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Review

Solubility Characteristics and Microstructure of Bitumen: A Review

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Abstract: This is a comprehensive review of the significance of solubility theories, internal stability, and external compatibility within petroleum science and pavement engineering. The historical development and future trends of solubility methods in bitumen are discussed, emphasizing the importance of separating bitumen components based on solubility to establish a link with chemistry. The paper also highlights the development of solubility theories and various characterization tests for bitumen, as well as the distribution of functional groups of solvents and their parameters. Additionally, it explores the generation of solubility profiles for different types and aging states of bitumen based on solubility data and statistical correlation, and the use of stability diagrams to assess the internal stability of bitumen in different states. The potential for continued research in this field is emphasized to bridge the gap between fundamental chemistry and practical application, leading to improved formulations and enhanced performance of bitumen in various applications, ultimately resulting in more durable and stable pavement structures.

Keywords: bitumen aging; bitumen component separation; compatibility; Hansen solubility parameters

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1. Introduction

For more than a century, the quality and durability of highways has been of central interest to industrialized nations in order to ensure the reliable transport of people and goods. Often, pavement engineers and petroleum chemists have offered different perspectives on the application of bitumen for this purpose. Due to the chemical complexity of bitumen, the establishment of long-term chemical standards for the identification and quality control of bituminous concrete is essential [1]. The composition of bitumen varies significantly depending on the oil source and refining process. Additionally, the wide range of molecular components present in various types of bitumen complicates chemical characterization. Most theories on bitumen's chemical composition focus only on identifiable compound types and their interrelationships [2]. The stability among different components in bitumen determines its rheology, temperature sensitivity, aggregate adhesion capacity, and service life as a road construction material [3]. Since the stability of bitumen depends on the mutual solubility of all molecules in the binder, it is unlikely that general properties can be related to isolated fractions [4]. Separation techniques based on the solubility of bitumen components are commonly employed by researchers, manufacturers, and quality control personnel. These techniques often involve precipitation schemes to separate bitumen into fractions [5]. Fractional precipitation is perhaps the most widely used technique in bitumen analysis, with numerous schemes developed, each with its own rationale. Some of these schemes have been accepted as standard methods, while others are used to define the fractional precipitation of asphalt. The SARA (Saturates, Aromatics, Resins, and Asphaltenes) technique is the most widely used method for separating bitumen into its four main fractions [6]. However, the separation of bitumen into these four components is based on polarity rather than chemical composition [7]. Asphaltene to maltene ratios do not always correlate well with the rheological and chemical properties of bitumen. Thus, any linear, sequential fractionation scheme is not necessarily applicable to understanding the properties of bitumen [8]. In the fractionation of oxygen and low molecular weight compounds, these molecules do not easily associate with others containing polar functional groups. Therefore, the missing link in understanding the correlation between SARA fractions and microstructure lies in the intricate interplay between molecular polarity and intermolecular interactions. These connections are crucial because the formation of microstructures in petroleum-related substances is significantly influenced by the varying polarities of the molecules within these fractions [9].

The current bitumen models have yet to address the interaction between resin and asphaltene components. Consequently, analyzing the structural model of bitumen from the perspective of solubility is crucial [10,11]. The chemical structural changes in bitumen due to external influences are a significant factor in studying bitumen aging. Currently, the understanding of bitumen aging is primarily based on component regulation theory and solubility theory [12]. Component regulation theory, based on the traditional four components of bitumen, suggests that chemical aging occurs through the transformation of SARA components. This theory can guide the application of rejuvenators to aged asphalt. However, it fails to explain the physical hardening caused by wax crystallization at low temperatures and asphaltene deposition during transportation [13]. Solubility theory, rooted in chemical thermodynamics, posits that bitumen aging is due to an increase in the difference in solubility parameters between components, leading to decreased compatibility. This theory originates from modern colloid theory. Girdler described the bitumen system as a colloid, with asphaltene dispersed in lower molecular weight alkenes [14]. The colloidal structure of bitumen comprises solid particulate asphaltenes as the dispersed phase, liquid aromatic and saturated components as the dispersion medium, and semi-solid colloids as peptizers [15]. The balance between gel and sol characteristics is critical for bitumen performance under varying conditions [16]. Gel characteristics provide stability and resistance to deformation, while sol characteristics enable flow and workability during application [17]. Dickie and Yen proposed a macrostructure for bitumen that aligns with this view [18]. The influence of asphaltene polydispersity, the colloidal steric hindrance effect, and the aggregation effect can further elucidate the overall instability caused by changes in asphaltene structure. Yen also posited that asphaltenes and resins share similarities in composition and polarity, and colloidal interactions between these compounds can result in variations in the measured molecular weight of asphaltene molecules using different techniques [19]. As research on polymer solutions deepens, some researchers have begun to use polymer solution theory (Flory–Huggins theory) to explain the structure of asphalt. This theory suggests that bitumen is a high molecular weight polymer solution, with high molecular weight asphaltene as the solute and low molecular weight resin as the solvent. The stability of the solution depends on the asphaltene content and the difference in solubility parameters between asphaltene and resin [20].

The viscoelasticity of bitumen is attributed to the continuous breaking and reforming of intermolecular bonds between small polar molecules. In bitumen, molecules such as asphaltenes, resins, and other polar components are interconnected by these secondary bonds. These bonds allow for the constant rearrangement of molecular structures, enabling bitumen to exhibit both viscous and elastic behaviors depending on the rate and magnitude of applied stress [21]. Hansen solubility theory offers a useful framework for understanding molecular interactions, including the formation of secondary bonds such as hydrogen bonds, dipole-dipole interactions, and van der Waals forces [22]. The theory classifies these interactions based on three main parameters: dispersion forces (related to London dispersion forces), polar forces (related to dipole-dipole interactions), and hydrogen bonding. Through the development and application of solubility theory, researchers have linked the physical and chemical parameters of asphalt-solvent systems (dispersed or cosolvent media) to molecular mechanisms such as aggregation, precipitation, and phase separation induced by external factors [23]. Various theoretical models have been established based on solubility theory, including compatibility models, solid models, colloid thermodynamic models, and thermodynamic micelle models. By applying the principles of Hansen's solubility theory, researchers can gain insights into the molecular interactions that govern the behavior of bitumen and develop strategies to optimize bitumen formulations for specific applications and performance requirements [24].

Bitumen solubility is a fundamental aspect of bitumen technology that influences various processes, including component separation, aging behavior, and rejuvenation. However, a consensus on the solubility system has yet to be reached. To enhance the understanding of solubility theory in bitumen applications, this paper reviews recent advancements and provides a comprehensive overview of the use of solubility theory in bitumen component separation, aging mechanisms, polymer-modified bitumen research, and the compatibility of bitumen with rejuvenators. Additionally, the historical and future developments of the solubility approach in the context of bitumen are analyzed. The effects of functional group solubility and further extensions of solubility theory on bitumen are briefly discussed. By studying bitumen solubility, researchers can deepen their understanding of bitumen chemistry and develop innovative approaches to improve the performance and longevity of bitumen pavements. This study aims to provide a preliminary basis for comprehensive and realistic internal and external compatibility systems for bitumen.

2. Scope and Objective

The objective of this study is to deliver a concise yet comprehensive overview of bitumen and its solubility. To achieve this, a targeted search was conducted using specific keywords to gather relevant and suitable literature. The keywords employed in this search include: bitumen, asphalt binders, solubility, and compatibility. The inclusion criteria for selecting literature were as follows: the article must focus at least 50% on bitumen solubility, be written in English, pertain to crude oil or pavement engineering/applications, and be peer-reviewed. This study used VOSviewer software (v1.6.20) to construct and visualize bibliometric networks. VOSviewer is a powerful tool that can construct and visualize bibliometric networks using data from literature search databases [25]. The image shown in Figure 1 is a bibliometric map generated by VOSviewer which uses a co-occurrence network of terms extracted from the titles and abstracts of at least 200 highly relevant articles over the past three decades. The top 70% of the most relevant terms were selected as keywords, represented by the 40 terms listed in the figure, and grouped into three clusters represented by different colors. The blue cluster primarily represents research related to solubility in asphaltene engineering, including the solvent properties between different components, such as saturated and aromatic fractions, as well as the effect of various solvents like toluene on their solubility. The green cluster focuses on research into the properties of asphalt in pavement engineering, discussing the compatibility of different additives and the interactions between internal components of asphalt, with a focus on the application of solubility parameters. The red section discusses the impact of solubility on asphalt production in crude oil engineering, including two-phase structural characteristics, as well as the effects of pressure, solvents, and diffusion characteristics on asphalt production and performance. Based on the results of the quantitative literature analysis and the current state of research on solubility in asphalt, this study conducts a literature review structured around the theoretical framework presented in Figure 2.

