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# Characterisation of Asphaltenes and Modelling of Flocculation – State of the Art

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**Résumé — Caractérisation des asphaltènes et modélisation de la floculation – État de l'Art** – Ce travail présente un état de l'art concernant la floculation des asphaltènes avec deux grands items : la caractérisation des asphaltènes dans différents milieux et la modélisation de la floculation. Cette revue commence par une caractérisation des asphaltènes proprement dite puis des caractérisations de ces derniers dans des solvants synthétiques ou des bruts. Nous insistons sur les techniques de détermination de masses molaires et de diffraction. L'incidence d'un ajout de bon/mauvais solvant est également discutée. La seconde partie de cette revue concerne la modélisation de la floculation. Elle examine les différents modèles de la littérature avant de présenter celui de Szewczyk et Béhar (1999) et son intégration dans un simulateur de réservoir. Les modèles disponibles requièrent encore des données expérimentales délicates à acquérir et un effort de recherche doit être réalisé pour améliorer cet état de fait.

**Abstract — Characterisation of Asphaltenes and Modelling of Flocculation – State of the Art** — This document describes a state of the art concerning the flocculation of asphaltenes with two major sections: characterisation of asphaltenes in various environments and modelling of flocculation. This review starts with the characterisation of asphaltenes as such, then their characterisation in synthetic solvents or crudes. Emphasis is placed on molar mass determination and diffraction techniques. The impact of adding a good/poor solvent is also discussed. The second part of this review is dedicated to modelling. We first examine the various models in the literature before describing the Szewczyk and Béhar (1999) model and its integration in a reservoir simulator. The models available still require experimental data which is difficult to collect and further research is needed to improve this situation.

## INTRODUCTION - REMINDER OF THE STAKES

Increasing the recovery rate of condensates and crudes is one of the major goals for the petroleum industry: the current average recovery rate is about 35% and only about 10% for the heavy crudes. This recovery rate is even more difficult to maintain when deposits form during the production steps. Asphaltenes may be responsible for the formation of these deposits, hence their nickname: the “cholesterol of petroleum” (Kokal and Sayegh, 1995). Asphaltene flocculation phenomena may also be observed when transporting crude oils. The data collected in the references of Leontaritis and Mansoori (1988), Novosad and Costain (1990) and Kabir and Jamaluddin (1999) demonstrate that the reservoir fluids concerned vary considerably and that it is difficult to anticipate *a priori* the risk of flocculation (see Table 1).

The presence of asphaltene deposits may result in productivity losses and sometimes even production shutdowns due to the following phenomena. Pressure loss during production, or a change in the composition of the fluids in the reservoir during recovery operations enhanced by injection of gas (*e.g.* CO<sub>2</sub>) or liquid hydrocarbons (condensates, naphthas) may destabilise the asphaltenes initially dissolved in the oil *in situ*, which could lead firstly to an increase in its viscosity and secondly to the formation of a deposit causing partial or total blocking of the porous medium. This plugging of the reservoir rock causes a drop in productivity. Production must then be stopped and mechanical cleaning carried out, when possible, or aromatic solvents injected, possibly containing specific additives (Kabir and Jamaluddin, 1999) designed to dissolve the deposits formed and thereby efficiently unblock the porous medium (known as “squeeze” operations). These solvents plus additives can also be injected as a preventive measure. Although their activity has now been demonstrated, their modes of action are not yet fully understood and controlled. Formation of deposits in the wells may result in complete blockage and hence production shutdown. Blocking of the reservoir effluent evacuation pipes leading to the upgrading installations may also have dramatic consequences for the field operator (Leontaritis, 1996).

In order to estimate the scale of these problems, a study was conducted in 1994 by the Institut Français du Pétrole (IFP) with international oil companies. Although conducted a relatively long time ago, it produced valuable information regarding the position of the companies with respect to the difficulties involved in the exploitation of asphaltenic crudes and tar mats. The high response rate convincingly confirmed the importance which the oil companies attach to solving the problems caused by asphaltene flocculation and the formation of deposits. The main conclusions of this study are given below:

- asphaltene deposits are found in about 20% of all the reservoirs in operation;
- problems are extremely frequent in the reservoir or the well, and less so in the surface facilities. Although

solutions exist for the reservoir/well zone, most operators consider them as unsatisfactory;

- operation of oil fields presenting difficulties involves an additional cost of about 0.5 \$/bbl. In deep sea wells, this additional cost may be extremely high;
- about 80 % of the operators considered there was a need to carry out research and development work but less than half of them had an R&D department. The oil companies would like to see research carried out in the following areas, in descending order of priority:
  - formation of deposits;
  - study of industrial solutions;
  - characterisation of deposits;
  - location of deposits.

Note that a physico-chemical phenomenon often has to be characterised before its formation can be studied. In addition, it appears that numerous operators would like to have tools (experimental methodologies, kinetic and thermodynamic models) enabling them to more accurately estimate the production trend of a field, after the formation of deposits, during the decompression and enhanced recovery phases.

Asphaltene deposition may also occur during the conversion of heavy products (Higuerey *et al.*, 2001). In these processes, asphaltenes undergo pressure and temperature variations as well as changes in their structure and polydispersity over time. As conversion proceeds therefore, the residues processed become less stable, sometimes precipitating to such a point that they block up the pipes and the exchangers. Studies conducted on asphaltenes to investigate the conversion mechanisms have been described in several publications: Merdrignac *et al.* (2004), Bartholdy and Andersen (2000), Wiehe (1992 and 1993). Many questions are still unanswered, however, since prediction of flocculation phenomena remains a challenge:

- what is the maximum conversion rate possible for a given crude without destabilising the effluents?
- how can we establish a relation between the stability of asphaltenes and their reactivity?
- how can we integrate these phenomena in the kinetic models?

Most of the work described in this report, carried out during studies concerning the upstream oil industry, has led to a better understanding of flocculation phenomena in reservoirs. It will be possible to apply this insight into flocculation phenomena in the downstream industry, to provide faster solutions to the existing stakes. Speight (2004 a and b) has already proposed this approach.

To investigate asphaltene flocculation and the formation of deposits, scientists and oil companies have conducted multidisciplinary studies for the last fifty years on the following themes:

- characterisation of asphaltenes;
- characterisation of asphaltene solutions;

TABLE 1  
Asphaltene deposits on site

Country	Algeria	Venezuela	Venezuela	Aegean Sea
Area		East	West	North
Field name	Hassi messaoud	Mata-Acema	Macaraibo	Prinos
°API	42.3	16-36	30	≈ 28
% asphaltene	0.062%	0.9 - 9.8% (nC7)	10%	4.5%
Operation which caused flocculation	Production	Closure of a well and/or acid treatment	Production	Production
Solution proposed	Injection of solvent modification of production conditions	Addition of an oil from the Boscan field API = 9-12% asphaltene = 17.2%	Modification of production conditions	Injection of solvent
Company				
Source	Haskett and Tartera (1965)	Lichaa (1977)	Lichaa (1977)	Adialis (1982)

Country	USA	USA	Canada	Norway
Area	California	Mississippi	Saskatchewan (south east)	North Sea (280 km south west of Stavanger)
Field name	Ventura Avenue	Little Creek	Midale	Ula
° API	?	?	29	39
% asphaltene	?	?	5.5% (nC <sub>6</sub> ) (+10% wax)	0.57% (nC <sub>7</sub> )
Operation which caused flocculation	Production acid treatment injection of CO <sub>2</sub>	Injection of CO <sub>2</sub>	Injection of CO <sub>2</sub>	Production
Solution proposed	Mechanical cleaning of the pipes modification of production conditions oil circulation	Mechanical cleaning of the pipes	Modification of production conditions	Modification of production conditions
Company			Shell	BP
Source	Tuttle (1983)	Tuttle (1983)	Novosad and Costain (1990)	Thawer <i>et al.</i> (1990)

Country	Mexico	Kuwait
Area		
Field name	Tecominoacan	Burgan (Magwa)
° API	37	36 - 40
% asphaltene	1% (nC5)	0.5% (nC7)
Operation which caused flocculation	Production at bubble pressure	Production
Solution proposed		Injection of solvent (tank oil de-asphalted with an available condensate) Injection of water to maintain the pressure
Company		
Source	Escobedo and Mansoori (1992)	Kabir and Jamaluddin (1999)

- characterisation of asphaltenic crudes;
- flocculation in tank oils;
- flocculation in a reservoir fluid;
- modelling of flocculation phenomena.

Structured around these six themes, this article will attempt to outline a state of the art for each one. The first three sections describe the current images of asphaltenes in various environments. The fourth and fifth sections describe flocculation in crude oils while the last section describes the various models proposed to date. Studies in asphaltenes and resins in a source rock or a reservoir fluid can also help solve geochemical issues. This type of work will not be discussed in this document. The reader is invited, however, to refer to the following documents for further information: Pelet *et al.* (1986); Huc *et al.* (1984); Tissot and Welte (1984).

## 1 CHARACTERISATION OF ASPHALTENES

### 1.1 Introduction

A reservoir fluid consists of numerous hydrocarbon molecules, as illustrated on the diagram in Figure 1, which shows the analytical path generally taken at *IFP* to characterise the various molecules and fractions contained in a crude. For further details concerning the techniques used to characterise petroleum products and their fractions, the reader can consult the state of the art proposed by Merdrignac and Espinat (2006).

Asphaltenes are defined as being the insoluble fraction of a crude after adding a large excess of *n*-alkane (at least

40 volumes per volume of fluid, Speight and Moschopedis 1981). It is therefore a solubility class; consequently, there are no asphaltene molecules as such, but molecules forming the asphaltenes. Ancheyta *et al.* (2002) demonstrated that the quantity of asphaltenes precipitated varies with the volume of solvent added, becoming constant after reaching a solvent / oil ratio of 40 ml/g. The quantity of asphaltenes precipitated also varies with the chain length of the *n*-alkane used. Several authors (Hotier and Robin, 1983; Corbett and Petrossi, 1978; Mitchell and Speight, 1973) have demonstrated that the quantity of asphaltenes precipitated varies very little for *n*-alkanes heavier than *n*-heptane and increases significantly for shorter *n*-alkanes. This probably explains the existence of numerous normalised operating protocols corresponding to precipitations using *n*-heptane (ASTM D3279, IP 143, NFT 60 115). The de-asphalted oil is known as maltenes and contains resins, considered to be the peptising agents of asphaltenes (Koots and Speight, 1975; Swanson, 1942). The resins can also be separated from the maltenes by adsorption (Andersen and Speight, 2001).

Once it has been extracted from the crude, the asphaltene fraction can be studied either as it is or after further fractionation (Szewczyk *et al.*, 1996; Andersen, 1994; Merdrignac and Espinat, 2006). In both cases, the asphaltenes can be characterised by determining:

- the mass fractions of the carbon, hydrogen, oxygen, nitrogen (Szewczyk *et al.*, 1996) and of the various heteroatoms by elemental analysis;
- their molecular groups by  $^{13}\text{C}$  Nuclear Magnetic Resonance;
- their molar masses by various methods.

