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¹H Diffusion-Ordered Spectroscopy (DOSY) Nuclear Magnetic Resonance (NMR) as a Powerful Tool for the Analysis of Hydrocarbon Mixtures and Asphaltenes

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Heavy crude oils are more and more of interest for the oil industry to meet the growing worldwide energy demand. Asphaltenes, which are the heaviest and least reactive molecules in crude oils, have received great attention over the last few decades, because they are responsible for many problems occurring during hydrotreatment and hydroconversion. ¹H diffusion-ordered spectroscopy (DOSY) nuclear magnetic resonance (NMR) based on pulsed field gradient (PFG) sequences is a powerful tool to analyze polydisperse samples. The key advantage of such a technique compared to traditional NMR diffusion sequences, such as pulsed field gradient spin-echo (PFGSE), is to obtain both physical and chemical information in a single experiment. ¹H DOSY NMR has been carried out on different types of samples to obtain a deeper insight into the physicochemical properties of petroleum samples, because diffusion coefficients are both sensitive to molecular weights and sizes. The application of DOSY NMR to analyze hydrocarbon mixtures and asphaltenes is assessed. It is shown that both solute and solvent diffusion coefficients decrease with an increasing concentration of solute. Different types of intermolecular interactions were observed on petroleum samples depending upon the sample concentration. Dilute and semi-dilute regimes have also been detected. ¹H DOSY spectra applied to diesel and asphaltene samples in toluene are presented and interpreted to demonstrate the potential of DOSY techniques to analyze heterogeneous petroleum samples. The data obtained for the diesel sample enable us to establish that monoaromatics were connected to long alkyl chains, whereas di- or triaromatic molecules were linked to shorter hydrocarbon chains. However, a clear conclusion could not be reached for the asphaltene sample because there were only a few aromatic protons that were not detected. This observation is most consistent with a continental model of these asphaltenes.

1. Introduction

For the last 2 decades, governments have had to face the growing worldwide energy demand, especially in the transportation field. Heavy crude oils are therefore more and more of interest for the oil industry both in terms of exploring and upgrading. However, these crude oils are composed of complex hydrocarbon molecules that can be characterized according to their polyaromaticities, their amount of heteroatoms, or even their metal amount. Asphaltenes are defined as the part of crude oil that is insoluble in *n*-alkane, such as *n*-pentane or *n*-heptane, and soluble in toluene. They are composed of highly polyaromatic species with alkyl side chains but also heteroatoms (N, S, and O) and metals (Ni and V),¹ which make them the most polar and heaviest petroleum fraction. Asphaltenes are responsible for many problems during oil production, transport, and even refining.^{2–5} In fact, they play a major role in the formation of deposits affecting the production of crude oils.⁶ These macromolecules are known to self-associate and aggregate, leading to fouling and plugging.⁵ Last but not least, asphaltenes

are responsible for catalyst deactivation because of coke formation during hydroconversion processes.^{7,8} Their reactivity is directly linked to their molecular properties: molecular weight, structure, molecular interactions, and self-aggregation.¹ Obtaining a better understanding of these products is required to develop new catalysts and novel conversion processes.

Despite more than 40 years of research on asphaltenes, some questions are still under discussion: what are the molecular weight of asphaltenes, their particle size, and their chemical structure? The complexity of the study is due to the nature of asphaltenes themselves: they are composed of polydispersed entities in terms of both molecular weight and chemical composition, and their self-association depends upon their

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(1) Gawrys, K. L.; Blankenship, G. A.; Kilpatrick, P. K. *Energy Fuels* **2006**, *20*, 705–714.

(2) Ancheyta, J.; Centeno, G.; Trejo, F.; Marroquin, G. *Energy Fuels* **2003**, *17*, 1233–1238.

(3) Groenzin, H.; Mullins, O. C. *J. Phys. Chem. A* **1999**, *103*, 11237–11245.

(4) Rogel, E. *Langmuir* **2004**, *20*, 1003–1012.

(5) Merdignac, I.; Espinat, D. *Oil Gas Sci. Technol.* **2007**, *62*, 7–32.

(6) Rogel, E.; Leon, O.; Torres, G.; Espidel, J. *Fuel* **2000**, *79*, 1389–1394.

(7) Hauser, A.; Marafi, A.; Stanislaus, A.; Al Adwani, A. *Energy Fuels* **2005**, *19*, 544–553.

