Hansen solubility parameter concept provides a good tool for selection of suitable polymers, based on predictions of compatibility between different polymers and bitumen. If the HSP of a particular polymer is not known, it can easily be determined with a simple solubility test as described above. To illustrate the usefulness we may compare two types of polymers with known HSP with the HSP of bitumen. To make it simple we selected two polymers, polyethersulfone (PES) and polyethylensulfide, for which solubility data are presented in Chapter 5 and Chapter 18, respectively. Neither of these polymers is a common modifier for bitumen. The solubility ellipsoids of the two polymers compared to the HSP sphere of Venezuelan bitumen are illustrated in Figure 9.6. It is evident that PES is not soluble in bitumen, as the solubility ellipsoid is almost completely outside the ellipsoid of bitumen. In case PES is mixed with bitumen it will be dispersed rather than dissolved.
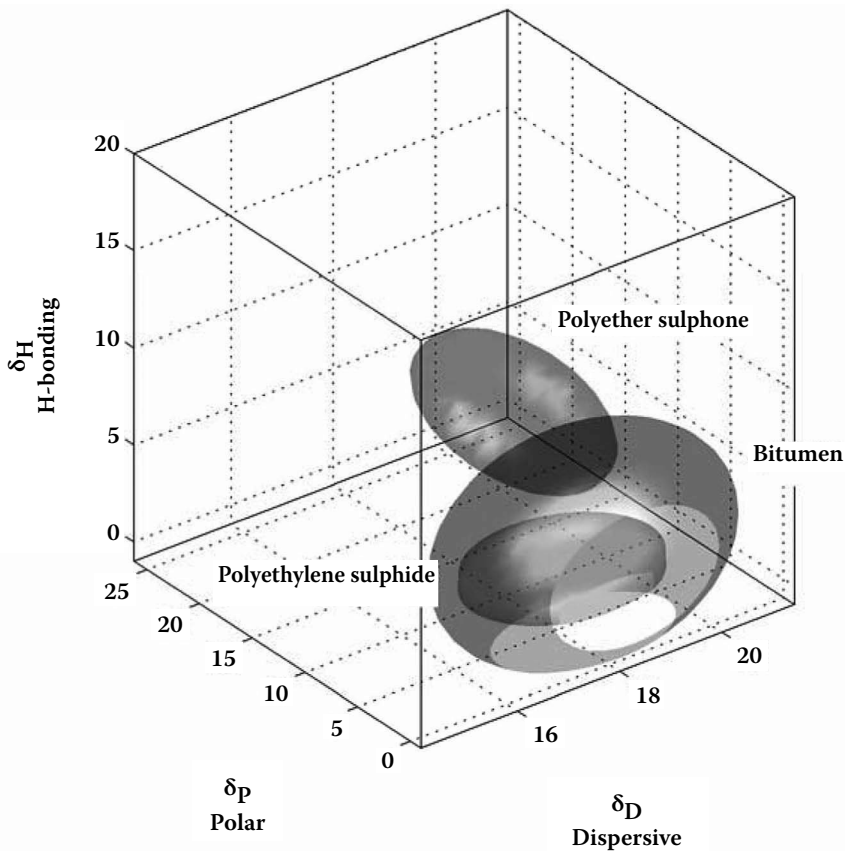