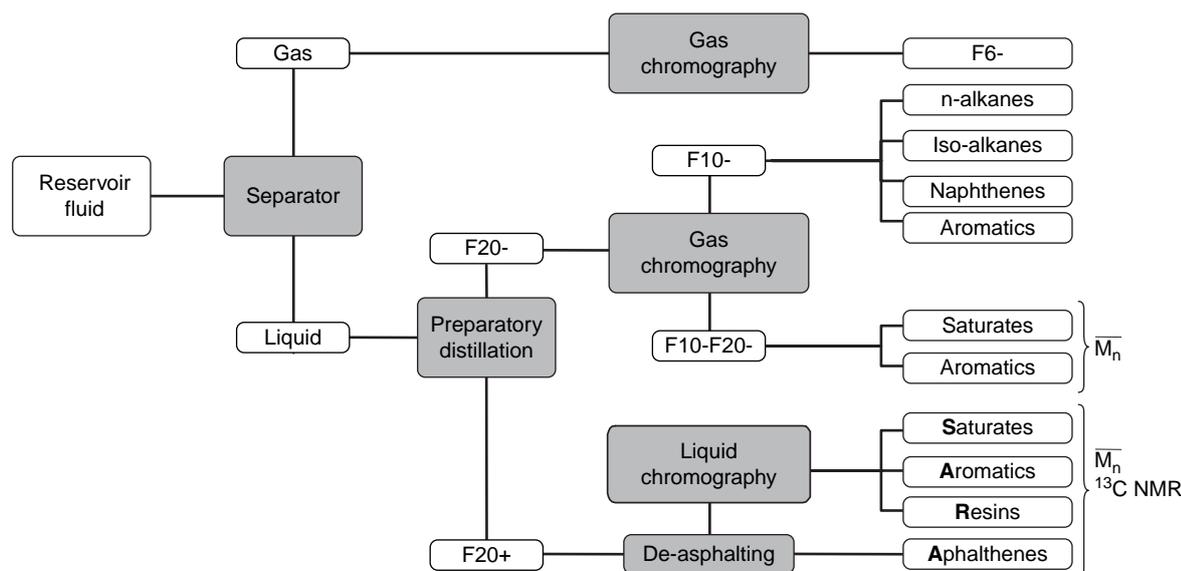


Figure 1

Example of a fractionation method used with an oil.

TABLE 2

Elemental composition of asphaltenes precipitated using various solvents (taken from Speight and Moshopedis, 1981)

Source	Precipitating Medium	Composition (wt%)					Atomic ratios			
		C	H	N	O	S	H/C	N/C	O/C	S/C
Canada	<i>n</i> -pentane	79.5	8.0	1.2	3.8	7.5	1.21	0.013	0.036	0.035
	<i>n</i> -heptane	78.4	7.6	1.4	4.6	8.0	1.16	0.015	0.044	0.038
Iran	<i>n</i> -pentane	83.8	7.5	1.4	2.3	5.0	1.07	0.014	0.021	0.022
	<i>n</i> -heptane	84.2	7.0	1.6	1.4	5.8	1.00	0.016	0.012	0.026
Iraq	<i>n</i> -pentane	81.7	7.9	0.8	1.1	8.5	1.16	0.008	0.010	0.039
	<i>n</i> -heptane	80.7	7.1	0.9	1.5	9.8	1.06	0.010	0.014	0.046
Kuwait	<i>n</i> -pentane	82.4	7.9	0.9	1.4	7.4	1.14	0.009	0.014	0.034
	<i>n</i> -heptane	82.0	7.3	1.0	1.9	7.8	1.07	0.010	0.017	0.036

TABLE 3

Elemental composition of asphaltenes precipitated using various solvents from a Venezuelan crude (taken from Coustet Pierre, 2003)

	Precipitating medium		
	<i>n</i> -pentane	<i>n</i> -heptane	<i>n</i> -nonane
%C	83.2	82.7	82.6
%H	8.0	7.5	7.7
%N	2.7	1.8	3.0
%O	1.4	1.5	1.8
%S	5.1	4.9	4.9
Losses	-0.4	1.6	0.0
H/C	1.15	1.10	1.11

The purpose of these measurements is to define an average representation of the molecules forming the asphaltenes.

## 1.2 Elemental Composition

The main analysis methods implemented to determine the elemental composition of a heavy oil fraction have been described in a state of the art by Barbelet *et al.* (1979). Table 2, extracted from the work carried out by Speight and Moschopedis (1981), indicates that the elemental carbon and hydrogen composition of asphaltenes in oils from various geographic origins remains constant (% carbon =  $82\% \pm 3\%$ , % hydrogen =  $8.1\% \pm 0.7\%$ ).

TABLE 4

Elemental and percentage analysis of asphaltene metals precipitated using various solvents (taken from Ancheyta *et al.*, 2002)

Solvent	Maya		Isthmus		Olmeca	
	<i>n</i> -C <sub>5</sub>	<i>n</i> -C <sub>7</sub>	<i>n</i> -C <sub>5</sub>	<i>n</i> -C <sub>7</sub>	<i>n</i> -C <sub>5</sub>	<i>n</i> -C <sub>7</sub>
Elemental analysis (wt%)						
Carbon	81.23	81.62	83.90	83.99	86.94	87.16
Hydrogen	8.11	7.26	8.00	7.30	7.91	7.38
Oxygen	0.97	1.02	0.71	0.79	0.62	0.64
Nitrogen	1.32	1.46	1.33	1.35	1.33	1.34
Sulphur	8.25	8.46	6.06	6.48	3.20	3.48
Atomic ratios						
H/C	1.198	1.067	1.144	1.043	1.092	1.016
O/C	0.009	0.009	0.006	0.007	0.005	0.006
N/C	0.014	0.015	0.013	0.014	0.013	0.013
S/C	0.038	0.039	0.027	0.029	0.014	0.015
Metals (wppm)						
Nickel	268.7	320.2	155.4	180.4	81.9	157.7
Vanadium	1216.6	1509.2	710.3	746.6	501.0	703.8

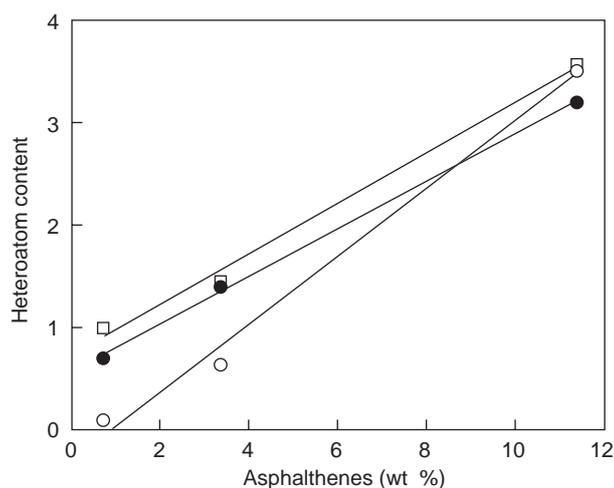


Figure 2

Percentage of asphaltenes against the quantity of heteroatoms present in the oils, open circles metals: (Ni + V) in ppm  $\times 10^2$ , black circles: nitrogen by % weight  $\times 10^{-1}$ , and open square: sulphur by % weight.

According to the same authors, the oxygen and sulphur percentages cannot be used as reference values since the exposure of asphaltenes or oil to atmospheric oxygen or to the sulphur contained in some minerals may lead to incorrect results. Table 3 lists data acquired on asphaltenes extracted from a Venezuelan crude (Coustet Pierre, 2003).

The hydrogen and carbon percentages agree with the figures given in Table 2. Table 4 lists data acquired by Ancheyta *et al.* (2002) on three oils. Their results agree with those of the previous authors. In addition, they show that the

percentages of sulphur, metals (nickel + vanadium) and nitrogen in oil are related to the percentage of asphaltenes (see Fig. 2). Similarly, Tissot and Welte (1984) show that there are linear relations between the main components of an oil and the total sulphur percentage: the best linear correlation coefficient is obtained for aromatic compounds.

In conclusion, asphaltenes are characterised by constant hydrogen and carbon percentages and an H/C ratio lower than that of the oil containing them (Ancheyta *et al.*, 2002; Tuttle, 1983). Leon *et al.* (1999) demonstrated that asphaltenes extracted from unstable crudes exhibit a hydrogen deficit compared with asphaltenes extracted from stable crudes. By using opacimetry techniques to determine the stability of their crudes (see Section 4.3), the authors demonstrate that their stability increase corresponds to an increase in the H/C ratio of the asphaltenes. Lastly, for more detailed information concerning the aromaticity of asphaltenes, the positions of heteroatoms and metals, the recent book published by Speight (1999) provides an exhaustive state of the art. Leon *et al.* (1999) demonstrated that asphaltenes extracted from unstable crudes displayed greater aromaticity and a higher degree of condensation than asphaltenes extracted from stable crudes. As for the H/C ratio, she establishes a relation between aromaticity and degree of condensation and the stability of the crudes.

### 1.3 Molecular Groups

Several studies have been conducted at the IFP on the structure of asphaltenes by proton (<sup>1</sup>H) and carbon (<sup>13</sup>C) Nuclear Magnetic Resonance (NMR) (Bouquet *et al.*, 1984; Dereppe *et al.*, 1975). <sup>13</sup>C NMR can be used to characterise the CH<sub>3</sub>, CH<sub>2</sub> and CH molecular groups belonging to aliphatic chains

TABLE 5

Physicochemical properties of various asphaltene molecules proposed in the literature

Property	values			
	Groenzin and Mullins (2000)	Speight (1981)	Zajac <i>et al.</i> (1994)	Murgich <i>et al.</i> (1996)
Formula	H <sub>98</sub> C <sub>72</sub> S <sub>1</sub>	H <sub>79</sub> C <sub>80</sub> N <sub>2</sub> O <sub>1</sub> S <sub>2</sub>	H <sub>63</sub> C <sub>57</sub> N <sub>1</sub> S <sub>1</sub>	H <sub>159</sub> C <sub>138</sub> N <sub>3</sub> O <sub>2</sub> S <sub>2</sub>
Molecular weight (amu)	995.64	1149.67	794.2	1955.95
Molecular volume (Å <sup>3</sup> )	794.6	892.7	637.3	1574.6
Elemental analysis (%)				
C	86.86	83.58	86.2	84.74
H	9.92	7.01	8	8.19
N		2.44	1.76	2.15
O		1.39		1.64
S	3.22	5.58	4.04	3.28
Number of fused aromatic rings	7	14	9	24
C <sub>A</sub>	30	47	29	70
C <sub>S</sub>	42	33	28	68
H <sub>A</sub>	11	9	6	19
H <sub>S</sub>	87	70	57	140

and the CH, CH<sub>substituted</sub>, C<sub>condensed</sub> molecular groups belonging to aromatic rings. With these groups it is possible to produce an image of the structure of asphaltenes (Ancheyta *et al.*, 2002) and estimate the thermodynamic quantities of fractions (Szewczyk, 1997) using correlations based on the group contribution concept.

#### 1.4 Other Research Work

Other methods have been used to characterise the structure of asphaltenes:

- chemical methods;
- diffusion methods such as X-ray diffraction (Pedersen *et al.*, 2002);
- thermal decomposition methods.