(8) Matsushita, K.; Marafi, A.; Hauser, A.; Stanislaus, A. *Fuel* **2004**, *83*, 1669–1674.

concentration.⁹ The influence of chemical composition is not well-defined either: how can asphaltene fractions with a similar chemical composition present very different behaviors?

Asphaltenes characterization is still a challenge because they are composed of thousands of heavy compounds. Many analytical techniques can be used to analyze asphaltenes,^{5,10–13} but their tendency to form aggregates depending upon their concentration, the solvation, and finally the analytical method makes the determination of physical properties by conventional techniques¹⁴ very difficult. Nuclear magnetic resonance (NMR) is an excellent tool to analyze petroleum samples.^{15,16} It is widely used to measure carbon aromaticity and obtain mean carbon parameters.¹⁷ However, the ¹H and ¹³C NMR petroleum spectra are crowded and overlapped because of the main presence of aromatic, naphthenic, and aliphatic functions. Thus, a chemical structure appears difficult to define. Two main structural models of average molecules have been proposed: the continental¹⁸ and the “archipelago”^{19–22} models. The first model, also called the “island model” or the “like your hand model” shapes the asphaltenes as a condensed aromatic molecule composed of a single aromatic core substituted by some alkyl chains, whereas in the second model, the asphaltene molecule consists of several smaller aromatic cores interconnected by alkyl chains and thioether bridges. The introduction of new NMR techniques, such as diffusion-ordered 2D NMR spectroscopy (DOSY),²³ which employs pulsed field gradient (PFG) sequences, have been used for complex and heterogeneous mixtures, such as biological samples,^{24–26} polymers,^{27,28} for measuring protein–ligand interactions,²⁹ or even complexes.^{30,31} This new technique is expected to enable an in-depth physicochemical characterization

Table 1. Physical Properties of Samples A–D

	physical properties		
	boiling points fractions (°C)	density	refractive index
sample A	160–410	0.8378	1.4654
sample B	265–375	0.8864	1.4954
sample C	375–565	0.9116	1.5136
sample D	>565	1.05	n/a

of complex mixtures of petroleum distillates³² and heavy oils because it is both sensitive to molecular weight and structure. It aims at measuring self-diffusion coefficients, which can yield structural and dynamic information (molecular size and also aggregation states), in complex mixtures. Ostlund et al.³³ have already presented that it was possible to measure the self-diffusion coefficients of asphaltenes by pulsed field gradient spin–echo nuclear magnetic resonance (PFGSE NMR). However, in the literature, only one reference³² shows a DOSY spectrum of an aromatic petroleum fraction, in the distillate boiling range.

In the present study, ¹H DOSY NMR experiments were carried out on different types of fractions ranging from kerosene cuts to fractions that have an initial boiling point above 560 °C. Diesel cuts, diluted in toluene, were first investigated, because they contain light hydrocarbon molecules and, thus, can therefore be considered as a more simple system for our investigation. The influence of sample concentration on the diffusion coefficient is presented in this paper. It illustrates that various types of intermolecular interactions between solvent and solute are highly dependent upon solute concentration. An experiment on the asphaltene sample has also been carried out. Asphaltenes and diesel ¹H DOSY spectra are presented to demonstrate the potential of these types of sequences to obtain physicochemical information in only one experiment. Polyethylene glycol and polystyrene analyses were performed to validate the method because these compounds have been extensively studied in the literature.^{27,34,35}

2. Experimental Section

2.1. Chemicals. Deuterated toluene (D, 99.8%) used for NMR measurements was supplied by Eurisotop. Petroleum samples A, B, C, and D and asphaltenes were provided by IFP. Asphaltenes were extracted from crude oils from the addition of *n*-heptane.

2.2. Petroleum Sample Preparation. Distillation is the most common method used to fractionate petroleum samples. The goal is to separate hydrocarbons according to their volatility. The True Boiling Point method (ASTM D2892) is a preparative distillation used to isolate subfractions between the initial boiling point and 400 °C. Above this temperature, potstill distillation (ASTM D5236) is employed under vacuum to obtain fractions whose boiling point is less than 550 °C. The heaviest fraction that remains after potstill distillation is called the vacuum residue. In the present study, a 160–410 °C boiling point sample labeled sample A and different cuts from the same feedstock (identified as samples B–D) were analyzed. Physical properties of samples A–D are listed in Table 1.

A sample of asphaltenes was also analyzed after deasphalting according to a standard analytical procedure derived from the standard NF T60-115. They were extracted from crude oils from the addition of 50 volumes of *n*-heptane used as a flocculant at 80 °C.