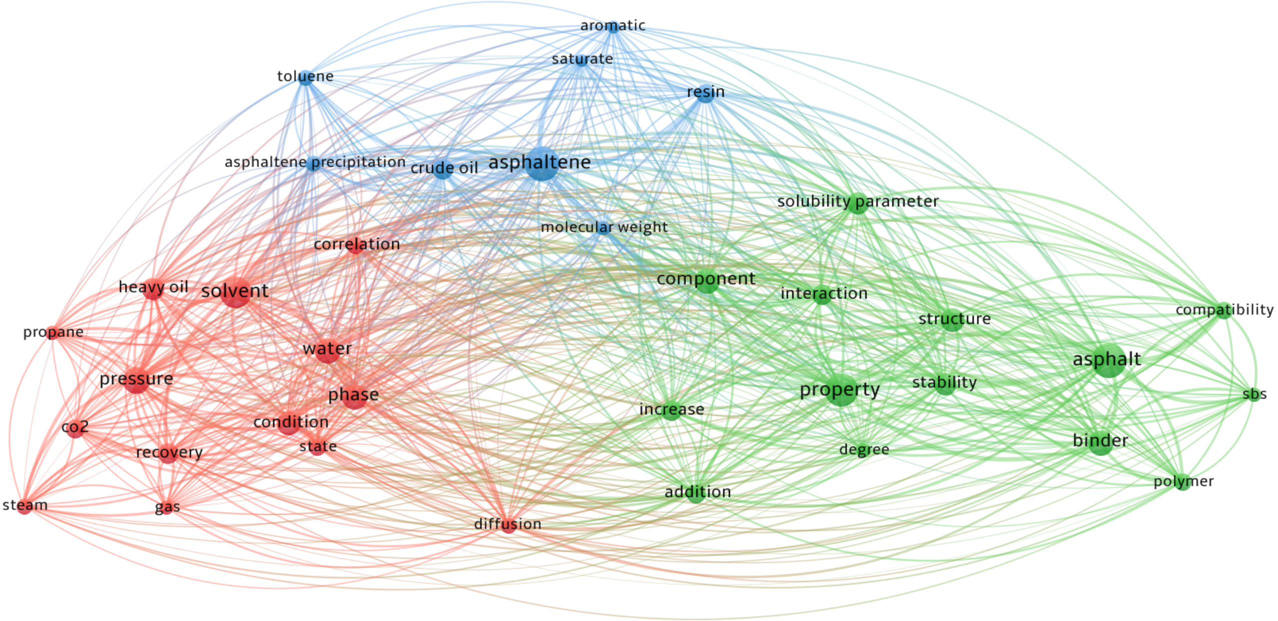


Figure 1. Visualization of the bitumen solubility network constructed using full counting.

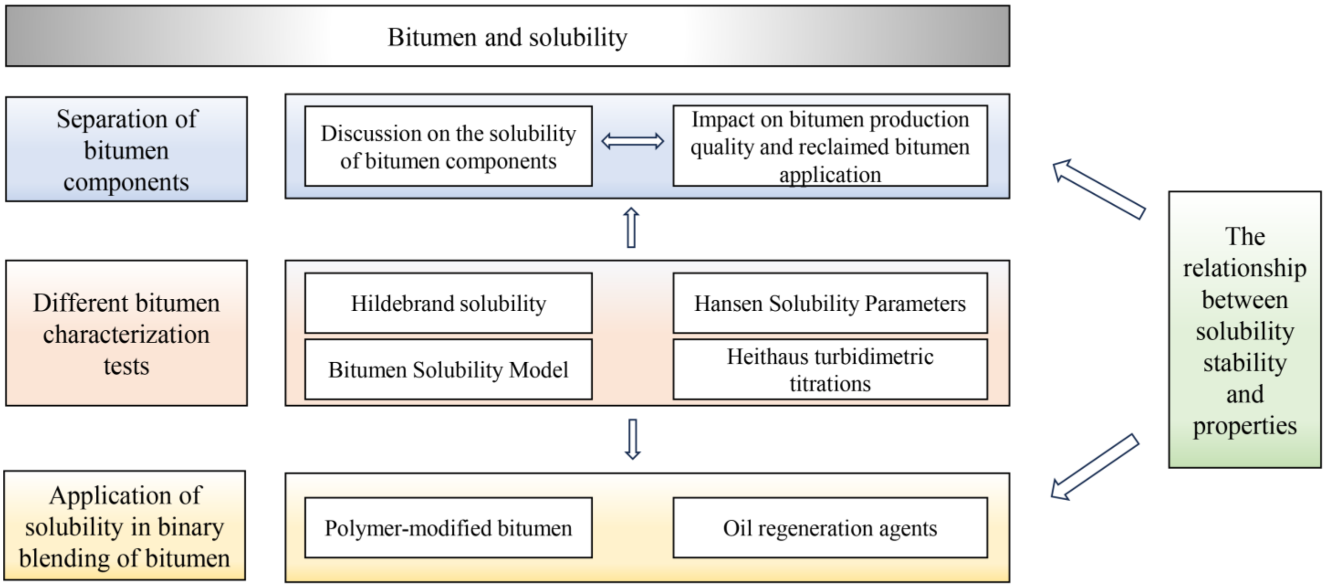


Figure 2. Theoretical review framework.

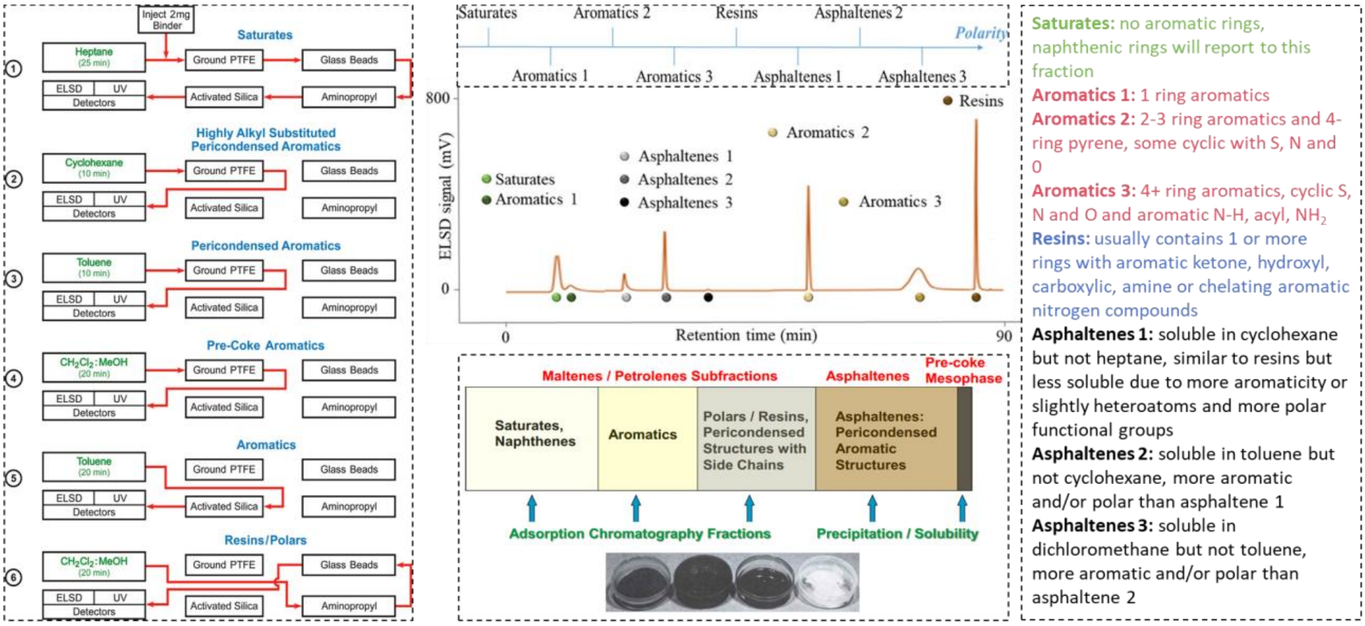
3. Separation of Bitumen Components Based on Solubility

Asphalt comprises millions of diverse organic molecules and heteroatoms, resulting in significant variations in polarity, molecular weight, H/C ratio, and aromatic content. The relationship between the chemical composition of asphalt and its performance on roadways is a crucial area of research [26]. Understanding this relationship facilitates the optimization of asphalt formulations, enhancing durability, stability, and performance across diverse conditions [27]. However, current research faces challenges in translating the molecular structure of bitumen binder into specific physical and chemical properties. Bitumen is fractionated into uniform components through various separation processes. These classical separation processes, which have been extensively utilized, can be categorized into three types based on the methodologies employed: (i) separation by partial solvent, (ii) selective adsorption-desorption (Corbett method), and (iii) chemical precipitation [28]. Table 1 outlines different chemical analysis methods used to examine the classical separation components of bitumen. These methods, whether employed individually or in combination, provide comprehensive information about the composition, structure, and properties of the classically separated components of bitumen [29].

Table 1. Tests to analyze bitumen composition.

Test Categories	Test Analysis
Fractionation by precipitation	Solvent precipitation, Chemical precipitation
Fractionation by distillation	Vacuum distillation, Thermogravimetric analysis
Chromatographic separation	Gas chromatography, Inverse gas-liquid chromatography, Liquid chromatography (adsorption, ion exchange, coordination, thin layer, size exclusion)
Chemical analysis	Spectrophotometric techniques (infrared, ultraviolet, nuclear magnetic resource, X-ray fluorescence, emission, neutron activation), Titrimetric and gravimetric techniques, Elemental analysis
Molecular weight analysis	Mass spectrometry, vapor pressure osmometry, and size exclusion chromatography
Indirect compositional analysis	Internal dispersion stability tests