For further details on these techniques and their results, the reader is invited to consult the reference written by Speight and Moschopedis (1981).

#### 1.5 Image of the “Asphaltene Molecule”

Although improvements are always possible, the main chemical characterisation tools are now thoroughly understood. These techniques can be used to globally describe the asphaltenes as molecules formed from condensed polyaromatic rings containing most of the heteroatoms and carrying alkyl chains. Several authors have proposed an image of the asphaltene molecule. Pacheco-Sanchez *et al.* (2004) listed four different images of asphaltene molecules: Groenzin and Mullins (2000); Speight (1981); Zajac *et al.* (1994) and Murgich *et al.* (1996), whose main characteristics are given in Table 5.

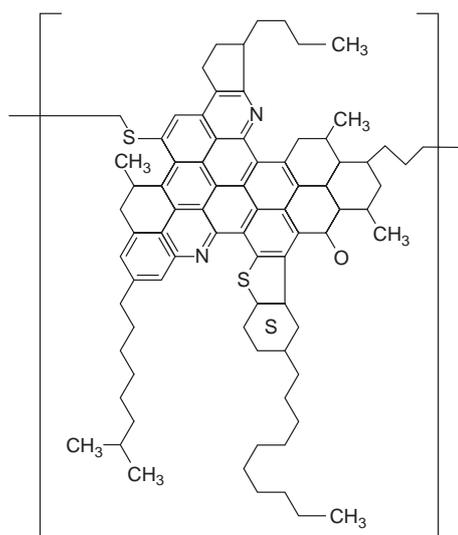


Figure 3  
Asphaltene molecule (taken from Speight and Moschopedis, 1981).

It is also worth mentioning the work of Leon *et al.* (1999), who propose four asphaltene molecules: two corresponding to stable crudes and two to unstable crudes. Speight and Moschopedis (1981) propose the image of asphaltenes shown in Figure 3.

It became clear, however, that the instability of a crude oil, leading to the formation of deposits, cannot be predicted by the chemical composition of its component fractions alone. This observation initiated research work on the characterisation of asphaltene solutions. The parameters investigated are the molar mass, the polydispersity (by mass or size) and the aggregation state involving molecular groups of widely varying dimensions.

## 2 CHARACTERISATION OF ASPHALTENE SOLUTIONS

### 2.1 Introduction

Like the study of asphaltenes, the study of asphaltene solutions depends on the asphaltene separation method since the quantity and type of solvent added to a crude to precipitate the asphaltenes affect not only the quantity of asphaltenes but also their nature. The asphaltene deposits obtained by precipitation, in fact, also contain resins. Consequently, the asphaltene purification step also has an impact on the results obtained (Speight 2004 a and b). Lastly, the nature of the solvent used to redissolve the asphaltenes, as well as the quantity of asphaltene dissolved and the temperature chosen for the study, also affect the measurements. Speight and Moschopedis (1981) investigated the impact of the isolation, purification and dissolution method on the asphaltene molar mass determined by tonometry. Hirschberg *et al.* (1984) demonstrated that in solution, the parameters governing asphaltene solubility and precipitation were the properties of the asphaltenes, the presence of resins, the temperature and the pressure. Depending on the measurement methods, which will involve different properties, the molar mass or the size of the aggregates in an asphaltene solution will vary and no method can produce absolute values.

### 2.2 Determination of molar masses

Vellut *et al.* (1998) have published a bibliographic review of the various techniques for measuring the molar masses of macromolecules. They distinguish between the thermodynamic colligative methods (the property studied depends on the solute concentration for diluted solutions), such as vapour pressure osmometry (tonometry), cryometry, ebulliometry, osmometry (osmotic pressure) and viscosimetry, the separation methods (size exclusion chromatography, supercritical fluid chromatography, liquid chromatography, ultracentrifugation, ultrafiltration), and the spectroscopic methods. The reader can also refer to Cooper's publication (1989) for more extensive information concerning these experimental techniques.

Working together with university teams, several teams from the *Institut Français du Pétrole* have helped develop experimental techniques to determine the molar masses of heavy petroleum fractions. Jointly with the Laboratoire de Chimie Analytique I of Lyon University, directed by Professor J. Jose, several thermodynamic measurement methods have been developed as part of two theses: Blondel-Telouk (1994), and Vellut (2000). Blondel-Telouk *et al.* (1995) developed an apparatus based on the drop in vapour pressure when adding a solute to a solvent. This is the principle of a tonometer. In this case, however, the authors propose a more accurate apparatus (uncertainty less than 2%) than those commercially available (uncertainty = 10%). Vellut *et al.* (1998) developed another apparatus based on a differential ebulliometry method. As part of Vellut's thesis, the average molar masses of about thirty petroleum fluids were measured (tank oils, atmospheric distillation residues, petroleum cuts : saturates, aromatics, resins and asphaltenes) in toluene (% weight of solute of 0.1 to 1%, preparation 48 hours before). The experimental uncertainties (average relative deviations) obtained are estimated at  $\pm 2\%$ . The molar mass ranges determined are as follows:

- for tank oils, from 600 to 700 g/mol;
- for saturates, from 450 to 550 g/mol;
- for aromatics, from 500 to 600 g/mol;
- for C<sub>20+</sub> cuts, from 500 to 750 g/mol;
- for resins, from 550 to 650 g/mol;
- for asphaltenes, from 700 to 3000 g/mol;

Another technique involving much more sophisticated equipment was tested with Professor T. Chiba's team at Okkaido University, as part of the same thesis: mass spectrometry (MS) with Time of Flight measurement of ions obtained according to one of these two modes:

- Matrix Assisted Laser Desorption Ionisation (MALDI);
- Laser Desorption (LD).

In both cases the sample to be studied, either mixed with a specific solvent or alone, is deposited on a platinum or gold target and subjected to laser radiation. If the average molar mass of asphaltenes is measured using these techniques, most fractions studied have a value of about 2000 g/mol. Lastly, if the ebulliometry results are compared with the mass spectrometry results, average relative deviations ranging from 6% for asphaltenes and 19% for resins are observed. These results can be considered as satisfactory, especially since MS is applied to solid samples whilst ebulliometry is used to study the same fractions dissolved in a solvent. Since this comparison was carried out using about fifty petroleum cuts taken from 16 tank oils from a wide range of geographical locations, it can be considered as highly reliable, both quantitatively and qualitatively. Methods have also been developed using separation techniques. For instance, size exclusion chromatography is used to determine the molar masses of asphaltenes, residues and effluents of hydroconversion

processes. Merdrignac *et al.* (2004) demonstrated that size exclusion chromatography, although unsuitable for absolute determination of molar masses for these compounds, can be used to compare the molar mass distributions under given analytical conditions. Light, X-ray and neutron scattering techniques (Ravey and Espinat, 1990; Espinat, 1991) have also been used in the determination of molar masses.

Speight *et al.* (1985) have published a critical review of the experimental techniques and the results in the literature. They also provide a summary of the advantages and disadvantages of each experimental technique. Their conclusion is that no universal method is available to characterise the molar mass, the size of the aggregates in an asphaltene solution. They consider, however, that the results of Moschopedis *et al.* (1976) are the most accurate. These authors determined the molar mass of asphaltenes by vapour pressure osmometry for a large number of oils, in various solvents. They demonstrate that the molar masses measured in benzene, dibromomethane and pyridine correspond to associated molecules. In contrast, the molar masses of asphaltenes determined in nitrobenzene are practically constant and equal to  $1800 \pm 300$  g/mol. The authors conclude that the molar mass of the "asphaltene molecule" must correspond to this value.

### 2.3 Colloidal Structure of Asphaltenes in Solution

One of the images most frequently used to represent asphaltenes in solution is that of colloids. They are defined as particles of size between molecular scale and the micron, dispersed in a solvent by Brownian motion. This approach offers the advantage of being independent of the intimate details of the structure at molecular level. The colloids can be represented by statistical entities with few macroscopic parameters. Many colloids display a fractal spatial distribution between two sizes, one low and the other high. The fractal dimension, which represents the compactness of the structure, can vary between 1 (linear structure) and 3 (compact structure). Several techniques can be implemented to characterise the colloidal behaviour of asphaltene solutions. We will describe three of them which have been used recently at the *IFP*: small angle scattering, electron microscopy and viscosimetry.

Small angle scattering is a powerful tool which can be used to determine the structure of colloids from nanometric to submicronic scale. The radiation sources used are X-rays (Small-Angle X-Ray Scattering, SAXS), neutrons (Small-Angle Neutron Scattering, SANS) and visible light. Since asphaltenes are absorbent materials, these techniques are limited to dilute asphaltene solutions. The principle used in these techniques consists in measuring the brightness of the scattered beam against wavelength ( $\lambda$ ) and angle of observation ( $\theta$ ) which define the wave vector  $Q$  according to:

$$Q = \frac{4\pi}{\lambda} \sin \theta$$

Espinat *et al.* (1998) provide an exhaustive description of the information which can be deduced from scattering measurement. The results of such measurements can be divided into two types: those which are dependent on an interpretation model and those which are not. Fairly reliable values of average volume by weight, molar mass by weight and radius of gyration can be deduced from experimental measurements without using distribution models. In contrast, Barré *et al.* (1997) demonstrated that the experimental scattering spectra could be reproduced using different distributions of realistic colloids (spheres, discs, ellipses, etc.). The results of approaches such as these must therefore be interpreted with caution, and the method used to obtain them should always be borne in mind.

Electron microscopy is an excellent technique to study the structure of samples. Since the sample must be kept at very low pressure ( $10^{-5}$  torr) when using electron beams, this technique is restricted to solids. With suspensions, evaporation of the liquid inevitably leads to a change in the sample structure. One way of getting round the problem is to solidify the liquid by cooling and carry out the microscopic examination at low temperature. This approach was used by Espinat *et al.* (1998). It reveals the fractal structure of asphaltenic residues in toluene and *n*-heptane mixtures. It is important to mention a recent study conducted by Acevedo *et al.* (2004) which corroborates the results obtained by SAXS using a microscopy method, therefore not involving a colloid representation model.

Viscosimetry is the third colloid characterisation method examined. Intrinsic viscosity is a typically colloidal property. It reflects the effect of submicronic particles present in a homogeneous and Newtonian solvent. The experimental results obtained in viscosimetry indicate that viscosity is a linear function of the asphaltene volume fraction, as long as it remains below 2-3%, and that it increases much more quickly as soon as the asphaltene volume fraction exceeds 7-8%. In diluted state therefore, there exists a region where the relative viscosity,  $\eta_r = \eta/\eta_0$  the ratio between the solution viscosity and the solvent viscosity, is linear depending on the particulate volume fraction  $\Phi$ . The intrinsic viscosity can therefore be defined as:

$$[\eta] = \lim_{\Phi \rightarrow 0} \left( \frac{\eta_r - 1}{\Phi} \right)$$

Various interpretations have been put forward to explain the values obtained (Reerink, 1973). They give a geometric image of the asphaltene particles (solvated spheres, ellipses, etc.).