(9) Espinat, D.; Rosenberg, E.; Scarsella, M.; Barre, L.; Fenistein, D.; Broseta, D. Colloidal structural evolution from stable to flocculated state of asphaltene solutions and heavy crudes. In *Structures and Dynamics of Asphaltenes*; Plenum Press: New York, 1998; pp 145–202.

(10) Yen, T. F.; Erdman, J. G.; Pollack, S. S. *Anal. Chem.* **1961**, *33*, 1587–1594.

(11) Groenzin, H.; Mullins, O. C. *Energy Fuels* **2000**, *14*, 677–684.

(12) Klein, G. C.; Kim, S.; Rodgers, R. P.; Marshall, A. G.; Yen, A. *Energy Fuels* **2006**, *20*, 1973–1979.

(13) Gawrys, K. L.; Blankenship, G. A.; Kilpatrick, P. K. *Langmuir* **2006**, *22*, 4487–4497.

(14) Norinaga, K.; Wargadalam, V. J.; Takasugi, S.; Iino, M.; Matsukawa, S. *Energy Fuels* **2001**, *15*, 1317–1318.

(15) Pekerar, S.; Lehmann, T.; Mendez, B.; Acevedo, S. *Energy Fuels* **1999**, *13*, 305–308.

(16) Dickinson, E. M. *Fuel* **1980**, *59*, 290–294.

(17) Merdignac, I.; Quoineaud, A. A.; Gauthier, T. *Energy Fuels* **2006**, *20*, 2028–2036.

(18) Ruiz-Morales, Y.; Mullins, O. C. *Energy Fuels* **2007**, *21*, 256–265.

(19) Speight, J. G. Asphaltene constituents. In *The Chemistry and Technology of Petroleum*; CRC Press: Boca Raton, FL, 2007; pp 315–344.

(20) Murgich, J.; Abanero, J. A.; Strausz, O. P. *Energy Fuels* **1999**, *13*, 278–286.

(21) Strausz, O. P.; Mojelsky, T. W.; Lown, E. M. *Fuel* **1992**, *71*, 1355–1363.

(22) Gray, M. R. *Energy Fuels* **2003**, *17*, 1566–1569.

(23) Morris, K. F.; Johnson, C. S. *J. Am. Chem. Soc.* **1992**, *114*, 3139–3141.

(24) Barjat, H.; Morris, G. A.; Smart, S.; Swanson, A. G.; Williams, S. C. R. *J. Magn. Reson., Ser. B* **1995**, *108*, 170–172.

(25) Hinton, D. P.; Johnson, C. S. *J. Phys. Chem.* **1993**, *97*, 9064–9072.

(26) Morris, K. F.; Johnson, C. S. *J. Am. Chem. Soc.* **1993**, *115*, 4291–4299.

(27) Chen, A.; Wu, D.; Johnson, C. S. *J. Am. Chem. Soc.* **1995**, *117*, 7965–7970.

(28) Jerschow, A.; Muller, N. *Macromolecules* **1998**, *31*, 6573–6578.

(29) Lucas, L. H.; Larive, C. K. *Concepts Magn. Reson., Part A* **2004**, *20A*, 24–41.

(30) Ambrus, A.; Friedrich, K.; Somogyi, A. *Anal. Biochem.* **2006**, *352*, 286–295.

(31) Viel, S.; Mannina, L.; Segre, A. *Tetrahedron Lett.* **2002**, *43*, 2515–2519.

(32) Kapur, G. S.; Findeisen, M.; Berger, S. *Fuel* **2000**, *79*, 1347–1351.

(33) Ostlund, J. A.; Andersen, S. I.; Nyden, M. *Fuel* **2001**, *80*, 1529–1533.

(34) Chari, K.; Antalek, B.; Minter, J. *Phys. Rev. Lett.* **1995**, *74*, 3624–3627.

(35) Hakansson, B.; Nyden, M.; Soderman, O. *Colloid Polym. Sci.* **2000**, *278*, 399–405.

2.3. Sample Preparation for DOSY NMR Experiments. Samples A–D were prepared at different concentrations ranging from 0.1 to 80 wt % in toluene- d_8 for sample A, from 1 to 30 wt % for sample B, and from 1 to 20 wt % for samples C and D. The asphaltene sample was analyzed at 1 wt % in toluene- d_8 . Each mixture was added to 5 mm NMR tubes and stored at 4 °C.

2.4. DOSY NMR Measurements. DOSY NMR experiments were performed on a Varian INOVA Unity 600 narrow bore spectrometer equipped with a Performa II gradient pulse amplifier and fitted with a triple resonance (HCN) probe capable of producing up to 60 G cm^{-1} .