Although classic bitumen separation procedures follow the principle of solvent solubility differences, these changes are insufficient to explain chemical trends under the influence of external environments [30]. Further refinement of bitumen components based on solubility differences is needed to analyze these changes in chemical trends. Solvent fractionation schemes rely on the thermodynamic principles governing solubility [31]. Bitumen contains numerous complex and high-molecular-weight hydrocarbons, exhibiting a variety of intermolecular forces that confer stability to the material [32]. These forces include London dispersion forces, permanent and induced dipole interactions, repulsive forces, and hydrogen bonds among nonpolar molecules. Solvent fractionation entails precipitating specific components using a non-solvent to disrupt the mixture's thermodynamic equilibrium, with macromolecular substances typically precipitating first. The most prevalent fractionation method in bitumen analysis is the determination of asphaltenes, which are identified using n-pentane, n-hexane, n-heptane, or insoluble naphtha, depending on the precipitant employed. The fraction of bitumen excluding asphaltenes is known as maltene. The maltene fraction can be further subdivided into oil and resin components [33]. Some researchers have conducted more complex separations of bitumen or heavy oil based on solubility characteristics in early research [6,34,35]. However, these analyses do not reveal the detailed chemistry of individual fractions and cannot fully describe the internal stability and properties. The Hansen solubility bitumen separation method first dissolves the bitumen in a solvent or solvent mixture with a Hansen solubility parameter (HSP) similar to the desired fraction. The mixture is then subjected to a series of cooling and filtration steps, resulting in the separation of the bitumen into different fractions. The HSP of the different fractions is determined by analyzing their solubility in various solvents and comparing these values to those of known reference materials. The separated fractions can then be characterized and used for various applications, such as in the production of bitumen, lubricants, and other petrochemical products. Over time, the complex separations of bitumen components have become more mature and commercialized. As shown in Figure 3, the Western Research Institute has developed original technology for the continuous component separation of bitumen, termed the Saturates, Aromatics, Resins, and Asphaltene Determinator (SAR-AD), based on solubility theory [36]. The SAR-AD is a high-performance liquid chromatography method that can separate bitumen into eight components [37]. In the SAR-AD separation method, the maltene phase is divided into five specific fractions through chromatography: Saturates, Resins, and three types of Aromatics (Aro-1, Aro-2, Aro-3), each differing in polarity and molecular characteristics. Meanwhile, the asphaltene fraction is further classified into three subgroups based on their solubility in solvents with progressively stronger dissolving abilities: cyclohexane, toluene, and a dichloromethane:methanol (98:2) mixture [29,38].



Saturates: no aromatic rings, naphthenic rings will report to this fraction

Aromatics 1: 1 ring aromatics

Aromatics 2: 2-3 ring aromatics and 4-ring pyrene, some cyclic with S, N and O

Aromatics 3: 4+ ring aromatics, cyclic S, N and O and aromatic N-H, acyl, NH_2

Resins: usually contains 1 or more rings with aromatic ketone, hydroxyl, carboxylic, amine or chelating aromatic nitrogen compounds

Asphaltenes 1: soluble in cyclohexane but not heptane, similar to resins but less soluble due to more aromaticity or slightly heteroatoms and more polar functional groups

Asphaltenes 2: soluble in toluene but not cyclohexane, more aromatic and/or polar than asphaltene 1

Asphaltenes 3: soluble in dichloromethane but not toluene, more aromatic and/or polar than asphaltene 2

Column switching, solvent flow, time scheme for SAR-AD separations

Example of the modified automated SAR–AD separation profile

Figure 3. Example of the bitumen SAR-AD chromatogram described by polarity scale, adapted from [37,39], and copyright (2013) American Chemical Society and MDPI.

Asphaltenes, the downstream products of crude oil refining, have consistently been present at various stages of production. Researchers across multiple disciplines have conducted extensive characterization studies on asphaltenes using physical, chemical, and other methodologies [40,41]. Asphaltenes are broadly characterized as polar, polyaromatic hydrocarbons with high molecular weight, derived from crude oil. They exhibit solubility in aromatic solvents like toluene but remain insoluble in lower alkanes, such as n-pentane or n-heptane [42]. In pavement engineering, the primary concern regarding asphaltenes is their precipitation and role in chemical aging during bitumen transportation and use [43]. As illustrated in Figure 4, the intricate structure of asphaltenes requires a multifaceted approach to understand their behavior. This includes examining the diversity of colloidal aggregation models (e.g., the Yen-Mullins model) and analyzing both specific and nonspecific molecular interactions. These interactions encompass hydrogen bonding, dipolar forces, van der Waals forces, and π-π stacking, all of which play crucial roles in governing the self-assembly, stability, and macroscopic properties of asphaltenes [44,45]. The further separation of asphaltenes during component separation processes depends significantly on solvent solubility [46,47]. Due to the varying applications of asphaltenes across different fields, there is no consensus on the choice of solvents. This approach tends to direct fractionation by introducing polar forces, hydrogen bonding, and dispersion forces as factors determining the solubility of asphaltene components in the mixture [48]. The Venezuelan FIRP laboratory considers solvents with different carbon numbers as a common strategy to improve asphaltene characterization by isolating them into solubility fractions [49]. This approach presents two key benefits: it simplifies the analysis of the material by breaking it down into more manageable components, and it offers a distribution of asphaltene properties instead of a single averaged value. However, a notable limitation lies in the significant overlap among the resulting fractions, which can complicate precise interpretation of their distinct characteristics. The asphaltene fractions precipitated by n-heptane and n-pentane exhibit significant differences [50]. The former has a lower H/C ratio, indicating higher aromaticity. The N/C, O/C, and S/C ratios of the asphaltene fraction precipitated by n-heptane are generally higher, attributed to the higher proportion of heteroatoms in this fraction. Figure 4 illustrates the main characteristics of the C_5 (precipitated by n-pentane) and C_7 (precipitated by n-heptane) asphaltene fractions and their relationship with molecular weight. The higher aromatic content and heteroatom concentrations in C_7 fractions can lead to more pronounced oxidative aging, affecting the long-term durability of bitumen pavements. The macromolecular properties of asphaltenes are determined by various analytical techniques that produce two- and three-dimensional structures. Asphaltenes in crude oil are organized into micellar-like structures, reflecting their natural state of dispersion within the oil matrix [48]. Their solubility, as the densest and most complex fraction, is governed by a delicate interplay with the lighter components of bitumen, maintaining a balance that prevents aggregation or precipitation [51].

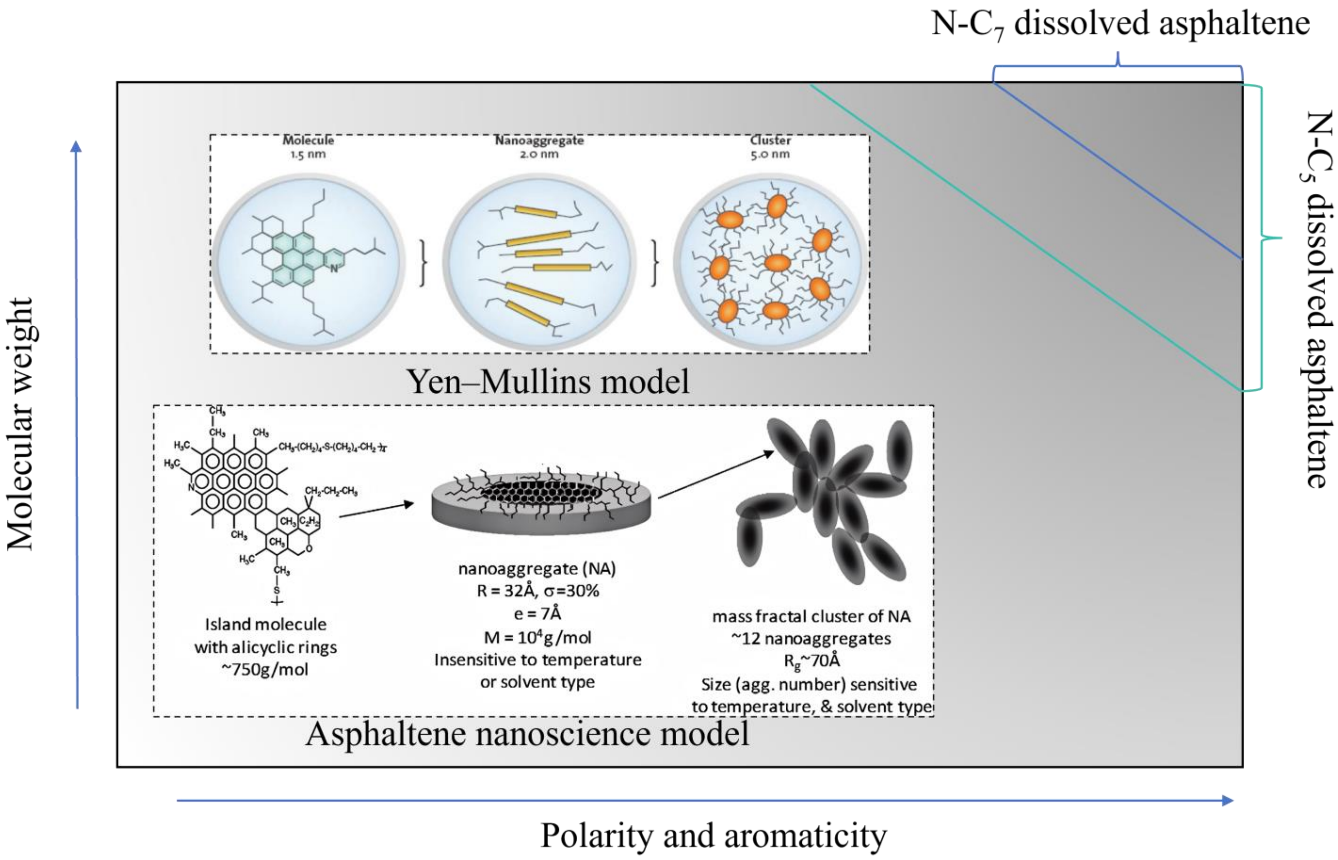


Figure 4. Asphaltene model and different solvents on asphaltene precipitation, adapted from [19,52], and copyright (2012) American Chemical Society and Taylor & Francis license.