Concerning the modelling of these colloidal structures, several models determining the aggregation kinetics of the particles and of the resulting structure can be found in the literature. For example, the DLCA (Diffusion Limited Cluster Aggregation) model which assumes that aggregation is controlled by particle diffusion, and the RLCA (Reaction

Limited Cluster Aggregation) model which assumes that a limitation exists via a potential barrier.

There is still disagreement, however, concerning the colloidal nature of asphaltenes. For Sirota (2005), asphaltenes are molecules which may lead to traditional liquid-liquid demixing. The asphaltene-rich phase is often below its glass transition, resulting in a solid appearance with a fractal morphology, hence its colloidal appearance. Based on this approach, Sirota interpreted the diffraction experiments by fluctuations in compositional homogeneities.

Micelles, examples of aggregated colloids of finite size, form a special case of colloidal systems. When the molecules display chemical dissymmetry, with a lyophilic part and a lyophobic part, the formation of micelles depends on external conditions (temperature, concentration or chemical nature of the solvent). At low concentrations, these molecules are separated from each other, whereas at high concentrations, they form complex structures known as micelles. The transition between these two regimes is known as the Critical Micelle Concentration (CMC).

## 2.4 Critical Micelle Concentration

Andersen and Speight (1994) published a concise bibliographic review of the studies in the literature and the various experimental techniques employed to determine the critical micelle concentration of an asphaltene solution. Leon *et al.* (1999) measured the critical micelle concentrations of asphaltene solutions in various solvents (cyclohexane, tetrahydrofuran, carbon tetrachloride) ranging from 1 to 18.6 g/l. They show that the highest micelle concentrations are found in asphaltenes extracted from stable crudes, irrespective of the solvent used. Andersen and Birdi (1991) demonstrate that the resins added to the asphaltene/solvent medium participate in the formation of micelles and are not involved as co-solvent.

## 2.5 The Solubility Parameter

Numerous approaches based on the Flory-Huggins theory (see *paragraph 6*) use an asphaltene solubility parameter, even though asphaltenes do not respect the assumptions underlying this model. This solubility parameter, introduced by Hildebrand, describes the cohesion energy of a molecule according to:

$$\delta = \sqrt{\frac{\Delta H_{vap.} - RT}{v_m}}$$

where  $\Delta H_{vap.}$  is its vaporisation enthalpy,  $v_m$  its molar volume,  $T$  the temperature and  $R$  the perfect gas constant. Several methods are available to determine the solubility parameter of a constituent (Andersen and Speight, 2001). This parameter

can be estimated from equations linking the composition and structure of asphaltenes to their solubility parameter (Leon *et al.*, 1999). Rogel (1997) suggests another calculation method based on molecular modelling. The principle is as follows: the experimental data obtained (molar mass, elemental analysis, NMR) are compared with the data obtained by molecular dynamics on a sample of 10 000 molecules. After choosing the molecules forming the fraction studied, its solubility parameter is calculated using a group contribution method. Rogel (1997) demonstrates that the solubility parameters calculated for asphaltenes and resins increase when the H/C ratio of the fraction drops, the largest solubility parameters corresponding to the unstable asphaltenes. Based on the behaviour of pure components, Laux *et al.* (2000) propose a group-contribution correlation to calculate the asphaltene solubility parameter. Lastly, the asphaltene solubility parameter can be determined using solubility tests in different solvents (Yen, 1984). The solubility parameter depends linearly on the Critical Micelle Concentration in apolar solvents (Andersen and Birdi, 1991). Consequently, the aggregation behaviour of asphaltenes can be related to their structure and composition.

## 2.6 Study of Asphaltene Aggregation on Adding a Poor Solvent

Jointly with the University of Paris VI and the Laboratoire Central des Ponts et Chaussées, the Institut Français du Pétrole took combined measurements of viscosity and small-angle neutron and X-ray scattering (SANS and SAXS) with diluted solutions of Safanyia asphaltenes (Fenistein *et al.*, 1998), either in pure toluene or in toluene + *n*-heptane mixtures. The two techniques implemented can be used to obtain complementary characteristics regarding the structure of asphaltene aggregates in solution. If we examine the effect of the solvent, at a given asphaltene volume fraction, SANS measurements reveal progressive aggregation of asphaltenes as heptane is added. In addition, superimposition of spectra corresponding to small size reveals the structural similarity of asphaltenes at this scale. The measurements taken using neutron scattering also indicate that there is a significant increase in the size (radius of gyration and effective volume) and the molar mass of asphaltenic aggregates in solution on adding *n*-C<sub>7</sub>, so providing a “microscopic” interpretation of the results observed. If we now examine the variation in intrinsic viscosity of asphaltene solutions as a function of the heptane/toluene ratio, we first observe a drop in this viscosity before a large increase near the flocculation point. This indicates that dilution first occurs in the region surrounding the asphaltenes, and therefore possible deaggregation of these compounds, then a reaggregation effect resulting in flocculation above a certain heptane concentration. In conclusion, Fenistein (1998) demonstrates that the asphaltene concentration on these measurements is incompatible with a flattened

object model. In contrast, these measurements are coherent with a fractal aggregation structure of dimension equal to 2. A large fraction of solvent is trapped in the structure, resulting in high intrinsic viscosity. By studying the addition of flocculant, he gives the following image of asphaltene flocculation. In the solvent, the asphaltene structure is open, solvated and fractal with a dimension of 2. The asphaltene aggregation mode is compatible with the RLCA (Reaction Limited Cluster Aggregation) model. Above the flocculation point, large compact structures appear.

## 2.7 Image of Asphaltene Solutions

The hypothesis of a micelle type structure was proposed for the first time by Pfeiffer and Saal in 1940. They suggested that asphaltenes form the centre of a micelle peptised by maltenes, the micelles possibly agglomerating into larger clusters. Using numerous experimental techniques, Yen (1981) proposes a more accurate image of asphaltenes in solution (see Fig. 4). Firstly, the asphaltenes combine to form elemental particles which in turn combine to form a micelle. The combination of these micelles may then lead to larger particles or even flocs. This model has been confirmed in numerous publications: Sheu and Storm (1995); Espinat *et al.* (1998), Savvidis *et al.* (2001).

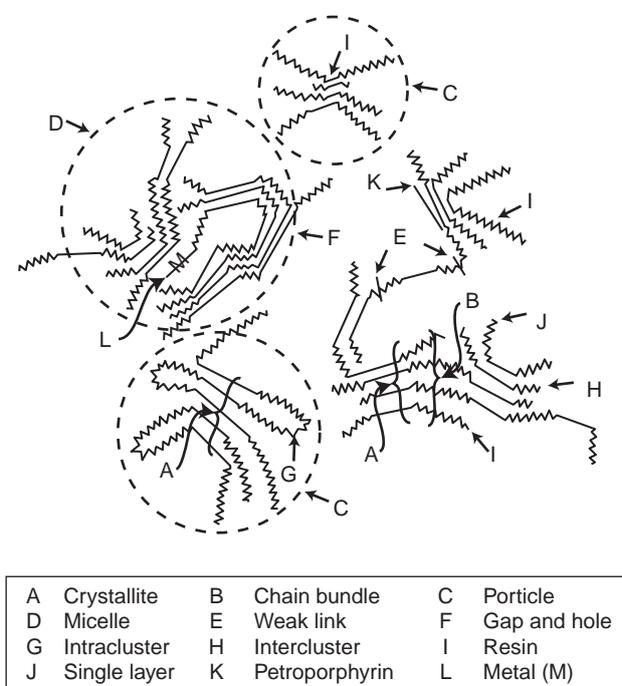


Figure 4

Image of asphaltene aggregates in solution (taken from Yen, 1981).

### 3 CHARACTERISATION OF ASPHALTENIC CRUDES

It seems appropriate to question whether the study of molecules of asphaltenes, or their aggregation state in solution in good solvents, can be transposed to the study of real crude oils. Few characterisation techniques are in fact applicable to this complex environment (small-angle X-ray scattering, viscosity).

Espinat *et al.* (1984) demonstrated the benefit of using X-ray scattering (SAXS) with crudes, whereas by using small-angle neutron scattering (SANS), Ravey *et al.* (1988) and Overfield *et al.* (1989) confirmed the presence of aggregates in oils and characterised their physical dimensions and shapes according to solvent quality. Still using scattering techniques, Espinat and Ravey (1993) observed that the size of micelles depends on the temperature, the solvent type and the asphaltene concentration. According to these authors, the size depends on a reversible thermodynamic equilibrium between primary particles and aggregates. For mixtures of maltenes and asphaltenes, Fenistein *et al.* (1998) find the same compact flocculated and open fractal structural types as with asphaltene + toluene synthetic mixtures.

Using small-angle X-ray scattering and viscosity measurement techniques, Hénaut *et al.* (2001) studied fluids “recombined” from maltenes and asphaltenes extracted from an oil by addition of *n*-pentane. They show that the behaviour of heavy oils is similar to that of polymer solutions. For low asphaltene concentrations, the relative viscosity of maltene/asphaltene mixtures increases with the asphaltene concentration. Above a certain concentration known as the overlap concentration in the polymer domain,  $C^*$ , the relative viscosity increases sharply and the radius of gyration measured by scattering decreases.

Having described the properties of asphaltene in synthetic media, we develop in the following the behaviour of asphaltene in natural media, either tank oil (crude oil at atmospheric conditions *i.e.* without dissolved gases) or bottom oil (crude oil at reservoir conditions).

## 4 FLOCCULATION IN A TANK OIL

### 4.1 Introduction

Standardised measurement of the asphaltene content of a tank oil and characterisation of asphaltenes in good/poor solvent solution cannot be used to predict the onset of flocculation, the kinetics of this phenomenon, or the size of the flocculated aggregates. However, this information is crucial for oil companies in order to assess the risk of flocculation, hence the need to characterise flocculation in tank oils. The most important notion is that of flocculation point, which is defined as being the minimum quantity of flocculant which precipitates the asphaltenes in the crude/solvent medium.

Mousavi-Dehghani *et al.* (2004) propose various descriptions of this flocculation point.

### 4.2 Detection of Flocculation Point by Direct Observation

#### Filter Drop Spreading Method

A drop of the flocculant-crude-solvent mixture to be studied is sampled and placed on a filter paper. After a few minutes drying, the stain observed stabilises by evaporation and diffusion through the paper. The filter drop spreading method is based on the fact that the flocculated particles diffuse more slowly than the surrounding liquid when the mixture is placed on a filter paper. The following results can be obtained:

- A uniform stain indicates that there are no particles in suspension, *i.e.* no flocculation has yet occurred in the mixture;
- A black area in the centre of the stain indicates the presence of flocculated asphaltenes. This technique forms the basis of ASTM D4740.

The flocculation point can be detected by studying various flocculant-crude-solvent mixtures containing an increasing quantity of flocculant.

#### Optical Microscopy

The particles in suspension are observed directly in the preparation studied. A drop of the solution to be studied is sampled and observed under optical microscope. These studies are carried out under normal light (detection of asphaltenes) or under polarised light (observation of paraffins).

#### Drawbacks of these Methods

The three main drawbacks with these methods are given below. It is difficult to accurately observe the appearance of a precipitate due to the lack of progressivity of these methods, which tend to produce “all or nothing” results. The measurements are long and difficult to automate. Lastly, a systematic error may be introduced into the results of the optical microscopy test, due to evaporation of the diluents during observation.