The pulse sequence used for the diffusion measurements was the Doneshot³⁶ sequence and will be detailed in section 3.1. The gradient pulse strength (g) was varied in 50 linear steps from 0 to 60 G cm^{-1} to obtain complete signal attenuation. According to Price,³⁷ the use of a standard sample of known diffusion coefficient is the easiest way of calibrating gradients. In these experiments, gradients were calibrated against the HOD diffusion constant at 25 °C (D_2O , 99.9%, $D = 19.0 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$).^{37,38} The calibration was confirmed by measuring adenosine triphosphate (ATP), sodium dodecyl sulfate (SDS), and glucose diffusion coefficients in a mixture in D_2O at 22 °C according to ref 26. Measuring these diffusion coefficients was preferred to measuring those of n -heptane or n -dodecane, because ATP, SDS, and glucose are heavier and will better reflect heavy petroleum molecules than the n -alkane solvents. In the Doneshot sequence based on a stimulated echo, the gradient pulse duration (δ) and the diffusion delay (Δ) were kept constant, ranging from 1.5 to 3.5 ms for δ and from 0.08 to 0.5 s for Δ . Spectra were measured at 20 °C with a 90° pulse duration of 6.30 μs and a relaxation delay of 30 s.

Published DOSY spectra generally use either mono- or multi-exponential fittings. One of the main advantages of the fitting method resides in the possibility to apply least-squares fitting, leading to simple algorithms and, as a result, to fast processing. However, such techniques are not suitable for complex samples because they require an estimate of the number of components. In our study, we will be confronted with spectral superposition and polydisperse molecules because hydrocarbon mixtures are composed of thousands of unknown components. For polydisperse samples, CONTIN^{39,40} could have been used to process the DOSY NMR spectra. However, this software shows a lack of resolution to enable a separation of the different species presenting similar sizes.^{41,42} NMR data were processed with the NMRnotebook software, with a DOSY module incorporated from NMRtec SAS. The Maximum Entropy (MaxEnt) Laplace inversion has been implemented in the software by Delsuc.⁴¹ This module gives access to the whole diffusion spectrum without any knowledge of the number of species present in the sample and is therefore well-adapted for polydisperse mixtures. The goal is to build the inverse Laplace transform by maximizing the entropy of spectral distribution and comparing it with the real spectrum. According to the authors, this software provides a high-quality spectrum, ensuring resolution, accuracy, and reliability of the results.

The diffusion coefficients reported are median values of the distribution. The error estimations reported in this work were obtained by difference between maximum and minimum diffusion values of the considered distribution.

The experimental techniques used were checked against the known diffusion behavior of poly(ethylene glycol)s and polystyrene oligomers in D_2O and toluene, respectively.

3. Theoretical Basis

3.1. DOSY NMR Theory. Diffusion ordered spectroscopy (DOSY)^{23,42} is a method devised by Morris and Johnson,²³ which derived from the pulsed field gradient spin–echo nuclear magnetic resonance (PFGSE NMR) sequence of Stejskal and Tanner⁴³ based itself on the nuclear spin–echo concept of Hahn⁴⁴ and Carr and Purcell.⁴⁵ DOSY was introduced to identify the molecular components of a mixture sample and obtain at the same time information on their size. It aims at measuring diffusion coefficients, which are of fundamental importance because they are very sensitive to molecular size and shape. It also provides information on the molecular weight and molecule aggregation status. The main advantage of this technique is its ability to construct a two-dimensional spectrum, in which the first dimension is a conventional NMR spectrum with the species chemical shift and the second one represents their diffusion coefficients. One of the sequences available for Varian Inova spectrometers is the Doneshot³⁶ sequence. On the basis of a PFGSE sequence, it is described by its authors as a powerful technique for analyzing mixtures. The Doneshot sequence presents several advantages compared to the bipolar pulse pair stimulated echo (BPPSTE), from which it derives. First of all, it allows diffusion measurements in just one shot and with only one transient per gradient strength without any phase cycling. The sequence is composed of extra balancing gradient pulses in addition to asymmetric bipolar field gradient pulse pairs to select a unique coherence transfer pathway and minimize at the same time the eddy current effect. Other gradients occur at the beginning and the end of the diffusion delay to keep the deuterium lock signal focused and minimize field-frequency lock disturbance. A thorough description of the sequence is given by Pelta et al.³⁶ In practice, while increasing gradient strengths, the intensity of the signal is attenuated because of diffusion according to an exponential function. Thus, the relationship between the signal amplitude (I) while applying gradient (g) in the z direction, the signal amplitude at zero gradient (I_0), and the diffusion coefficient (D) in the same direction is given by eq 1,³⁶ derived from the Stejskal–Tanner equation