FIGURE 9.6 Solubility ellipsoid for bitumen compared with solubility ellipsoid for polyether sulfone and polyethylene sulfide.
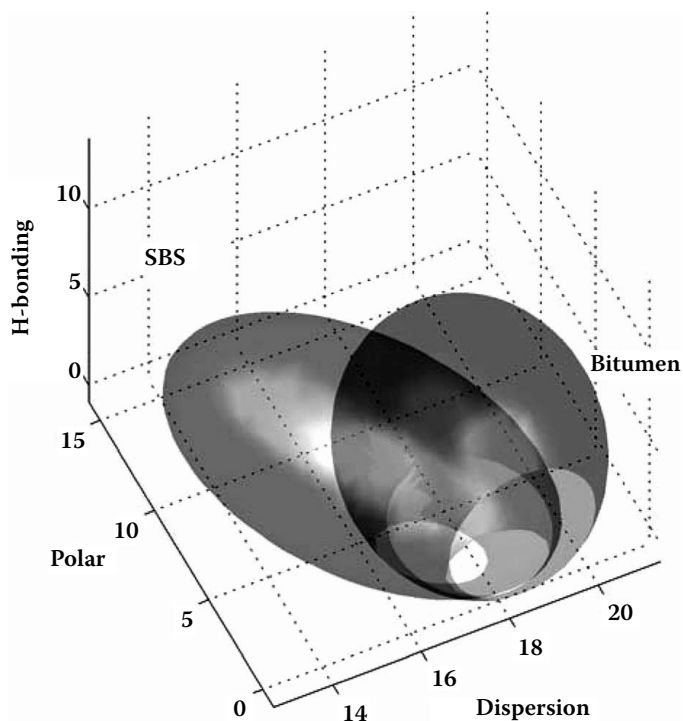
FIGURE 9.7 Solubility ellipsoid of bitumen compared to a solubility ellipsoid of SBS.

The effect will be an increase in stiffness at temperatures where PES will act as a solid filler. In case of polyethylenesulphide the solubility ellipsoid is inside the ellipsoid of bitumen, and thus polyethylenesulphide is expected to be completely soluble (compatible). As the polymer is completely soluble we do expect the effect to be related to the concentration of the modifier. No problem with storage stability is foreseen.

None of the polymers discussed above have been frequently used for modification of bitumen. The polymer most commonly used for bitumen is styrene butadiene block copolymer (SBS) or similar polymers based on styrene and butadiene. This polymer gives a good modification effect at fairly low concentration (3–5%). The major advantages are increased stiffness at fairly high temperatures (60°C) and improved flexibility at low temperature. The higher stiffness will decrease the risk for rutting (permanent deformation). This risk is highest on hot, sunny summer days. The HSP of SBS was determined with a solubility test as above and the solubility ellipsoid was plotted together with bitumen in Figure 9.7. It is evident that there is a considerable overlap between the SBS and the bitumen. This implies partial solubility. In reality the situation is even more complicated as SBS consists of two different kinds of polymer segments based on butadiene and styrene, respectively. Each of these segments has different HSP. SBS belongs to the group of thermoplastic elastomers. These become plastic-like and can be processed at higher temperatures, at the same time having rubber-like properties at room temperature because of physical crosslinking caused by polystyrene and polybutadiene being mutually insoluble. The polystyrene blocks have a glass transition temperature of approximately 100°C, and therefore SBS is fairly workable at temperatures above 100°C but is still rubber-like at lower temperatures. It has been proposed that the same mechanism is also giving a good effect in bitumen, with the polystyrene being soluble/compatible in bitumen at the mixing temperature (180°C) but becoming less soluble or insoluble at lower temperatures. The effect is the same physical crosslinking as in pure SBS. Figure 9.7 supports this
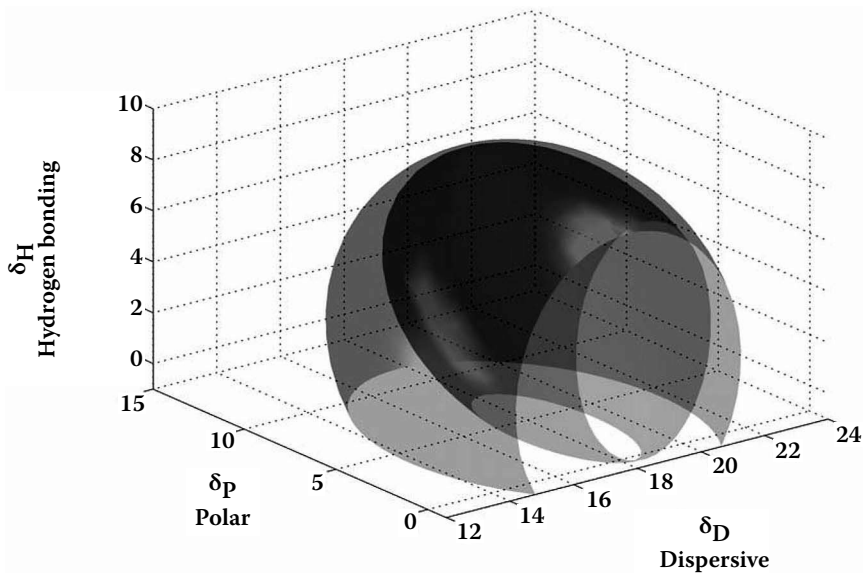
FIGURE 9.8 Comparison between a heavy Venezuelan crude oil (Laguna) and a light crude oil (Leadon) from the North Sea.