### 4.3 Observation of Flocculation Point by Light Scattering

Studies have been conducted in the *Institut Français du Pétrole* (Hotier and Robin, 1983; Hotier, 1982) to determine this flocculation point by light scattering. The authors even patented the method (FR2566909, 1986). The same technique has been used by other authors (Fuhr *et al.*, 1991; Reichert *et al.*, 1986).

Hotier et Robin (1983) suggested the use of light scattering to determine the flocculation point, since this technique is more progressive, it can be automated and it is easier to implement than the previous methods. Since the crudes used are first diluted (to allow light to pass through the crude/solvent medium), the flocculation point can be studied as a function of the quantity and type of solubilising agent used. The authors propose two experimental methods.

#### Opacimetry

This method is based on measurement of the intensity transmitted by a crude/solvent solution. The intensity of the light transmitted first increases due to dilution by addition of flocculant. The formation of particles then opacifies the medium by scattering the light rays in all directions, stopping the increase in the luminous flux transmitted. This event indicates the flocculation point.

#### Nephelometry

This method is based on measurement of the scattered intensity, for example at an angle of 90°. The scattered light remains virtually constant until the flocculation point is reached. As soon as the flocculation point is reached, a sudden increase is observed in the scattered light, indicating the flocculation point. Lastly, some authors have suggested that, in addition to the flocculation point, the variations in aggregates over time should also be observed (Rahmani *et al.*, 2005).

Light scattering can no longer be used when the quantity of asphaltenes in the crude studied is too low. In this case another method, known as capillary viscosimetry, can be used.

#### 4.4 Observation of Flocculation Point by Capillary Viscosimetry

Its detection principle is based on an increase in the pressure loss across the ends of a capillary tube containing a flocculant-crude-solvent mixture. Depending on the authors, this increase is related:

- either to the presence of asphaltene aggregates in the medium and corresponds to approaching the flocculation point (El Mohamed *et al.* 1988, De Boer *et al.* 1995, Escobedo and Mansoori, 1995, 1997; Ali and Islam, 1998).
- or to the appearance of a layer of flocculated asphaltenes on the surface of the capillary tube. This increase can then be used to determine the thickness of this layer of asphaltenes formed (Broseta *et al.*, 2000).

Capillary viscosimetry has proved to be an extremely sensitive method to monitor flocculation and the formation of deposits, since it is able to detect flocculation in a mixture containing approximately 0.04% by weight of asphaltenes (Broseta *et al.*, 2000).

#### 4.5 Other Methods

Prunelet *et al.* (2004) demonstrated that nuclear magnetic resonance (NMR) could be used to determine a flocculation point in an asphaltene solution and they extended this method to tank oil in a patent (FR2834792). Other methods are available to determine the flocculation point, *e.g.* interfacial tension measurement (Vuong, 1985), electrical conductivity measurement (Fotland *et al.*, 1993) and filtration (Rassamdana *et al.*, 1996, Jiang *et al.*, 1990).

#### 4.6 Results of the Studies

Information has been obtained on the various parameters influencing the flocculation point and the quantity of flocculated asphaltenes by studying flocculation in flocculant-crude-solvent mixtures. These parameters are:

- the chain length of the *n*-alkane used as flocculant;
- the type of solvent used;
- the temperature;
- the pressure.

Hotier and Robin (1983) demonstrate, for the series of *n*-alkanes, that the maximum flocculation point is obtained with *n*-heptane, then that it drops as the number of carbons increases, whereas the percentage of flocculated asphaltenes decreases with the number of carbon atoms. Ghouloum and Oskui (2004) obtain the same result and demonstrate that the flocculation point in a tank oil at 20°C and 208 bar drops with the number of carbon atoms for the following series of flocculants: CO<sub>2</sub>, C<sub>2</sub>, C<sub>3</sub>, *n*-C<sub>4</sub>, *n*-C<sub>5</sub>, *n*-C<sub>6</sub>, *n*-C<sub>7</sub>. Reichert *et al.* (1986) test four solvents: toluene, a gas oil, a highly aromatic diesel and a slightly aromatic diesel, and demonstrate that with the bitumen studied, highly aromatic diesel is the best solubilising agent.

Hotier and Robin (1983) and Fuhr *et al.* (1991) study the effect of temperature on the flocculation point. They demonstrate that the flocculation point decreases slightly, which indicates that the crude becomes more unstable as the temperature rises. Burger and Robin (1983) observed the same tendency on Hotier - Robin type equipment adapted to operate at high pressure and temperature. Lastly, Briant (1963) demonstrated that the quantity of flocculated asphaltenes also increased with temperature. In contrast, with heavy oils, Gharfeh *et al.* (2004) observe that the crude becomes more unstable with temperature in the presence of heptane and that the same crude becomes more stable in the presence of naphtha. Ghouloum and Oskui (2004) observe that the crude becomes more stable with temperature. In conclusion, the results in the literature indicate no clear trend since temperature affects not only the solubilities of the components in a mixture, but also the molar volumes (see *paragraph 6*).

Briant (1963) studied the effect of pressure and demonstrates that increasing the pressure decreases the quantity of flocculated asphaltenes in the medium.

## 5 FLOCCULATION IN A RESERVOIR FLUID

Fewer experimental studies have been conducted on reservoir fluids due to the additional technical difficulties involved (pressure regulation) (Lhioreau *et al.*, 1967) and the representativeness of the samples studied. Fotland (1996), for example, demonstrates that it is best to study reservoir fluid sampled at the reservoir pressure. Some authors quantify the quantity of flocculated asphaltenes in a mixture after flashing. Quantification of the asphaltenes is then open to discussion: does it correspond to the asphaltenes flocculated under the temperature and pressure conditions in which the mixture was studied? (Burke *et al.*, 1990; Jiang *et al.*, 1990)

### 5.1 Observation of Flocculation Point by Gravimetry

This method consists in stabilising a mixture in a cell for 24 hours, under the temperature and pressure conditions generally corresponding to the reservoir conditions, so that the flocculated asphaltenes have time to settle. The percentage of asphaltenes is then measured:

- either in the upper phase of the cell. In this case, the quantity of non-flocculated asphaltenes is being determined (Jamaluddin *et al.*, 2001);
- or on the walls and at the bottom at the cell. In this case, the quantity of flocculated asphaltenes is being determined (Burke *et al.*, 1990).

In both cases, this method can be used to determine the flocculation point as well as the quantity of asphaltenes participating in flocculation.

### 5.2 Observation of Flocculation Point by Light Scattering

Jamaluddin *et al.* (2001) used the near infrared ( $\sim 1600$  nm) and measured the signal transmission. During depletion, at pressures greater than the flocculation point, the light transmitted increases since the fluid density decreases. Once the flocculation point has been reached, the light transmitted decreases due to the presence of larger and larger asphaltene particles in the medium, dropping down to zero around the bubble point. When the light transmitted starts to increase slightly as the pressure is reduced, the redissolution threshold has been reached. Hammami *et al.* (2000) obtained the same type of results on oils from the Gulf of Mexico. Like the previous authors, they observe that although this technique can be used to determine the flocculation point, and with certain precautions the redissolution threshold, observation of possible reversibility may prove difficult due to the deposits which form on the surface of the cell and which take a long time to dissolve. Aquino-Olivos *et al.* (2001) used the same technique to determine the effect of inhibitors on the flocculation point of reservoir fluids. Lastly, Gharfeh *et al.* (2004) used

this technique on diluted heavy oils, infrared radiation being unable to cross the heavy oils otherwise, then added a flocculant.

### 5.3 Observation of Flocculation Point by Filtration

This method consists in stabilising a mixture in a cell for 24 hours, under the temperature and pressure conditions generally corresponding to the reservoir conditions. An aliquot portion of the mixture is then filtered under equilibrium pressure and temperature conditions and the percentage of flocculated asphaltenes is measured:

- either on the filter. In this case, the quantity of flocculated asphaltenes is being determined (Jiang *et al.*, 1990);
- or in the filtrate. The quantity of non-flocculated asphaltenes is being determined. Knowing the total quantity of asphaltenes present in the mixture, the quantity of flocculated asphaltenes is determined by subtraction (Szewczyk and Behar 1999, Edmonds *et al.*, 1999).

In both cases, this method can be used to determine the flocculation point as well as the quantity of asphaltenes participating in flocculation.

### 5.4 Other Research Work

Other methods can be used to determine the flocculation point in reservoir fluids, for example electrical conductivity measurement (Fotland, 1996) and acoustic resonance (Jamaluddin *et al.*, 1998). Negahban *et al.* (2003) use a high-pressure microscope to observe the size of asphaltene aggregates during depletion. At high pressure, Joshi *et al.* (2001) measure the spectrum between 2500 and 800 nm of a reservoir fluid as a function of time in order to determine whether flocculation occurs, the size of the existing particles and their sedimentation rate. Lastly, Zou and Shaw (2004) use X-rays to determine the phases involved and the densities of the phases in a vacuum residue/*n*-alkane mixture. Their measurements are based on the fact that the intensity of a transmitted X-ray image is a function of the elemental composition, density and thickness of the sample and the apparent densities were obtained through calibration.

### 5.5 Conclusions

Jamaluddin *et al.* (2001) compared several experimental techniques used to determine the flocculation point or even the quantity of asphaltenes flocculated during depletion of a reservoir fluid. Table 6 summarises the advantages and disadvantages of the methods described above, mainly drawn from their results.

The effect of pressure on flocculation of a crude oil under reservoir conditions is now known. Several studies show that the flocculation point is generally located at a pressure

TABLE 6

Comparison of experimental techniques used to determine a flocculation point in a reservoir fluid Results of studies

Technique	Gravimetry	Acoustic resonance	Light diffusion	Filtration
Flocculation point	X	X	X	X
Bubble point	(X PVT cell)	X		(X PVT cell)
Redissolution threshold	X		X	X
% flocculated asphaltenes	X			X
Volume	High	Low (10 cm <sup>3</sup> )	Low (30 cm <sup>3</sup> )	High
Execution time	Long (x times 24h)	Fast	Fast	Long
Operating conditions	No stirring	No stirring	Stirring	Stirring
Remark	Imprecise flocculation point		Interpretation of results difficult Asphaltene deposit on walls	Flocculation point underestimated

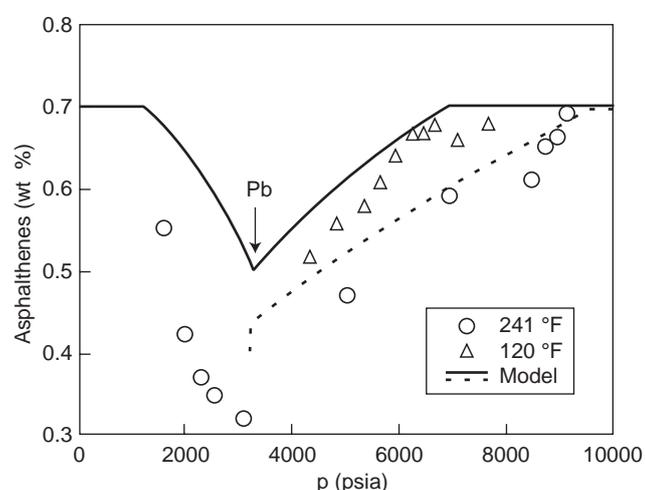


Figure 5

Percentage of soluble asphaltenes in a reservoir fluid during depletion (taken from Kahir and Jamaluddin, 1999.)

greater than the fluid saturation pressure and that maximum flocculation occurs at the saturation pressure (Jamaluddin *et al.*, 2001; Hammami *et al.*, 2000; Jiang *et al.*, 1990). Kabir and Jamaluddin (1999), Edmonds *et al.* (1999), Szweczyk and Béhar (1999) determined experimentally the percentage of soluble asphaltenes in a reservoir fluid during depletion and obtained the graph shown on Figure 5, extracted from studies conducted by Kabir and Jamaluddin (1999).