$$I = I_0 e^{-D\gamma^2 g^2 \delta^2 [\Delta + \delta(\alpha^2 - 2)/6 + \tau(\alpha^2 - 1)/2]} \quad (1)$$

where δ and Δ are the width of the field gradient pulses and the diffusion delay, respectively, γ is the magnetogyric ratio ($2.675 \times 10^8 \text{ rad T}^{-1} \text{ s}^{-1}$ for ^1H), α is the imbalance factor, and τ is the time between the midpoints of the individual gradient pulses in one diffusion-encoding period. From eq 1, it is possible to determine the translational self-diffusion coefficient (D) of the different compounds of the mixture.

4. Results and Discussion

4.1. Concentration Effect on Petroleum Samples. Figure 1 shows the self-diffusion coefficient of sample A as a function of the sample A concentration in a solution of toluene analyzed at 20 °C. A wide range of concentrations has been covered and is presented here.

Average diffusion coefficients have been obtained on aliphatic peaks ranging from 0.7 to 1.5 ppm for the petroleum sample and at 7.15 ppm for toluene as presented in Figure 2.

(36) Pelta, M. D.; Morris, G. A.; Stchedroff, M. J.; Hammond, S. J. *Magn. Reson. Chem.* **2002**, *40*, S147–S152.

(37) Price, W. S. *Concepts Magn. Reson.* **1998**, *10*, 197–237.

(38) Antalek, B. *Concepts Magn. Reson.* **2002**, *14*, 225–258.

(39) Provencher, S. W. *Comput. Phys. Commun.* **1982**, *27*, 213–227.

(40) Provencher, S. W. *Comput. Phys. Commun.* **1982**, *27*, 229–242.

(41) Delsuc, M. A.; Malliavin, T. E. *Anal. Chem.* **1998**, *70*, 2146–2148.

(42) Johnson, C. S. *Prog. Nucl. Magn. Reson. Spectrosc.* **1999**, *34*, 203–256.

(43) Stejskal, E. O.; Tanner, J. E. *J. Chem. Phys.* **1965**, *42*, 288–292.

(44) Hahn, E. L. *Phys. Rev.* **1950**, *80*, 580.

(45) Carr, H. Y.; Purcell, E. M. *Phys. Rev.* **1954**, *94*, 630.

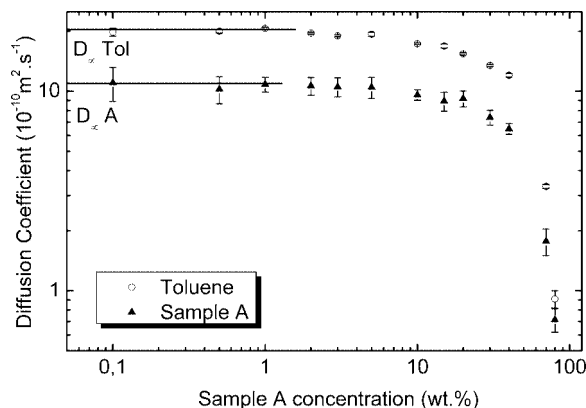


Figure 1. Self-diffusion coefficient of sample A in solution in toluene- d_8 as a function of the solute concentration.

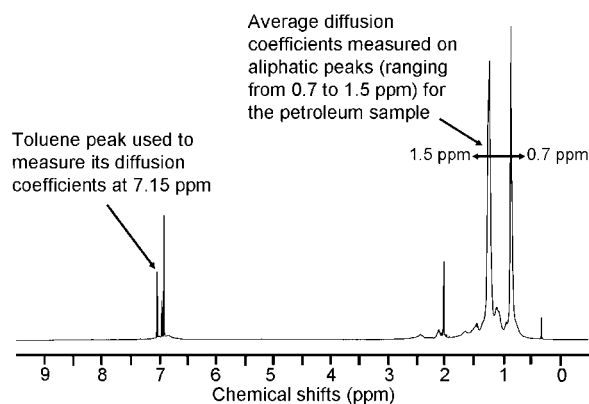


Figure 2. Sample A proton spectrum.