HSPs have been effectively applied to the separation of wax in bitumen. The West Research Institute's Waxphaltene Determinator (WD), depicted in Figure 5, can rapidly separate wax and asphaltenes based on solubility differences at varying temperatures [53]. The number 1~5 in Figure 5 provides a summary of the probable chemical identities associated with the various peaks observed in the further separated bitumen. The Waxphaltene Determinator separation process is not easily adaptable for preparative-scale applications due to the significant temperature fluctuations involved. Building upon this, Ding enhanced the wax separation method using reduced pressure chromatography and the principle of solubility parameter similarity in bitumen. Ding also conducted microscopic experimental analyses to determine the impact of different wax components on the thermal reversible aging of bitumen [54]. The transfer of components and asphaltene aggregation following chemical aging, as well as the crystallization behavior of light component waxes after physical hardening, can exhibit varying effects and cracking behavior in pavement applications [55].

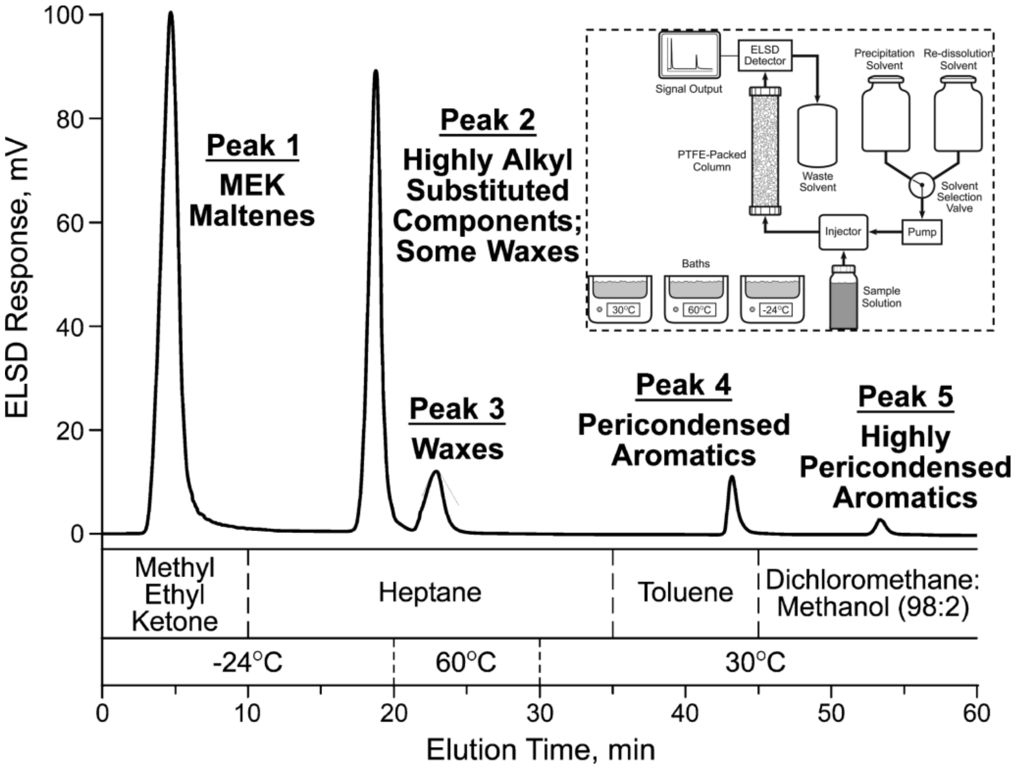


Figure 5. Waxphaltene determinator flow schematic and separation for bitumen sample [53], copyright (2010) American Chemical Society.

4. Solubility Theories and Different Bitumen Characterization Tests

The earliest application of solubility theory in petroleum science was to understand asphaltene precipitation. Asphaltenes become insoluble in crude oil and precipitate out under certain conditions, such as changes in temperature, pressure, or composition. However, the complexity of this system has impeded the development of sophisticated predictive models. Asphaltene precipitation solubility refers to the concentration at which asphaltenes begin to precipitate from the oil phase [56]. From a petrochemical perspective, asphaltene solubility is crucial to understanding bitumen solubility. Early studies of bitumen solubility relied on empirical observations and basic solvent tests [57]. Schabron suggests that changes in the physicochemical properties of light components in bitumen may significantly affect system stability. Thermal processes and external factors reduce the solvent capacity of the bitumen medium for heavy and polar molecules, resulting in the formation of saturated products [58]. Consequently, the solubility parameters of both the dispersing and solvent phases are altered, ultimately leading to phase separation [59]. Initially, asphaltene solubility was considered indicative of the compatibility of asphaltenes in a medium. Within the asphaltene fractions, molecules with lower solubility parameters facilitate the solubilization of asphaltenes with higher solubility parameters in the dispersion medium. The molecular interactions among asphaltene components determine their behaviors, directly affecting their production and application. The thermodynamic method of describing asphaltene solubility involves the concept of solubility parameters, also known as cohesive energy density. Solubility parameter data correlate with the precipitation of asphaltenes [60]. Scatchard's initial work in 1931 laid the foundation, but it was Hildebrand and Scott who significantly refined the concept in their work on Regular Solution Theory, providing a more comprehensive framework [61]. The solubility parameter is indeed a measure of the energy required to vaporize a substance, which reflects the internal cohesive forces within the liquid. The cohesive energy density (the amount of energy per unit volume) is essentially the quantity from which the solubility parameter is derived [62]. Materials with similar solubility parameters tend to be more compatible and have greater miscibility, while materials with vastly different solubility parameters may experience phase separation [63]. The relationship between the solubility parameter (δ) and the cohesive energy density is fundamental to understanding the intermolecular forces in a substance. Within the framework of regular solution theory, the solubility parameter is a critical parameter for evaluating these interactions. Mathematically, the solubility parameter δ is expressed as the square root of the cohesive energy density, which represents the cohesive energy per unit volume of the fluid. The Equation (1) can be written as [64]:

$$\delta = \sqrt{(-\frac{U}{V})} \tag{1}$$

U is the cohesive energy, while V represents the volume. The solubility parameter (δ) provides significant insight into the energy required to break intermolecular forces within a material and how it interacts with other substances. When two materials with different solubility parameters are mixed, the material with a higher δ value requires more energy to overcome its cohesive forces, which makes it harder for the two materials to mix. If the energy required to disperse the higher δ material is greater than the energy gained by mixing it with the lower δ material, immiscibility is more likely to occur [65]. In complex mixtures, such as blends or polymer solutions, the distribution of solubility parameters, or solubility profiles, becomes crucial in understanding the miscibility behavior. These profiles reflect the variation of solubility parameters across the components of the mixture, which can be used to predict and explain immiscibility or phase separation. The distance between solubility parameters can determine the solubility of two substances. Equation (1) can be further expanded to Equation (2):

$$\delta = \sqrt{c} = \sqrt{-\frac{U}{V}} = \sqrt{\frac{\Delta H - RT}{V}} \tag{2}$$

where c is the cohesive energy density, U is the cohesive energy, V represents the volume, ΔH is the heat of vaporization, R is the gas constant, and T is the temperature.

The original Hildebrand solubility parameter, which was primarily designed for nonpolar, non-associating systems, is insufficient for describing the solubility behavior of complex mixtures such as bitumen, which involves both polar and nonpolar interactions. To address this limitation, Arkel, Small, and Prausnitz expanded Hildebrand's concept by separating the solubility parameter into nonpolar and polar components [66]. This modification provides a more comprehensive framework for understanding solubility in solvents with varying polarities. Bitumen, especially its asphaltene fraction, exhibits unique solubility characteristics due to its high aromaticity and molecular weight [67]. Asphaltenes, which have lower solubility parameters, can promote the solubilization of other molecules with higher solubility parameters in dispersion media, highlighting the need for more sophisticated models [68]. The Hildebrand parameter, while effective for regular solutions, is inadequate for systems involving polar solvents with complex electrostatic interactions, hydrogen bonding, or π-π interactions. Therefore, a broader approach—such as determining a range of solubility parameters or employing extended models that account for both polar and nonpolar components—is crucial for accurately describing the solubility behavior of bitumen and other complex mixtures [69].

Hansen et al. introduced a three-component solubility parameter to provide a more nuanced and accurate description of solubility, particularly for systems that involve complex intermolecular forces [70]. Currently, the HSP system is a fundamental tool in fields such as polymer and petroleum science, where understanding the solubility behavior of compounds is crucial [22]. Bitumen, as a complex mixture, presents significant challenges in measuring its solubility under various states. Hansen's three-dimensional solubility parameter (Equation (3)) is based on the idea that the cohesive intermolecular forces of a material can be decomposed into three distinct types of interactions: dispersive forces, polar interactions, and hydrogen bonding. This approach offers a more detailed and accurate way to model solubility, especially for systems involving complex interactions beyond simple van der Waals forces [71].