Jamaluddin *et al.* (2001, 1998) observe a slight pressure drop after which the flocculation point appears when the temperature increases (see Table 7) and a reduction in the quantities of flocculated asphaltenes (see Fig. 5). Neghaban *et al.* (2003) confirm this temperature effect by observing flocculation in a reservoir oil at 130 °F and its absence at 190 °F and 250 °F. All the authors agree that the effect of temperature remains small compared with the effect of pressure. De Boer *et al.* (1995) confirm this results using a solubility model.

TABLE 7

Effect of temperature on the flocculation point of a reservoir fluid

Temperature	Bubblepoint pressure MPa (psia)		Solid onset MPa (psia)
	Visual	AR	
48 (120)	36.06 (5230)	35.57 (5159)	42.98 (6234)
57 (135)	36.41 (5280)	36.47 (5289)	42.58 (6176)
66 (150)	36.75 (5330)	36.89 (5351)	41.86 (6071)

## 6 FLOCCULATION MODELS

### 6.1 Introduction

The previous paragraphs provided an obviously non-exhaustive overview of the studies conducted on asphaltenes. The number of studies published on the subject since the 1930's is quite impressive. The various studies focused on the following two aspects:

- characterisation of the asphaltenes;
- determination of the flocculation conditions.

From an industrial standpoint, the aim of these studies is to define models capable of predicting the flocculation of asphaltenes in the various configurations encountered during the production of hydrocarbons.

Flocculation occurs in a wide range of situations. In the reservoir, asphaltene flocculation may be due to the following causes: a change of temperature, pressure, composition or due to the electrokinetic effect (Leontaritis, 1989). Generally, the temperature variations of a reservoir are low and can be ignored (in contrast, flocculation studies must be carried out at the reservoir temperature to be relevant). Changes of composition, whether due to a drop in reservoir pressure or injection of fluid during enhanced recovery operations, are the main causes of asphaltene flocculation. Asphaltenes are polar

molecules bearing electrical charges which are involved in the structure of aggregates (Leontaritis and Mansoori, 1987). During fluid flows, these electrical charges may be neutralised, resulting in destabilisation of the aggregates and therefore the onset of flocculation. This phenomenon is extensively described in the literature (Lichaa and Herrera, 1975; Leontaritis and Mansoori, 1987), and no further details will be given on this point in the remainder of this text.

In a reservoir, the flocculated asphaltenes are likely to deposit in the pores and passages of the porous matrix, thereby reducing its productivity. Note that asphaltene flocculation may occur without any formation damage. It is important to distinguish between asphaltene flocculation and deposition. The flocculation of asphaltenes in fluid phase is simply an indicator of their dangerousness. In this context, a flocculation model must be able to predict the thermodynamic conditions (pressure, temperature, composition) resulting in a risk of asphaltene deposition, ideally even before the reservoir goes into production. Another more curative application of such models consists in defining the possible treatment conditions to eliminate asphaltene deposits when they are formed and affect the reservoir productivity.

In the oil industry asphaltenes are also formed during hydrotreatment operations in refineries. In these units, the heavy residues produced during the conversion of petroleum cuts into lighter fractions also deposit on the equipment. Elimination of these products is extremely expensive and should be avoided. Once again, asphaltene flocculation models are essential to predict the operating conditions of the equipment. In this article, we will only discuss the context of hydrocarbon reservoirs, but the tools developed can also be applied to other situations.

## 6.2 Flocculation Reversibility?

We have seen that two factors may be primarily responsible for flocculation in the reservoirs: pressure and the change in composition of the hydrocarbon fluid. From a practical point of view, the second factor is the easier to implement experimentally and much data on this subject can be found in the literature. The effect of pressure is more difficult to implement and less data are available. In addition, these measurements are mainly taken on real fluids and the results are therefore considered as confidential by operators. In contrast, the composition effects are often tested on synthetic fluids and the data are more readily available.

Despite the number of studies dedicated to asphaltene flocculation, the stability of asphaltenes in oils has not yet been fully elucidated (Kokal *et al.*, 1992; Cimino *et al.*, 1995; Wang 2000). This situation leads to two consequences: currently, there are no clearly defined models and it is not yet known whether flocculation is reversible or irreversible.

Based on their own experiments Pfeiffer and Saal (1940), conclude that flocculation is irreversible. Wang *et al.* (1999)

assume that, under conditions far from the flocculation point, the flocculation process is difficult to reverse. Hirschberg *et al.* (1984) assume that flocculation is reversible, but only with very slow redissolution kinetics. Our own measurements add to this confusion. As proof, Figure 6 shows the variation in the content of asphaltene dissolved in a sample of bottom oil as a function of pressure. Starting from a pressure of 65 MPa, depletion continues to around the bubble pressure, then the pressure is increased again. We have also indicated the initial asphaltene content of the fluid. The figure shows that we do not return to the initial value after recompression, in spite of the fact that a relatively long time was allowed to reach equilibrium (the two measurement points at 65 MPa correspond to an interval of 72 hours).

The same study on a quite different crude shows the opposite behaviour with another fluid (see Fig. 7). In this case, we return to the initial state after the decompression and recompression phases.

It appears, however, that many recent studies are in favour of a phenomenon which is at least partially reversible. Chung *et al.* (1991) published results which showed that a quarter of the asphaltenes flocculated with *n*-pentane were redissolved. Kokal *et al.* (1992) show that with two Canadian oils, the precipitates formed could be redissolved by adding heavy oil. Ramos *et al.* (1997) also indicate that the flocculation process is reversible. Recent measurements taken in a PVT cell equipped with a laser solid detection system (SDS) indicated that flocculation can be reversed by alternating decompression and recompression steps (Hammami *et al.*, 2000). These measurements are extremely important since the results were obtained without sampling likely to modify the system. Ghloum and Oskui (2004) also demonstrated reversibility of flocculation with Kuwait oils.

During an internal study focusing on the influence of solvents, the variation of “tank oil + wax flocculant + aromatic solvent” ternary mixtures was examined. Several dozen mixtures were produced such that they lie within the flocculation domain. Solvent was added after 24 hours to bring all these mixtures into the solvation zone. In all cases, the precipitated asphaltenes were redissolved provided that sufficient time (about 48 hours) was allowed to reach equilibrium. In conclusion, asphaltene flocculation must be considered as a process which is at least partially reversible. The differences in the results obtained are probably due to the degree of destabilisation of the asphaltenes. The greater the degree of destabilisation, the less flocculation should be considered as reversible. In contrast, if the flocculation conditions remain close to the flocculation point, flocculation should be considered as reversible. In a recent study, Beck *et al.* (2005) demonstrated hysteresis between asphaltene precipitation and redissolution. This effect is increased in the presence of air due to oxidation reactions. Complete reversibility can be obtained, however, when the asphaltenes are destabilised as little as possible and these authors suggest that hysteresis is

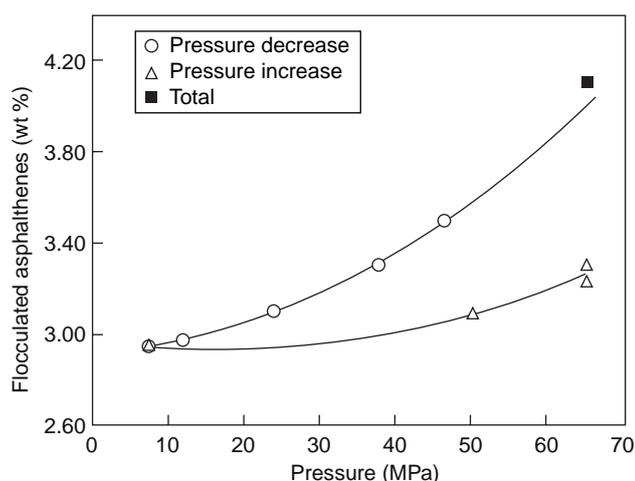


Figure 6

Contents of flocculated asphaltene in a crude *S*, during a decompression then recompression study.

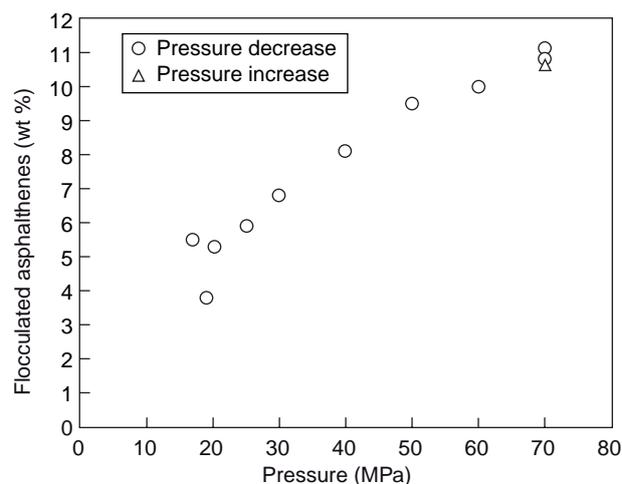


Figure 7

Contents of flocculated asphaltene in a crude *M* during a decompression then recompression study.

due to an energy barrier. When the asphaltene in solution are destabilised, they combine together to form large molecules. On attempting to redissolve them, the macromolecules may remain. The asphaltene return to their original size upon heating. These authors therefore consider that flocculation is reversible and that the hysteresis sometimes observed must be explained by an energy barrier.

### 6.3 The Various Classes of Flocculation Models

Before describing the model developed at the *IFP*, we will examine the four groups of models proposed in the literature, placing the emphasis on their hypotheses:

- the solubility models;
- the solid phase models;
- the colloidal models;
- the micellisation models.

#### Solubility Models

Historically the first, this type of approach was proposed by Fussel (1979), then taken up by Hirschberg *et al.* (1984). Initially, a traditional approach using a cubic equation of state is used to analyse the liquid - vapour behaviour of the fluid, neglecting the possible effect of precipitated asphaltene. In a second step, flocculation is taken into account as a liquid - liquid equilibrium. The asphaltene solution is considered as a two-constituent system: the asphaltene which may form a pure phase and the other constituents (including the resins) which form the oil phase. The phase separation is calculated using the Flory-Huggins model: the asphaltene molecules are therefore considered as a monodispersed polymer. In the simple case when only negligible quantities of asphaltene

are dissolved in oil, Hirschberg *et al.* obtain the following expression:

$$\phi_A = \exp\left(\frac{v_A}{v_L} \left[1 - \frac{v_L}{v_A} - \frac{v_L}{RT} (\delta_A - \delta_L)^2\right]\right)$$

where  $\phi_A$  is the volume fraction of asphaltene in oil,  $v_A$  and  $v_L$  are respectively the molar volumes of asphaltene and oil and  $\delta_A$  and  $\delta_L$  are the solubility parameters of asphaltene and oil. De Boer *et al.* (1995) demonstrated that the properties of the oil can be correlated with its density. The model therefore has two parameters specific to asphaltene.