picture as the part of the SBS ellipsoid located outside bitumen presumably represent the polysty-rene, although this has not been verified by experiments.

CRUDE OIL

Crude oil is found almost all over the world with large reserves in the Middle East, Russia, China, North America, Venezuela, and the North Sea, just to mention a few examples. It is produced by drilling wells in the ground or under the sea. Crude oil is pumped up to the surface where it is transported by pipeline or ships to refineries for further processing into desired products. The crude oils are very different, depending on origin. Some crude oils are very light and contain a large percentage of the most desired products, gasoline and diesel fuel, whereas other crude oils are heavy and bitumen-rich. The heaviest of the crude oils have such a high viscosity that they can not be pumped at normal ambient temperature but always have to be handled at higher temperature. Only a few selected crude oils can be used for production of high quality bitumen suitable for making asphalt for roads. Under certain conditions of storage and transport of crude oils there are sometimes problems with the formation of precipitates and/or deposits. These might decrease the capacity of pipelines by formation of solid contaminants in the crude oil. These deposits are sometimes blamed on asphaltenes and sometimes on waxes. The exact nature of these precipitates and the mechanism of their formation are not fully understood and is thus the subject for intense research. There are large economic benefits to be gained if the problem with deposits could be decreased. The use of HSP to study the precipitates in comparison with the solubility parameters of the crude oils is a good tool for better understanding of the precipitation mechanism. To have the complete picture it is also necessary to understand how temperature and pressure influence the HSP of different molecules in the crude oil.

The difference between two crude oils, heavy Venezuelan Laguna and medium Leadon from the North Sea, may be illustrated by 3D plots of the solubility ellipsoids of each crude oil calculated with the hsp3D program (Figure 9.8). It is shown that Leadon is covering a larger space than Laguna and is thus expected to have better solubility properties. This is probably an effect of Leadon being a lighter crude which contains more low viscosity oils. These are better solvents than the

higher molecular weight components of the Laguna. It is also seen that the solubility ellipsoid for the Laguna is located completely inside the solubility ellipsoid for the Leadon. This means that the Laguna crude should be completely soluble in the Leadon crude, and no problems with the formation of precipitates are to be expected by dilution of Laguna crude oil with Leadon crude oil.

TURBIDIMETRIC TITRATIONS

Although the determination and visualization of solubility parameters for bitumen and other mineral-oil-derived materials have proven to be very illustrative, there is still a desire for better precision. This has partly been met, as discussed above, by a better selection of test solvents and by better methods to optimize the ellipsoid. There are very obvious differences when it comes to practical applications, and particularly with modification with SBS polymers, among bitumens having very similar solubility ellipsoids (Table 9.2). Bitumens that are seemingly very similar with respect to solubility give still very different properties after mixing with SBS. One of the most important properties is the separation stability. Most mixtures of bitumen and SBS show a tendency for separation if they are stored at high temperature for a long time. A typical separation test is made at 180°C for 3 d. The separation is usually seen as the polymer floating to the surface, but sometimes, particularly at concentrations of SBS between 10 and 15%, a phase separation can take place, also in the bitumen. This is seen as a hard precipitate at the bottom of the bitumen tank. The separation tendency can be overcome by a proper selection of bitumen, alternatively by selection of a suitable polymer. The selection of components is mainly done on a "trial and error" basis, although there are some empirical rules. HSP may be an excellent tool for selection of suitable combinations of bitumen and polymer, but better precision is required than can be obtained with simple solubility testing with pure liquids. Improved estimation of the best solubility ellipsoid is required for optimal use of the HSP concept.