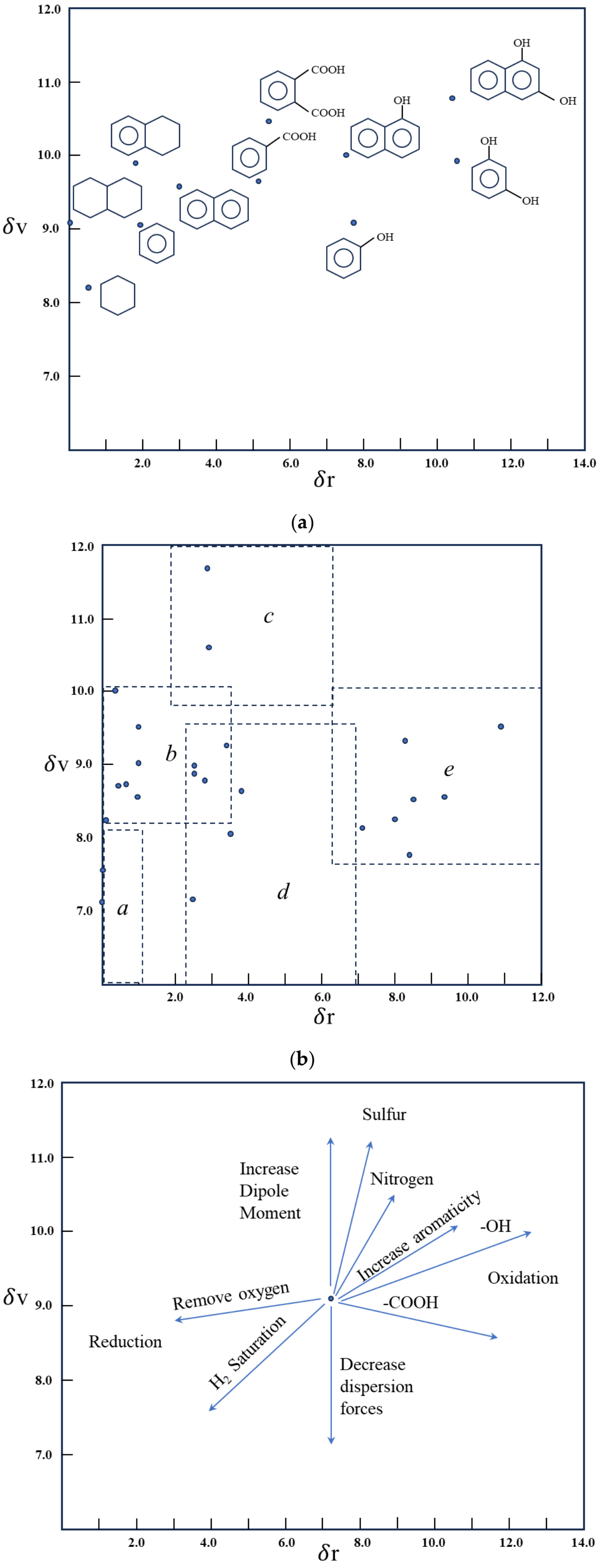
$$\delta = \sqrt{\left({\delta_{\mathrm{D}}}^2 + {\delta_P}^2 + {\delta_H}^2\right)} \tag{3}$$

where δ is the solubility parameter, δ_D is the dispersion solubility parameter, δ_P is the polar solubility parameter, and δ_H is the hydrogen-bonding solubility parameter. Most graphic expressions of solubility relationships are based on the parameters defined in Equation (3). The method proposed by Bagley and Scigliana employs two parameters [72,73], δ_r and δ_v in Equations (4) and (5), such that:

$${\delta_r}^2 = {\delta_H}^2 \tag{4}$$

$${\delta_v}^2 = {\delta_D}^2 + {\delta_p}^2 \tag{5}$$

where δ_r is called the residual solubility parameter and δ_v is the volume dependent solubility parameter. A graphic plot of substances according to their (δ_r,δ_v) coordinates shows corresponding relationships in their solubility characteristics. The solubility profile of a substance is a plot of the (δ_r,δ_v) coordinates of the solvents in which the substance is soluble and the corresponding degree of solubility. In addition to experimentally measuring physical properties to determine the Hansen Solubility Parameters (HSPs), a theoretically calculated group-contribution method has been proposed to estimate the solubility parameters, especially in complex systems like bitumen [74]. This method is based on a group solution model that calculates the HSPs by considering the chemical structure of the components within the material. The approach utilizes a thermodynamic method proposed by Wilson and Deal, which involves breaking down the chemical structure of the substance into smaller, functional groups (such as alkyl groups, aromatic rings, etc.) and estimating their contributions to the overall solubility parameters [75]. Group-contribution solubility parameters circumvent the need to determine an arbitrary solubility threshold, thereby enabling precise representation of solubility data. In other fields, these parameters are also known as Functional Solubility Parameters (FSP). Howell's studies have confirmed their applicability [76]. Figure 6a illustrates the various functional groups typically present in asphalt [77]. The solubility parameter values listed in Table 2 are based on Hansen's methodology and were calculated using Equations (4) and (5).



(a)

(b)

(c)

Figure 6. Solubility trend under (δ_r, δ_v) coordinates: (**a**) Group contribution for solubility. (**b**) Approximate domains of functional group populations. (**c**) Changes in Solubility Parameters.

Table 2. Solubility Parameters [78,79].

Solvent	Hansen Parameters			Bagley and Scigliana Parameters	
	δ_D	δ_P	δ_H	δr	δ_v
Cyclohexane	8.2	0	0.1	0.1	8.3
n-Heptane	7.5	0	0	0	7.5
n-Pentane	7.1	0	0	0	7.1
Diethyl ether	7.1	1.4	2.5	2.5	7.2
Ethyl acetate	7.7	2.6	3.5	3.5	8.1
2-Butanol	7.7	2.8	7.1	7.1	8.2
2-Propanol	7.7	3.0	8.0	8.0	8.3
1-Propanol	7.8	3.3	8.5	8.5	8.5
Ethanol	7.7	4.3	9.5	9.5	
Methanol	7.4	6.0	10.9	10.9	9 5
Ethylene diamine *	81	4.3	8.3	8.3	9.2
Pyridine	9.3	4.3	2.9	2.9	10.7
Trichloroethylene	8.8	1.5	2.6	2.6	8.9
Carbon Disulfide	10.0	0	0.3	0.3	10.0
Chrorobenzene	9.3	2.1	1.0	1.0	9.5
Benzene	9.0	0	1.0	1.0	9.0
Carbon tetrachloride	8.7	0	0.3	0.3	8.7
Trichloroethane	8.3	2.1	1.0	1.0	8.6
2-Butanone	7.8	4.4	2.5	2.5	9.0
Chloroform	8.7	1.5	2.8	2.8	8.8
Tetrahydrofuran	8.2	2.8	3.9	3.9	8.7
Acetone	7.6	5.1	3.4	3.4	9
Acetonitrile	7.5	8.8	3.0	3.0	11.6
Ethylbenzene	8.7	0.3	0.7	0.7	8.7
1-Butanol	7.8	2.8	7.7	8.3	7.7

* Ethylene diamine has been discontinued as a solvent.

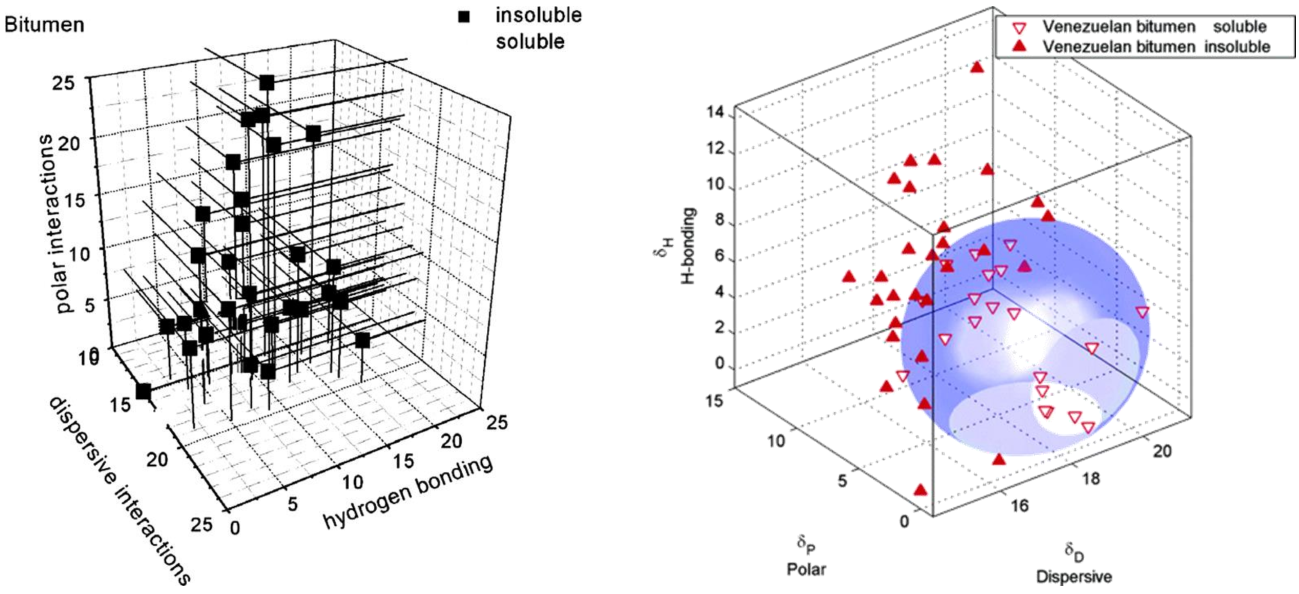
The distribution of the functional groups of the solvents, characterized by the δr and δv parameters in Table 2, falls into five well-defined regions (Figure 6b). Region *a* contains saturated hydrocarbons. Region *b* is predominantly occupied by halo hydrocarbons and aromatics. Region *c* includes nitrogen-containing compounds, while acids, esters, ethers, and ketones occupy Region *d*. Region *e* contains alcohols and phenols. The types or fractions of bitumen solubilized by the solvents within each of the regions outlined in Figure 6b are more homogeneous and identifiable than bulk asphalt. Consequently, visual and alphabetical interpretations of these subdomains (Regions *a*–*e*) can serve as more precise measurements of imbalances in the identifiable fractions of bitumen. These fractions play specific roles in the macroscopic structure of the system and have a direct relationship to the cementing properties of the sample. Solubility profiles for different types and aging states of bitumen can be generated based on solubility data and statistical correlation. Time-dependent condition ratings are used to evaluate the predictive capabilities of this characterization technique for refinery bitumen.