This approach would therefore suggest that flocculation is fully reversible. Since then, various modifications have been made to this approach: Mansoori and Jiang (1985) and Kawanaka *et al.* (1991) proposed a form allowing a polydispersity of asphaltene molecules to be considered. In their approaches, the Flory-Huggins model is replaced by the Scott and Magat model, to take into account a polydispersity of asphaltene. Cimino *et al.* (1995) discarded the assumption that the flocculated phase is composed solely of asphaltene.

#### Solid Phase Models

The first tests using this approach were proposed by Gupta (1986) and Thomas *et al.* (1992). Nghiem *et al.* (1993) proposed their approach considering that the phase which flocculates is solid and composed solely of asphaltene. The heavy oil fraction then consists of two constituents: a compound which is soluble in oil and another compound which precipitates. The liquid-vapour equilibria are analysed traditionally with a cubic equation of state. Since it is extremely easy to express the chemical potential of asphaltene in solid

phase, this model is easy to introduce in the reservoir simulators (Qin *et al.*, 2000), although experimental data are required to configure it.

### Colloidal Models

This type of model can be applied to two phenomena (Leontaritis and Mansoori, 1987): explaining the peptising role of resins around the asphaltenes and accounting for the electrokinetic effects. In this paper, we will concentrate on the first aspect. In this approach, asphaltenes are considered to be solid particles stabilised in a fluid by resin molecules. The asphaltene + resin system therefore forms colloids. The transfer of peptising agents from the colloid to the oil phase destabilises the colloids, resulting in asphaltene flocculation.

As with the other models, the liquid-vapour equilibrium calculations are made using a cubic equation of state. The chemical potential of the peptising agents (the resins) in the oil phase can therefore be calculated and this potential compared with that of the resins in the asphaltene phase. The flocculation point is determined by equating these two potentials. Once again, the Flory-Huggins model is used to express the potential of the resins in the asphaltene phase. This choice is explained by the fact that resins and asphaltenes can be considered as polymers. In this type of approach, flocculation is considered to be an irreversible phenomenon. This approach applies when the asphaltene + resin structure dissociates. If these structures are not modified, or only slightly, this model is equivalent to a solubility model from the point of view of its physics. It should be emphasised that in the absence of resins, the asphaltenes must flocculate in any solvent; this is the main fault with this model. Note that this is the only lyophobic model (the asphaltenes are not solvated by the fluid), the other approaches are lyophilic.

### Micellisation Models

This approach, which is the most recent, was proposed by Victorov and Firoozabadi (1996) and by Pan and Firoozabadi (1996 a and b). In this case, resin and asphaltene monomers in oil (as traces), a solid phase composed of asphaltenes and resins, and micelles composed of a core of asphaltenes stabilised by a ring of resin and solvents, coexist. These micelles must be considered as reservoirs of asphaltenes which will be reduced in number when flocculant is added. The size of the micelle structure and its composition are calculated by minimising the Gibbs energy of the complete system. Whilst this approach excludes redissolution of asphaltenes with high dilution rates, it considers that asphaltene flocculation is reversible. In addition, it predicts the flocculation of asphaltenes and resins in the presence of propane. According to its authors, these two points constitute the main innovations of this approach. Note also that addition of resins or a solvent does not lead to an increase but, on the contrary, to a decrease in the size of the micelles, as demonstrated

experimentally by Espinat and Ravey (1993). The periphery of the micelles must therefore dissolve in the fluid matrix. This is coherent with the fact that asphaltenes are lyophilic and must therefore be stable in the fluid matrix. On the contrary, adding a flocculant such as *n*-heptane increases the size of the colloids. This effect would be due to a reduction in the surface tension of the fluid when the flocculant is added, allowing increased resin absorption (Storm *et al.*, 1996). This increase in the size of the colloids was demonstrated by Acevedo *et al.* (2004). These results are in complete contradiction with those of the colloidal approach put forward by Leontaritis and Mansoori. Although this approach helps us to understand the effect of resins on asphaltene precipitation, it is complex and requires a large number of experimental data. Wu *et al.* (1998) therefore propose another approach, which considers flocculation as a liquid-liquid equilibrium. Asphaltenes and resins are considered as pseudo pure components which can combine, whereas the other constituents of the fluid represent a continuous medium. In this case, the phase equilibria are represented by the SAFT equation of state (Chapman *et al.*, 1988). The same physical base was used by Edmonds *et al.* (1999), but in a simplified form which only considered two interactions: asphaltene-asphaltenes and asphaltene-resins, and recently Fahim and Andersen (2005) proposed a similar approach with the Cubic Plus Association (CPA) equation.

### 6.4 The Szewczyk and Béhar Model and its Integration in Athos Software

We will now give a brief description of the model developed at the *Institut Français du Pétrole* by Szewczyk and Béhar (1999). It belongs to the group of solubility models and is designed to satisfy three observations:

- reversibility of the flocculation phenomenon;
- flocculation considered as liquid-liquid demixing;
- presence of all the oil constituents in the flocculated phase.

In this model, all the constituents are assumed to be present in all phases and flocculation is considered as the appearance of a second liquid phase.

For pressures above the bubble pressure of the fluid, flocculation appears as a liquid-liquid phase separation. Below the bubble pressure, flocculation leads to the existence of a three-phase liquid-liquid-vapour equilibrium. The same equation of state is used to analyse the various phases, the Adboul *et al.* (1991) equation:

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+\gamma b)}$$

where  $v$ : the uncorrected molar volume;  
 $b$ : the covolume;  
 $a(T)$ : the interaction parameter.

As usual,  $P$  is the pressure of the system,  $T$  its temperature,  $R$  the universal gas constant and  $\gamma$  is a constant equal to 4.82843 for the Peng and Robinson equation. The attraction term  $a$  and the covolume  $b$  are expressed as usual, they include the critical parameters ( $T_c$  and  $P_c$ ) and the acentric factor of each constituent. To consider the entire mixture as a unique constituent obeying the same formalism (van der Waals, 1873), mixture rules are applied to determine the global parameters of the fluid (Péneloux *et al.*, 1989, Abdoul, 1987):

$$b = \sum x_i b_i$$

$$\frac{a(T, x)}{b(T)} = \sum x_i \frac{a_i(T)}{b_i} - E(T, x)$$

The excess function  $E$  consists of two terms, an energy term and a combinatory term, which are calculated by group contribution from the structure of the molecules.

From the compositional point of view, the fluid is divided into three types of constituents: the  $C_{10}$ , which are perfectly identified, the  $C_{11}$ - $C_{20}$  fraction and the  $C_{20+}$  fraction which is represented by its SARA (saturates, aromatics, resins, asphaltenes) composition. The structure of the simple molecules (methane, ethane, carbon dioxide, etc.) is known. The structure of the  $C_{11}$ - $C_{20}$  fraction is a combination of model molecules. Lastly, for the  $C_{20+}$  fraction,  $^{13}\text{C}$  NMR analyses together with molar mass measurements can be used to

determine the proportions of the various molecular groups ( $\text{CH}_3$ ,  $\text{CH}_2$ ,  $\text{CH}_{\text{aromatic}}$ , etc.) in the SARA fractions (Saturates, Aromatics, Resins, Asphaltenes).

This model must be adjusted on traditional Pressure – Volume – Temperature (PVT) data and a curve of flocculation as a function of pressure; it therefore requires a relative large number of data but allows more relevant extrapolations. Figure 8 shows the results of an experiment carried out to measure flocculation as a function of pressure. The measurements were taken in a PVT cell, the samples filtered and the quantity of asphaltenes present in the filtrates determined.

At high pressures, the asphaltene content is constant; it is the total quantity of asphaltenes in the fluid. At 45 MPa, flocculation starts: the content of residual asphaltenes in the filtrate drops until the bubble pressure of the fluid is reached. Below the bubble pressure, the appearance of the vapour phase makes the liquid more likely to solubilise the asphaltenes and at pressure of 10 MPa the asphaltenes are once again stable in the liquid. This figure also shows the variation in the flocculation curves against temperature. Note that only a temperature of 30 °C was used to adjust the model. The temperatures of 80 °C and 142 °C can be used to appreciate the model's extrapolation possibilities. We must also point out one of the features of the model developed. Whilst most of the other models consist in assembling a liquid-vapour model then attempting to demix the liquid so obtained, the approach adopted by Szewczyk and Béhar supplies all the equilibria, and therefore the proportions of the oil-gas and asphaltene phases, in a single calculation.

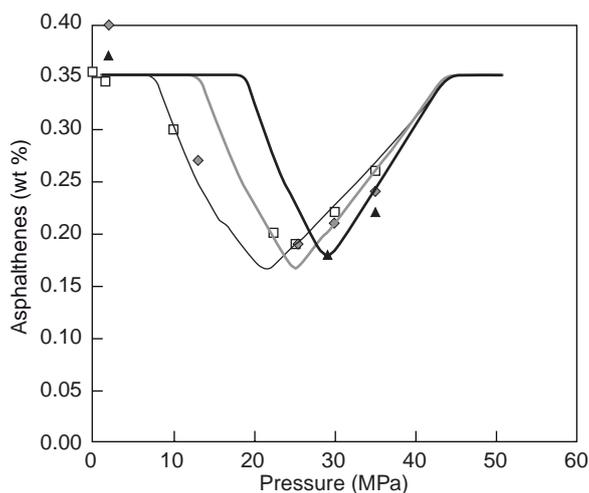


Figure 8

Variation in the quantity of flocculated asphaltenes against pressure; comparison of experimental data and of the Szewczyk and Béhar model (Square = 30 °C, diamond = 80 °C, triangle = 142 °C).

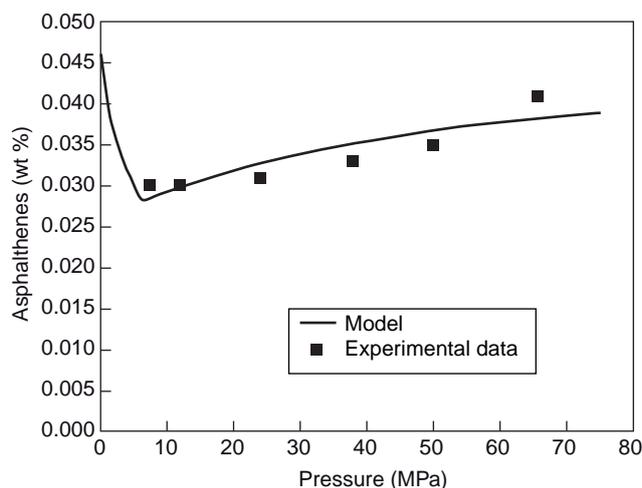


Figure 9

Variation in the quantity of flocculated asphaltenes against pressure; comparison of experimental data and of the Szewczyk and Béhar model. In this case, the model is used with a limited number of data.