BISOM TEST

The procedure discussed in the following has been developed at Nynas Bitumen based on turbidimetric titrations to precisely determine the boundary of the surface of solubility. The procedure is called BISOM, an acronym for BItumen SOlubility Model. The principle of the test method is visualized in Figure 9.9. The HSP ellipsoid of the bitumen is constructed using the "poor solvents" illustrated as solid triangles in the figure and the "good solvents" being illustrated with open triangles. Three nonsolvents have been selected. These have HSP placing them just outside the surface of the solubility ellipsoid. They may be seen as the black triangles in the center of the circles in Figure 9.9. In the case of BISOM titration the selected "poor solvents" are 2,2,4-trimethyl pentane (isooctane), 2-butanone (methyl ethyl ketone), and 2-ethyl hexanol. As bitumen is a high viscosity liquid or a semisolid material, it has to be diluted to decrease the viscosity to permit proper stirring during the titrations. For this purpose, a solvent with a solubility parameter as close to the center of the ellipsoid as possible has to be selected. For the BISOM titration we have selected toluene (or in some cases xylene) as the good solvent.

The titration is illustrated as arrows, going from the HSP of the good solvent toluene to any of the three poor solvents. The titration can be considered as a dilution of the bitumen with a mixture of a good solvent and a poor solvent. The HSP of the mixture is proportional to the concentration of each solvent. A precipitate will appear when the HSP of the mixture has a value placing it on the surface of the solubility ellipsoid.

An important effect to take into consideration in the turbidimetric titration of bitumen is the concentration effect. This comes from the fact that bitumen is kept homogeneous by the mutual solubility of all its different molecules. The effect is seen as a higher concentration of bitumen giving better solubility. This situation is contradictory to what is usually known for solubility of pure substances. To understand this phenomenon we must consider that the first sign of turbidity
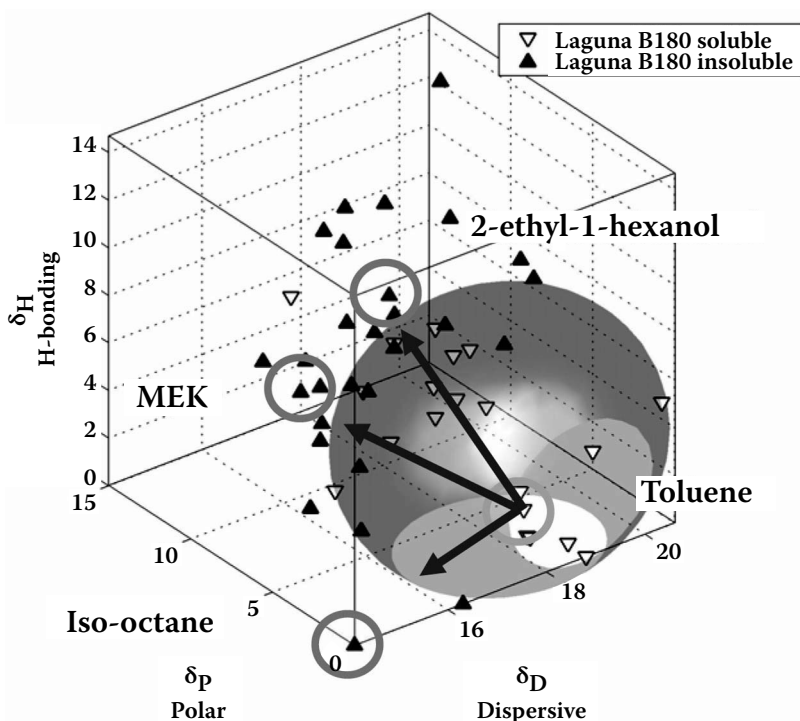
FIGURE 9.9 Summary of the BISOM titration with the "good solvent" and the three "poor solvents" titrants.

is interpreted as "insolubility," but more precisely, it is the insolubility of the molecule(s) that are least soluble in the particular titrant/solvent mixture that has been used.