The concept of solubility domain allows for the testing of various hypotheses regarding the oxidative process, including the debated cyclization and naphthenization of saturates, without the immediate need to identify each molecule. By selecting a sufficiently small starting population within a defined domain, researchers can observe shifts or spreads in this domain during oxidation. The initial domain can be chosen through various methods, such as precipitation, solvent extraction, or chromatographic separation. With solubility data, a plan for identifying specific substances can be devised. The solubility trend of bitumen can be inferred based on its behavior in different solvents and the contribution of functional groups to solubility. Figure 6c illustrates a scheme for estimating changes in solubility parameters, providing a visual representation of how the solubility of bitumen evolves under different conditions. The solubility trend of bitumen in different solvents, along with the role of functional groups in influencing solubility, helps in deducing the chemical changes that occur during oxidation.

Another method of characterizing solubility involves the three-dimensional HSPs, which analyze the interactions between solvents and asphalt. Interactions between induced dipoles are considered dispersive forces, while interactions between permanent dipoles and between permanent and induced dipoles are classified as polar forces [80]. Hansen parameters of various solutes and solvents can be represented in a three-dimensional plot with axes x, y, and z (δ_D, δ_H, δ_P), as shown in Figure 7a. Solute-solvent pairs are considered miscible when their positions in the solubility parameter space are close to one another. The distance (R_a) between the solvent (a) and solute (b) is commonly used to quantify their compatibility. It can be determined using Equation (6):

$$R_a = \left[4(\delta_{D1} - \delta_{D2})^2 + (\delta_{P1} - \delta_{P2})^2 + (\delta_{H1} - \delta_{H2})^2\right]^{1/2} \tag{6}$$

where R_a is the distance between a solvent and bitumen, δ_{D1} (or δ_{P1} or δ_{H1}) is the dispersion component of the solvent, and δ_{D2} (or δ_{P2} or δ_{H2}) is the dispersion component of bitumen.



(**a**) (**b**)

Figure 7. Different representations of the Hansen solubility diagram for bitumen: (**a**) axial diagram (x-y-z plot, where each axis is one of the Hansen solubility parameters); (**b**) ellipsoid diagram (Hansen fit, axis-aligned ellipsoid, and rotated ellipsoid are compared) [81], copyright (2004) American Chemical Society.

Experimental evaluation of a solute with various solvents, typically between 20 and 30 different types, and their classification as either "soluble" or "insoluble" through visual inspection or other methods, facilitates the determination of the Hansen parameter of the solute. In Figure 7b, the concept of solubility in the context of Hansen's solubility parameters can be visualized using a Hansen Sphere. The Hansen Sphere represents a hypothetical sphere in a three-dimensional space of solubility parameters (dispersive, polar, and hydrogen bonding components). The radius of this sphere is denoted as R_o, and the center corresponds to the solubility parameters of a given solvent. The determination of

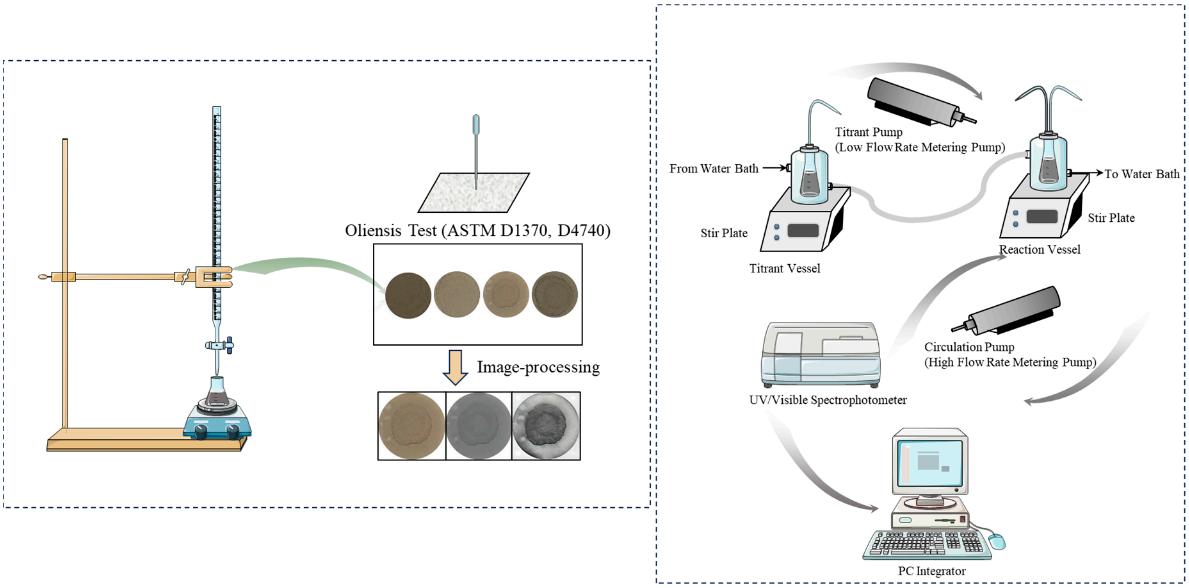
HSP using solvents with different degrees of analysis can be found in Redelius's work [81] and Hansen solubility software (HSPiP v6.0) [79].

To further quantify the solubility of materials and determine the solubility tendency and internal stability of different asphalts, Redelius proposed the "Bitumen Solubility Model" (BISOM) [82]. Early research established the interdependence between the mechanical behavior and the chemical composition of bitumen through precipitation methods. An advancement of this approach is the Oliensis spot test, which operates under the guidelines of ASTM D1370 [83] and D4740 standards [84], while also incorporating principles from Hansen solubility theory. According to Hansen's theory, when two liquids with different solubility parameters are mutually soluble, the solubility parameter of the resulting mixture will be proportional to the quantity of each liquid. This relationship is mathematically expressed by the following Equation (7):

$$\overline{\delta} = \frac{({}^{i}\phi\,{}^{i}\delta + {}^{j}\phi\,{}^{j}\delta)}{({}^{i}\phi + {}^{j}\phi)} \tag{7}$$

where ϕ is the volume fraction of each liquid i and j. Turbidimetric titrations can be employed to determine the solubility parameter of a substance. This involves titrating a solution of the substance with a non-solvent until precipitation occurs. For the Hildebrand parameter, it suffices to conduct two titrations using non-solvents with higher and lower solubility parameters to ascertain the substance's parameter. Heithaus initially proposed a specific turbidimetric titration method for bitumen to measure its "asphaltene peptization" and to identify the flocculation point via microscopy. Sreeram and Yuan's research focuses on optimizing and validating a novel method based on the visualization of the Spot test [29,85]. Binder stability was evaluated through turbidimetric titration using three distinct titrants: isooctane, methyl ethyl ketone, and iso-octanol. These titrants were selected for their varying polarity and solubility characteristics, which influence their interaction with the binder components. Detailed experimental procedures for this titration method can be found in the relevant literature [82,85,86]. The principle of turbidimetric titration involves preparing bitumen solutions in toluene and gradually adding a titrant until precipitation occurs. The settling point is reached when the least soluble component is no longer peptized by the surrounding components and separates from the bitumen matrix. By measuring the amount of titrant required for precipitation at different bitumen concentrations in toluene, it becomes possible to derive parameters to describe the state of peptization. These parameters provide insight into the stability and colloidal behavior of the bitumen system.

As bitumen was titrated with solvents (titrants) possessing distinctive solubility parameters according to the Hansen Solubility Parameter (HSP) Model, the parameter P was used to assess the stability of bitumen in these solvents. Specifically, parameter P serves as an indicator of the relative strength of the interactions within bitumen when exposed to these solvents, reflecting the overall compatibility of bitumen with the solvent based on its solubility characteristics. However, it is important to recognize that the parameters N and H do not solely represent polar and hydrogen-bonding interactions, as the titrants used were not exclusively polar or hydrogen-bond-driven. Instead, these parameters suggest a tendency of the solubility towards more polar or hydrogen-bonding interactions, though they are not strict indicators of such interactions in isolation. The titrations were conducted using toluene as the solvent for bitumen and three different titrants: iso-octane, methyl ethyl ketone (MEK), and iso-octanol. For each solvent/titrant pair, at least four different bitumen concentrations were titrated, and each titration was performed in duplicate to ensure consistency and accuracy. As shown in Figure 8a, this method, initially used for assessing bitumen's behavior in various solvents, was further developed into a turbidimetric titration test, which helps to detect changes in the solubility and phase behavior of bitumen. Different precipitants are used to increase the versatility of the method. Detection can be performed in many different ways: acoustic methods [87], viscosity [88], conductivity [89], optical microscopy [90], attenuated total reflection Fourier transform infrared (ATR-FTIR) [91], focused beam reflection (FBR) [92], fluorescence spectroscopy [93], dynamic light scattering [94], and NMR relaxation measurements [95]. A common method for continuously monitoring a titration involves using optical equipment like an ultraviolet (UV)-visible spectrophotometer. During the titration, the percent transmittance (%T) of the detected radiation changes. As shown in Figure 8b, the Western Research Institute (WRI) developed a novel method to detect precipitation points using a UV/VIS spectrophotometer at 740 nm, where precipitation is indicated by a decrease in transmittance [96].



(**a**) (**b**)

Figure 8. Two methods of bitumen Hansen solubility testing: (**a**) Heithaus turbidimetric titrations, reprinted from [97] with permission from Elsevier; (**b**) Automated Heithaus titrimetric from WRI.