This model served as a basis to develop a simpler approach for the Athos reservoir simulator software (Béhar *et al.*, 2003, Mougin *et al.*, 2003). This software carries out numerous computations for each mesh of the reservoir and uses highly simplified representations of fluids to minimise the computation time. Using our fluid database, we determined behaviour laws for these fluids as well as for the “child” fluids produced during successive pressure reductions. We demonstrated that it is possible to move from the flocculation curve of a given fluid to that of a child fluid by applying scaling laws.

The main drawback of the approach adopted by Szewczyk and Béhar is that it requires a large number of difficult-to-obtain data. Although this type of approach is suitable for research work, it is difficult to implement in an industrial context. Two approaches can be considered to overcome this problem:

- systematically study a large number of asphaltenic fluids to generate correlations for the various parameters of the model;
- look for alternative measurements simpler to implement in order to determine the parameters of the model.

The first option has been successfully implemented, as shown on Figure 9. In this example, we limited the number of data to be acquired: only the traditional PVT study and the curve of flocculation as a function of pressure were acquired. There was no need to determine the SARA analysis of the heavy fraction or its characterisation. This possibility of being able to predict the fluid behaviour with a minimum number of experimental data is also emphasised by Edmonds *et al.* (1999). The second research direction requires more prospective work and a return to measurements on simple systems, which we will now describe.

## 6.5 Determination of Flocculation Point by Refractive Index Measurement

As we have seen previously, the flocculation point is generally determined by adding a flocculant such as heptane; it is expressed as the quantity of flocculant to be added to the asphaltene solution to cause the formation of large aggregates. Figure 10 shows that the flocculation point of asphaltenes dissolved in various aromatic solvents depends on the dipolar moment of the solvent.

Three times more heptane is required to destabilise the asphaltenes in nitrobenzene than in paraxylene. Presented differently, however (see Fig. 11), these measurements show a certain invariant. If the refractive index (RI) of the mixture at the flocculation point is calculated, we observe that this threshold is virtually identical (1.4446) for all these solvents apart from pyridine.

The use of refractive indices was developed, in particular, by Buckley and her coworkers (Buckley, 1996; Buckley *et al.*, 1998; Buckley, 1999). In this approach the asphaltenes are considered as particles (*i.e.* colloidal) which interact through the solvent. The model assigns no special role to the resins, included in the solvent. Interactions between particles are attractive or repulsive. The attractive interactions include the van der Waals interactions as well as the specific interactions often mentioned in the literature: hydrogen bridge bonds,  $\pi$ - $\pi$  bond, etc. The repulsive interactions include the electrostatic interactions and, probably, the “steric” interactions (entropic repulsion which would be due to the presence of long aliphatic chains around the particle (see Yen’s model, 1979)).

In this type of colloidal system, aggregation occurs when the attractive forces are greater than the repulsive forces. The structure, growth mode and polydispersity of the aggregates

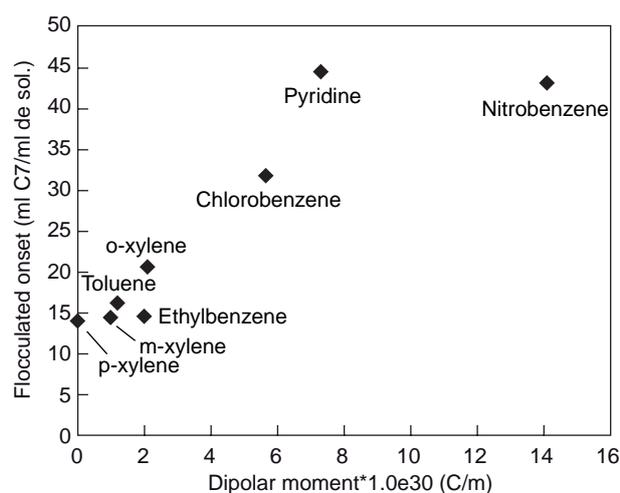


Figure 10

Influence of the dipolar moment of the solvent on the flocculation point.

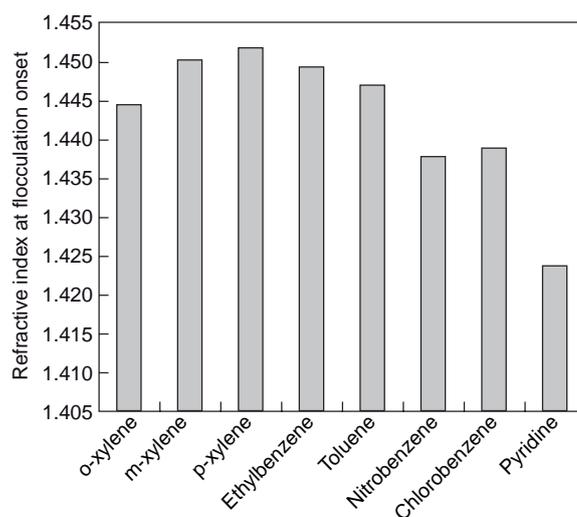


Figure 11

Refractive index at the flocculation point in the presence of various solvents.

are closely related to the shape of the particle interaction potential, and especially the presence and height of the potential barrier. At this point, it is worth referring to the extensively studied system of charged particles in aqueous medium: they are stable in an aqueous medium of low salinity—in this case, the electrostatic interactions prevail—and flocculate as soon as the water salinity exceeds a certain level, since the interactions are then masked by the salt. This analogy has been frequently mentioned to describe the structure and growth modes of asphaltenic aggregates (El Mohamed *et al.*, 1988; Yudin *et al.*, 1998; Fenistein *et al.*, 1998). Nevertheless, for asphaltenic systems, a tool similar to the DLVO theory (Derjaguin-Landau-Verwey-Overbeek, see Israelachvili, 1991, Chapter 12) is required for the aqueous colloids in order to quantitatively predict the shape of the interaction potential depending on composition or pressure.

According to Buckley and her coworkers, amongst the (numerous) interactions involved, only the London dispersive interactions are important and vary significantly with composition or pressure. They are expressed as a function of the distance  $r$  between particles, according to the law:

$$W(r) = -\frac{C}{r^6}$$

where the factor  $C$ , proportional to the Hamaker constant of the asphaltene/solvent system, is written as a function of the refractive indices of solvent and asphaltenes according to:

$$C = \frac{\sqrt{3}h\nu}{4} \frac{(n_a^2 - n_s^2)^2}{(n_a^2 + 2n_s^2)^2} a_a^6$$

In this expression,  $h$  is Planck's constant,  $\nu$  is the absorption frequency in the ultraviolet (assumed equal for asphaltenes and solvent);  $n_a$  and  $n_s$  are respectively the refractive indices of asphaltenes and solvent,  $a_a$  is the radius of an asphaltene aggregate. As we can see, the key quantity which controls the magnitude of the London dispersive interactions is the difference between the refractive indices of the asphaltenes and of the solvent. In a first analysis, for asphaltenes from a given origin, the flocculation point is therefore determined by dispersion forces for a given solvent + flocculant couple. A solvent of high polar moment requires more flocculant to bring the solvent + flocculant mixture to this state than a solvent of low polar moment. This result shows that asphaltene flocculation can be considered as only involving van der Waals forces. Since the asphaltene structure contains heteroatoms (see Section 2), we might have expected that polar effects, due for example to oxygen or sulphur atoms, should have been included. Buckley's and our own results show, however, that this is unnecessary, at least to a first approximation. It is likely that the heteroatoms only play a minor role in the interaction forces between asphaltenes and the solvent.

Using his measurements taken in solvent-flocculant-asphaltene systems, Wang (2000) proposes a rigorous thermodynamic model of flocculation based on the approach of solubility models with phase demixing. In this model the Gibbs energy of mixing the two phases is calculated by the Flory-Huggins model, according to:

$$\Delta G_m = RT(x_1 \ln \phi_1 + x_2 \ln \phi_2 + x_1 \phi_2 \chi)$$

where

$$\chi = \frac{v_1}{RT} (\delta_2 - \delta_1)^2$$

In these expressions, index 1 corresponds to the solvent + flocculant mixture and index 2 to the asphaltenes. This expression of the Gibbs energy can then be used to determine the expressions of the chemical potentials of the solvent + flocculant mixture and of the asphaltenes in each of the two phases. For a given composition mixture, it is then possible to determine whether the system is stable or whether it separates into two phases, *i.e.* whether flocculation occurs. By fully analysing the Gibbs energy profile as a function of the composition of the solvent + flocculant + asphaltene system, Wang also defines the metastability domain and the flocculation point. There are two free parameters in this approach:  $\delta$  the solubility parameter and  $v$  the molar volume of the asphaltenes. The main difference between the Wang model and the Wiehe and Kennedy (2000) model is the introduction of the molar volume. According to Wiehe and Kennedy, the flocculation point occurs at a unique solubility parameter, irrespective of the fluid mixture. This invariant is only meaningful, however, if the solvents and flocculants have similar molar volumes (Wiehe *et al.*, 2005).

## CONCLUSIONS AND PERSPECTIVES

Currently, the asphaltene deposits formed further to a reduction in reservoir pressure or during an enhanced gas recovery process are removed either by mechanical and/or chemical cleaning or by modifying the reservoir operating conditions (pressure, effluent composition). As the resulting costs may be high, there is an impact on the production economy of reservoirs containing crudes likely to precipitate asphaltenes. In addition to these financial aspects, the asphaltene deposits may cause serious accidents. Their deposition on production regulation valves has been known to cause major malfunctions of the well safety equipment. A plug of asphaltenes has even been violently ejected out of a well, accompanied by an eruption of crude oil. Similar hazards have also been reported on oil fields where the asphaltenes have prevented correct operation of safety valves fitted on the separators.

These examples clearly show that it is extremely important to identify possible flocculation of the asphaltenes in a crude, and their precipitation, before the design of the production and processing installations, both as regards the financial and the safety aspects. In this perspective, it is essential to develop a flocculation model. To represent the physics of this phenomenon under a wide range of conditions, the model must be based on as much experimental data as possible and must be as physical as possible. It is therefore vital that the behaviour of asphaltenes in solution or in crudes should be thoroughly understood and simulated.

We have described various aspects concerning the asphaltenes, whether considered alone, in solution in a good/poor solvent mixture, or in a crude. Since asphaltenes and their flocculation vary from one medium to another, numerous characterisation methods have been developed; their use has led to a better understanding of asphaltene structure and the conditions causing flocculation.

The compositional models used to calculate possible asphaltene flocculation rely on relatively simple bases, considering asphaltenes and resins as pseudo pure components. These models are poor predictors and require a minimum of experimental data under conditions similar to those of the reservoir. Note that models considering asphaltenes (and resins) as polymers or chains of oligomers have led to major breakthroughs over the last few years. In addition, another research direction consists in using flocculation measurements under ambient conditions to input data to models as a function of pressure ; this type of approach, designed to simplify experimental data acquisition, also seems promising.

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