The concentration effect was first described by Hithaus.[29] He developed a kind of turbidimetric test for what he called "peptization of asphaltenes." In this titration only one good solvent, toluene, and one poor solvent, *n*-heptane, were used. To account for the concentration effect, Heithaus performed the titration at several different concentrations of bitumen. The details of the calculations can be found in Reference 29, but Figure 9.10 gives an illustration of the principle.
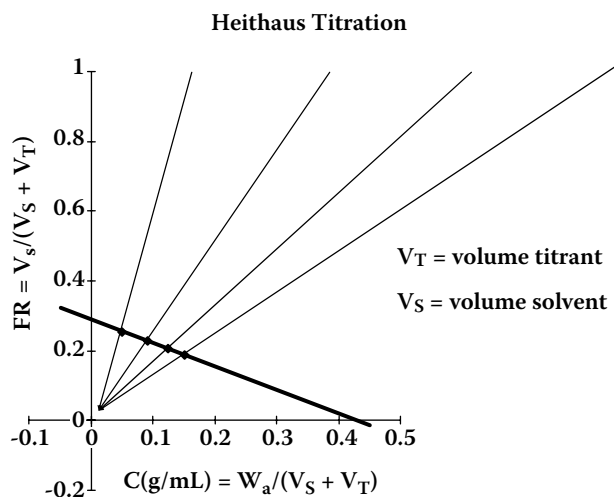

FIGURE 9.10 Illustration of the Heithaus titration of a Venezuelan bitumen.

In Figure 9.10 the dilution ratio FR = *volume solvent/total volume solvent and titrant* is plotted against C = *amount of bitumen/total amount of solvent and titrant*. At the start of the titration FR = 1 as no titrant (V_T = 0) has been added, whereas at the same time C is equal to the concentration of bitumen in the solvent. During the addition of titrant both FR and C become smaller and smaller. At infinite dilution FR = 0 and C = 0, but before this a precipitate has been formed, provided that the titrant has been properly selected. The point where the first sign of precipitate is noticed is marked with a black dot in the diagram. For each experiment the titration is repeated several times using different concentrations of bitumen. In Figure 9.10 the titration has been repeated four times, illustrated by the four titration arrows showing the decrease of the FR and the C value during the titration, and four black dots indicating the first sign of precipitation. A straight line is fitted through the four points using the least R-squared method. The equation for the line is used for extrapolation to find the intercepts for FR when C = 0 and for C when FR = 0. The meaning of the FR value at C = 0 is the ratio of solvent to titrant where there is solubility for all concentrations of bitumen. The solvent to titrant ratio can be used to calculate the HSP at the precipitation point for infinite dilution of the bitumen. The fact that a higher concentration of bitumen requires more titrant to reach the precipitation point confirms that the solubility of bitumen increases as the concentration increases. This effect is also visible with very dilute solutions. The meaning of the intercept for FR = 0 is the lowest concentration of bitumen that is needed to give full stability in pure titrant. It could also be expressed as the maximum titrant which can be added to bitumen without causing precipitation.

In practice the precipitation point at the BISOM titration can be determined by different methods. There are at least two commercial instruments which can be used for BISOM titrations although they are both originally developed for automatic Hethaus titration. The testing procedures used by the instruments are described in two ASTM standards. One of the instruments measures the transmission of light through a cuvette with a short beam length[30] and the other instrument uses variation in the intensity of a reflected beam of light (attenuated total reflectance principle [ATR]).[31] Both instruments can be equipped with more than one titrant for BISOM titration. There is a modified version of the ATR instrument[31] which is suitable for BISOM titrations.