With the increasing emphasis on performance and durability in road construction, solubility tests are critical to ensure the quality and uniformity of bitumen used in road surfaces. In contrast, petroleum engineering focuses on extraction, processing, and transportation, which leads to different methods and standards for evaluating solubility. Table 3 summarizes the varying interpretations of solubility across these fields. While petroleum engineering may prioritize optimizing the dissolution process for efficient extraction, road engineering concentrates on ensuring the quality and performance of binders.

Table 3. Different understandings of bitumen solubility in petroleum and pavement.

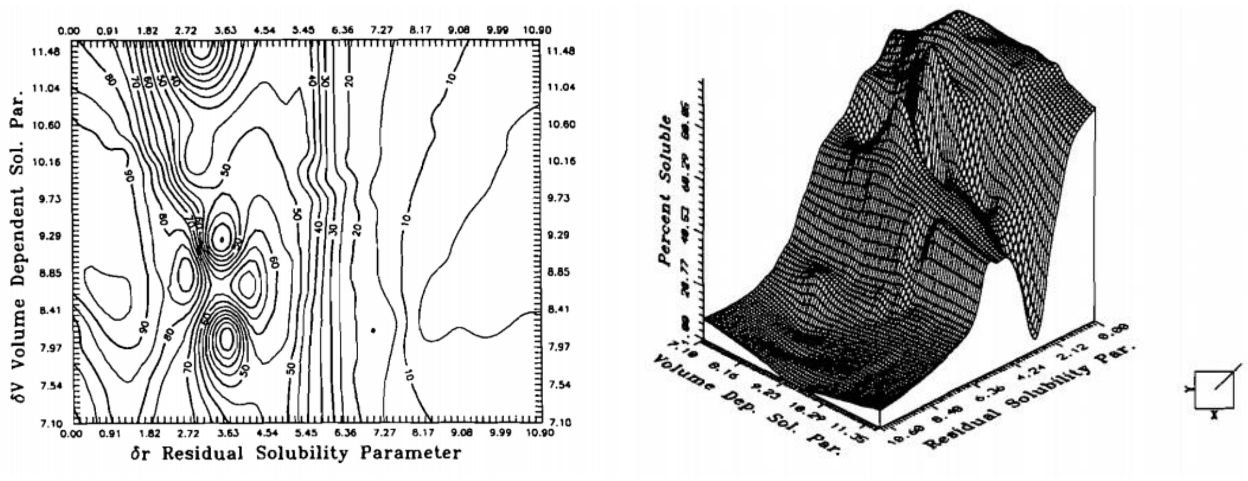
	Petroleum	**Pavement**
Solubility theory	Hildebrand and the Flory–Huggins theory	Hansen solubility theory
Solubility model	Asphaltenes model (size, shape, and specific intermolecular interaction)	Bitumen component compatibility model based on Hansen solubility
Characterization methods	Precipitation schemes	Miscibility studies
Research purposes	Precipitation of asphaltenes in crude oil	Durability of bitumen roads and stability of polymers

5. The Relationship Between Solubility Stability and Properties

5.1. Internal Stability Changes Caused by Oxidation

Understanding the relationship among solubility, stability, and the properties of bitumen is essential for optimizing its performance, especially in applications like petroleum and pavement engineering. Changes in bitumen's internal stability, particularly those caused by oxidation, can significantly affect its physical and chemical properties. Precipitation is a common phenomenon that often results from drastic changes in solubility characteristics. This makes precipitation a useful indicator for monitoring reactions within bitumen, as it is typically linked to significant shifts in solubility. However, solubility profile methods offer a more refined approach by detecting subtle changes in solubility characteristics that may not immediately result in precipitation. This capability allows for more sensitive monitoring of chemical reactions occurring in bitumen, which is crucial for assessing long-term performance and stability. Solubility parameters can be used in two ways: as isolated quantities, which require minimal mathematical complexity, or combined to create equations or graphical representations that describe the solubility behavior of bitumen in more detail. These methods provide a valuable tool for understanding and controlling the chemical interactions within bitumen, improving its suitability for various industrial applications.

In the early stages of bitumen solubility research, Hargen developed a model correlating solubility with the service life of bitumen pavement, based on extensive data [98]. The primary objective of solubility and compatibility theory is to identify the factors influencing compatibility and to quantify these parameters. The research demonstrated a correlation between bitumen samples extracted under different conditions and various solvents. Using software, a regression profile of the bitumen sample was generated, illustrating that changes in surface and volume in different regions of the profile often counterbalance each other, as shown in Figure 9. Consequently, the solubility map can be segmented into multiple regions, facilitating a more detailed analysis of the aging and deterioration processes. As bitumen ages, the solubility volume in this area increases, which aligns with the understanding that aging bitumen forms more oxidized material.



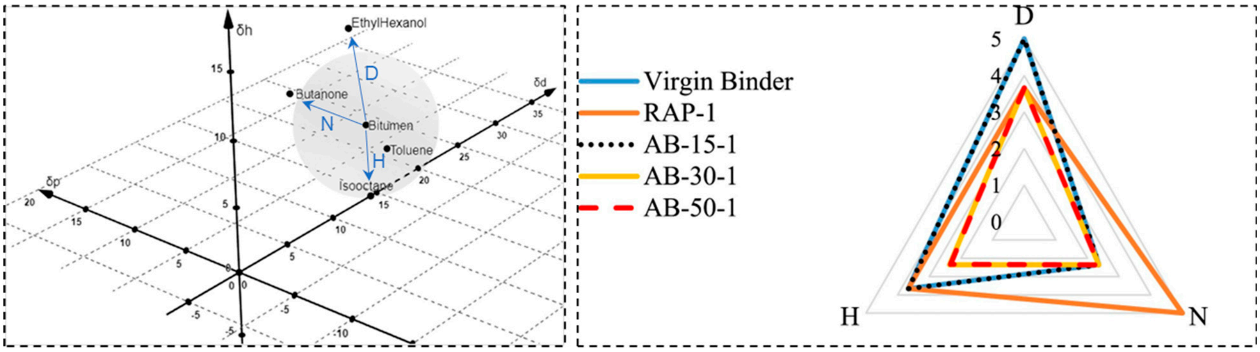
(**a**) (**b**)

Figure 9. Calculation of bitumen solubility trends under (δr, δv) coordinates: (**a**) Bitumen solubility surface. (**b**) Bitumen solubility volume [98]; copyright (2007) Taylor & Francis license.

The internal structural changes induced by bitumen oxidation significantly alter the solubility of bitumen. To further elucidate these solubility changes, Redelius, Sreeram, and Sogne employed HSPs to characterize the effects of oxidative aging on bitumen [82,85,99]. In these studies, they discussed the kinetics of bitumen oxidation and its impact on solubility, and examined the use of solubility curves to characterize bitumen oxidation and its sensitivity to oxidation. Additionally, Cui explored the diffusion process of oxygen within bitumen [100]. There are three primary hypotheses regarding the oxidation process. The first hypothesis posits that bitumen molecules undergo condensation during the reaction with oxygen, resulting in an increase in molecular size [101]. This hypothesis was tested using Gel Permeation Chromatography (GPC) experiments. Bitumen samples were dissolved in a solvent, typically tetrahydrofuran (THF), to reduce viscosity before being passed through a chromatography column [102]. It was found that specific molecules establish strong molecular associations, leading to a significant increase in molecular weight upon oxidation [103]. The second hypothesis posits that the reaction with oxygen increases the polarity of bitumen molecules, thereby enhancing their polar interactions [104]. The formation of carbonyl and sulfoxide groups during oxidative aging increases the polarity of certain bitumen molecules. However, this increase in polarity is insufficient to fully account for the significant hardening observed [105]. Infrared spectroscopy is widely employed to monitor the presence of carbonyl compounds and sulfoxides, facilitating the assessment of bitumen aging [106]. The third hypothesis posits that aging enhances aromaticity, which subsequently amplifies π-π interactions and dispersion forces [107]. Oxidation can result in the cleavage of carbon-hydrogen bonds in aliphatic compounds, leading to the formation of double bonds and ring structures [108]. These reactions often result in the formation of more stable aromatic structures. Oxidative hardening primarily occurs due to the strong intermolecular forces between polar molecules and oxygen-containing functional groups. Chemical oxidation can initiate polymerization and condensation reactions, where smaller molecules combine to form larger, more complex structures. This increase in molecular weight and the formation of large aromatic structures contribute to the hardening and embrittlement of asphalt.

The chemical composition of asphalt influences its durability through two primary mechanisms: the compatibility of interacting components and the resistance of bitumen to alterations induced by natural modification, such as oxidative aging [27]. The physical properties and performance of bitumen are influenced by molecular interactions among the asphalt components. These interactions include dispersive interactions, polar interactions, hydrogen bonding, and π-π interactions. While direct measurement of these interactions in the complex bitumen mixture is not feasible, the HSPs can empirically determine the dispersive, polar, and hydrogen bonding interactions. These parameters are represented as solubility spheres in a 3D graph. As depicted in Figure 10, Sreeram employed a three-dimensional titration solubility method and found that the most significant differences between unaged and aged adhesives were in polar interactions and dispersion forces [86]. It is generally recognized that as bitumen is subjected to progressively higher and more destructive temperatures, its hydrocarbons undergo dehydrogenation, its internal structure deteriorates, and its heavy ends become more focusable. This process of deterioration and increased flocculation is a clear indicator of compromised internal stability. These findings align with the current understanding of the properties of aged binders. However, a limitation of the titration procedure is that it only indicates relative differences in solubility trends among individual molecules of bitumen, rather than providing precise measurements [109].