The computer program hsp3D also has the possibility to handle HSP of solvents or solvent mixtures considered as being exactly on the surface of the ellipsoid. This is the case with HSP calculated from the ratio of good and poor solvents at the precipitation point. Thus, the BISOM data may be combined with solubility data for better precision. The BISOM data may easily be recalculated from FR_{max} to the FR value for the same concentration used in the solubility testing by using the equation for the line in Figure 9.10.

The results from a BISOM titration may be reported in different ways. The most simple is to give the FR_{max} for the intercept C = 0 and C_{min} for the intercept FR = 0. Heithaus[29] proposed further calculations of factors:

$$p_a = 1 - FR_{max} \tag{9.1}$$

$$p_0 = FR_{max} \left[\left(\frac{1}{C_{min}} \right) + 1 \right] \tag{9.2}$$

$$\mathbf{P} = \frac{p_0}{1 - p_a} \tag{9.3}$$

where p_a is considered to be related to the solubility of the molecules in bitumen with the lowest solubility, p_0 is related to the solubility power of the bitumen, and finally, **P** is a balanced stability index describing the internal stability of the bitumen. A higher number indicates a higher stability.

A high internal stability can be seen as a high allowance for blending with additives, polymers, solvents, or other types of bitumen or crude oil.

The interpretation of the BISOM titration is a determination of the internal stability of the bitumen or crude oil, rather than determination of HSP, although it is based on the principles of HSP. The BISOM could also be seen as an identification of those molecules that are the least soluble in the bitumen or crude oil, and how close to insolubility they are. To have a complete picture it is necessary to have several titrants with different HSP as the traditional determinations of internal stability using only *n*-heptane as precipitant will usually give an incomplete picture. It is not expected that the material precipitated by addition of *n*-heptane would be the same as that precipitated by the addition of 2-ethyl-1-hexanol or 2-butanone. The use of three titrants permits calculation of the HSP at three precipitation points, each of which could be considered to be on the surface of the solubility ellipsoid. It is, however, not possible to estimate the solubility ellipsoid from only three points on the surface, particularly since the exact center point is not known. If the HSP calculated from turbidimetric titrations are going to be compared to the HSP ellipsoid of the same material, the concentration at the solubility testing has to be taken into consideration. The precipitation point at a certain concentration can easily be estimated from data such as are reported in Figure 9.10.

CONCLUSION

- The Hansen solubility parameters of a complex material such as bitumen or crude oil can be estimated by determination of its solubility in a large number of solvents with known HSP.
- To have the best precision, the test solvents should be selected with respect to the material to be tested. It is preferred to have solvents near or at the borderline of solubility.
- The factor 4 in Equation 1.9 as a multiplier for the difference in the dispersion parameters for the materials being considered seems to be valid, also for complex mixtures like bitumen.
- Comparison of HSP for bitumen, asphaltenes, and maltenes confirms that asphaltenes are soluble in maltenes, and bitumen should thus not be considered as a colloidal dispersion as is frequently claimed.
- The best estimated HSP values for Venezuelan bitumen are D = 18.6 MPa$^{0.5}$, P = 3.0 MPa$^{0.5}$, H = 3.4 MPa$^{0.5}$.
- A computer program hsp3D can estimate the best fit to the solubility data and from this calculate the HSP.
- The program can also estimate the best coefficients for the ellipsoid model to illustrate the extension of solubility regions in a 3D diagram.
- Up to three different materials can be compared in the same 3D plot.
- The program is not limited to bitumen and crude oils, but could equally well be used for other types of materials.
- A procedure for turbidimetric titrations has been developed to further improve the precision to determine the surface of the HSP solubility ellipsoid. This procedure is called a BISOM titration.
- BISOM titration is well suited for measurement of the internal stability of complex hydrocarbon mixtures like bitumen or crude oils.
- BISOM titration is also a determination of the least soluble molecules in bitumen or crude oils.

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