A comprehensive understanding of bitumen solubility must relate it to the physical properties of asphalt. The rheological characteristics of bitumen at a specific temperature are influenced by both its chemical composition and the physical arrangement of its molecules. The solubility of bitumen, in relation to its rheological properties, is intricately linked to the three molecular forces proposed by Hansen: dispersion forces, polar interactions, and hydrogen bonding. These forces, along with the rheological data of bitumen, were analyzed statistically using the solubility titration model. The analysis revealed that the phase angle's shape with temperature, or the elastic behavior at a given stiffness, is closely associated with the parameters that determine hydrogen bonding potential and polar interactions. Specifically, increased hydrogen bonding and polar interactions contribute to the enhanced structural integrity of bitumen, reinforcing its viscoelastic properties and making it more resistant to deformation at varying temperatures. This finding highlights the importance of these molecular forces in determining bitumen's performance and stability [110]. Wang's research underscores the significance of increased asphaltene condensation and the diminished peptizing capacity of resins as pivotal factors in the phase separation of bitumen, primarily driven by molecular forces. This phase separation can negatively impact the rheological properties of bitumen. These findings provide important insights into the rheological characteristics of bitumen, which are vital for applications in paving and petroleum refining. The colloidal instability index (CI) of bitumen is a key measure for evaluating its colloidal stability, with the dispersion component being influenced by intermolecular forces [111]. Since molecules are composed of atoms, all molecules exhibit dispersion forces. Assuming that every molecule in a component of bitumen contributes to the overall dispersion force of that component, it is reasonable to assert that no single component has a significant relationship with the dispersion aspect. Currently, the application of bitumen solubility is confined to its chemical properties and is not correlated with the physical properties of bitumen or the performance of bitumen mixtures in road construction. This limitation has hindered the widespread promotion of bitumen solubility.



(**a**) (**b**)

Figure 10. Hansen solubility three-dimensional titration method: (**a**) HSP of toluene and titrants in the HSP sphere of bitumen. (**b**) Relative strength of internal stability of bitumen in different states [86], copyright (2020) Taylor & Francis license.

5.2. *Application of Solubility in Binary Blending of Bitumen*

A wide variety of polymers, including plastomers, elastomers, two-component curing systems, and even recycled rubber and plastics, have been tested as bitumen modifiers. However, due to the stringent requirements of bitumen products, only a few polymers are commonly used for this purpose. Two critical factors in polymer selection for bitumen modification are compatibility and cost efficiency. Compatibility refers to the polymer's stability against phase separation when mixed with bitumen, which is essential for maintaining a uniform structure and ensuring long-term performance [112]. Cost efficiency is another key consideration, as the goal is to achieve significant improvements in the properties of bitumen with minimal polymer content. In the road construction industry, where large volumes are used and price constraints are high, the modification level typically does not exceed 5% by weight. The Hansen Solubility Parameter (HSP) concept is a useful tool in selecting suitable polymers, as it allows for the prediction of compatibility between polymers and bitumen. If the HSP of a particular polymer is unknown, it can be determined through a simple solubility test, which helps guide the selection of compatible polymers for bitumen modification. This approach is both practical and efficient, particularly when considering the large-scale and cost-sensitive nature of road construction. The combination of solubility parameters and free energy theory provides a comprehensive approach to studying polymer-modified bitumen (PmB) [113]. Solubility parameters facilitate the evaluation of interaction strengths between components, whereas free energy theory elucidates the thermodynamic aspects of these interactions [114]. These factors aid in predicting the compatibility and stability of polymer–bitumen mixtures, and guide the selection of appropriate polymers to achieve the desired material properties.

The phase behavior of polymer-modified bitumen (PmB) directly and significantly affects its storage stability and morphology. Additionally, it has a substantial impact on other binder properties. The free energy theory evaluates the thermodynamic stability of PmB systems. The free energy of mixing determines the spontaneity of the mixing process and elucidates the polymer–solvent interactions and phase separation behavior in PmB. According to Zhu's research, applying solubility parameters and free energy theory assists in the design and formulation of PmB with customized properties for specific applications in Figure 11 [115]. This methodology can predict the long-term stability of PmB, optimize the selection of polymers and additives, and enhance PmB performance under various environmental conditions. In addition to polymer-modified asphalt, HSPs can be used to evaluate the compatibility between asphalt and oil regeneration agents. Hu discussed the compatibility between different types of emollient oils and asphalt using HSPs [116]. Sun studied the diffusion behavior of waste engine oil in asphalt based on the solubility parameter model [117], while Zhang focused on soybean oil [118]. By matching the solubility parameters of the oils with those of the emollients, the understanding of compatibility and chemical composition was further elucidated. When discussing the exudation effect of regenerated wax oil, Liu used solubility parameters to explain the phenomenon of incompatibility between asphalt and wax oil regenerants under certain conditions [97].

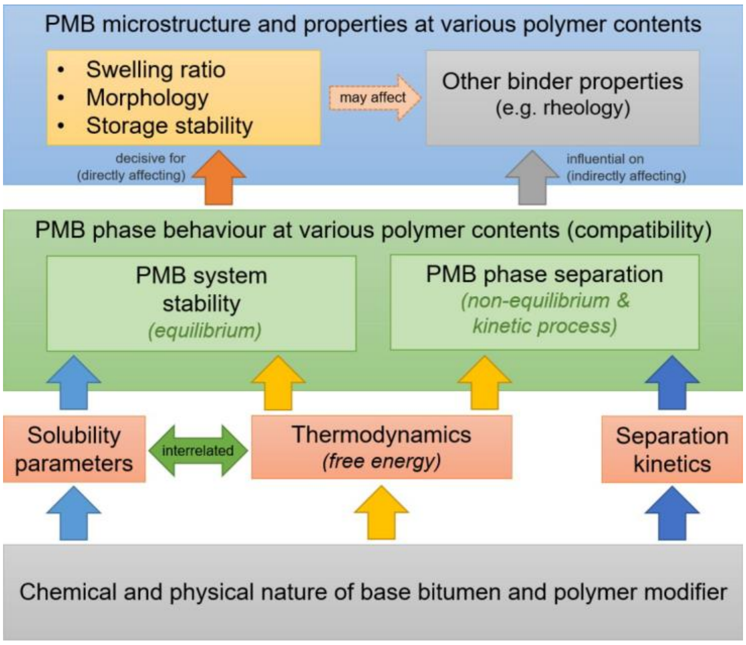


Figure 11. Stability of binary mixtures of polymer-modified bitumen [115], copyright (2019) Taylor & Francis license.

6. Research Gaps and Future Development

In numerous studies, the effect of different solvents' solubilities on the properties of bitumen in various states has been extensively discussed. The turbidimetric titration method, utilizing a selected titrant, effectively detected differences in internal stability and molecular interactions between aged and unaged adhesives. In Karlsson's research, FR_{max} and C_{min} were employed to evaluate the stability of the internal structure of bitumen, while also exploring the impact of solubility on the diffusivity of bitumen based on the structural stability changes induced by bitumen solubility [119,120]. Currently, there is a lack of research addressing the correlation between bitumen diffusion and bitumen solubility. However, Hansen posits that HSPs significantly influence diffusion, equilibrium absorption/swelling, and diffusion phenomena, which are crucial for determining certain polymer HSP methods. This perspective has been documented in studies on polymer blends. Thus, in future discussions on the diffusion behavior between bitumen and rejuvenators, the concept of solubility could be introduced to enhance the understanding of bitumen diffusion.

Advancements in analytical chemistry techniques have led to more systematic studies of bitumen solubility. Future studies are anticipated to characterize bitumen using solubility parameters in conjunction with chromatographic methods to better understand its composition and behaviour. The development of sophisticated analytical techniques, such as infrared spectroscopy and nuclear magnetic resonance (NMR) spectroscopy, has enabled researchers to investigate the molecular structure of bitumen and its solubility characteristics in greater detail [121]. This period has seen significant progress in understanding how different fractions of bitumen interact with solvents. Furthermore, advances in computational chemistry and modelling techniques have enhanced our understanding of bitumen solubility. Molecular dynamics simulations and quantum chemical calculations now allow researchers to predict solubility parameters, phase behaviours, and intermolecular interactions in bitumen with greater accuracy [122,123].

7. Summary and Conclusions

This article reviews the significance of solubility theories and properties in investigating asphalt's internal stability and external compatibility. Within the realms of petroleum science and pavement engineering, the historical development and future trends of solubility methods applied to bitumen are discussed. The separation technique for bitumen's various components based on solubility further links bitumen with chemistry. Based on this overview, the following can be summarized:

(1) Solvent fractionation and HSP are crucial for determining asphalt's solubility behavior. These methods, combined with the Bitumen Solubility Model (BISOM) and turbidimetric titrations, provide insights into asphalt's internal stability and mechanical behavior. While traditional methods like SARA fractionation have limitations in correlating chemical composition with properties, further separation of bitumen components based on various solubility methods can scientifically guide the production of high-quality asphalt.

(2) The impact of aging on bitumen solubility is significant, affecting its rheological properties and stability. By analyzing the solubility profiles of different bitumen types and aging states, predictive models for bitumen behavior can be developed. These changes can be understood through various hypotheses, such as molecular condensation, increased polarity, and increased aromaticity. Moreover, the solubility domain concept and group-contribution methods offer valuable insights into the interactions between various bitumen components and solvents.

(3) HSPs also aid in predicting the compatibility of bitumen with polymers, which is crucial for enhancing phase stability and performance in polymer-modified asphalt. Future advancements in analytical chemistry techniques will further refine our understanding of bitumen solubility.

In conclusion, the intersection of solubility, stability, and compositional analysis of bitumen paves the way for improved formulations and enhanced performance of bitumen in various applications, ultimately leading to more durable and stable pavement structures. Continued research in this field will bridge the gap between fundamental chemistry and practical application, ensuring better road performance and longevity.

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