Both coefficients (solvent and sample) are fully dependent upon sample A concentration.⁴⁶ The self-diffusion coefficients remain constant until the concentration reaches 10 wt %. In dilute solutions, the entities are isolated enough not to be influenced by the other molecules. In this range of concentrations, solute–solvent interactions are predominant and determine the limiting diffusion coefficient ($D_{\infty\text{tol}} \sim 20.2 \pm 0.2 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ for toluene, and $D_{\infty\text{A}} \sim 10.9 \pm 0.1 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ for sample A). This represents the regime where the Stokes–Einstein equation is applicable. As the concentration increases, obstruction effects can strongly modify the diffusion properties of solvent molecules. The contribution of solvent–solvent interactions is more and more important as the solute concentration becomes higher and can dramatically influence the solvent diffusion capacity. The self-diffusion coefficient of the solute measured D depends strongly and nonlinearly upon all types of intermolecular interactions:⁴⁷ attractive solvent–solute interactions and attractive solute–solute interactions. In fact, there is a continuous decrease in the diffusion coefficient beyond 10 wt %, which is attributed to a change of regime. The range of concentrations of 0–10 wt % stands for a dilute regime, whereas beyond 10 wt %, it is a semi-dilute regime. In fact, in more concentrated solutions, more attractive interactions are involved, leading to an increase in the friction of the solute⁴⁷ and thus a decrease of the diffusion coefficient. There are attractive solute–solute interactions, leading to an aggregation process, but also attractive solvent–solute interactions that slow the overall solvent diffusion and solvent obstruction effects as

described by Ostlund et al.³³ The two former effects are not distinguishable by NMR.

The Stokes–Einstein equation is often used to derive the hydrodynamic radius R_H of the solute from its diffusion coefficient D

$$D = \frac{k_B T}{6\pi\eta R_H} \quad (2)$$

where k_B is the Boltzman constant, T is the absolute temperature, and η is the fluid viscosity. According to eq 2 and using the diffusion coefficient of sample A at infinite dilution $D_{\infty\text{A}}$ and the toluene viscosity value at 293.15 K, an average hydrodynamic radius of the molecules in sample A is found: $R_H = 3.3 \text{ \AA}$. Nevertheless, this equation is only valid for spherical particles much bigger than the solvent molecules ($R_H > 5R_{\text{solv}}$), which is not the case in our studies. A new approach taking into account the shape and size of the solutes is required. The modified Stokes–Einstein equation⁴⁸ is

$$D = \frac{k_B T}{c(R_{\text{solv}}, R_H) f_s(a, b) \pi \eta R_H} \quad (3)$$

It has been proposed to set a factor c depending upon the ratio between the radius of the solvent (R_{solv}) and R_H ^{48,49} as equal to

$$c = \frac{6}{1 + 0.695(R_{\text{solv}}/R_H)^{2.234}} \quad (4)$$

The shape of the molecules must also be taken into account to be exact. f_s is the ratio between the minor (b) and the major (a) semi-axis of the ellipsoid considered. f_s depends upon the shape considered:^{48,50} prolate (cigar-like) or oblate (disk-like) ellipsoid molecules, as expressed by eqs 5 and 6, respectively

$$f_s = \frac{\sqrt{1 - (b/a)^2}}{(b/a)^{2/3} \ln\left(\frac{1 + \sqrt{1 - (b/a)^2}}{(b/a)}\right)} \quad (5)$$

$$f_s = \frac{\sqrt{(b/a)^2 - 1}}{(b/a)^{2/3} \arctan\sqrt{(b/a)^2 - 1}} \quad (6)$$

Our systems are composed of thousands of compounds presenting different shapes. Thus, it is not possible to establish an exact f_s value because of the complexity of the system. An average spherical particle is therefore assumed, and f_s is set equal to 1. Taking into account these hypotheses and the sizes of the molecules and the solvent, the hydrodynamic radius calculated for sample A is 4.2 Å.

Another approach consists of determining the molecular weights from diffusion measurements for our precise systems. A well-known relation^{28,35} between the diffusion coefficient D and the molecular weight M has been established according to Flory's scaling law ($R_g \propto M^{-\alpha}$, where R_g is the radius of gyration) and Stokes–Einstein equation (for a spherical particle, $R_g \propto R_H$)

$$D = KM^{-\alpha}, \quad \alpha > 0 \quad (7)$$

where K is a constant dependent upon the nature of the molecule and α is a coefficient dependent upon the shape of the particle-labeled shape factor. According to eq 7, the following formula can be deduced

$$\frac{D_1}{D_2} = \left(\frac{M_2}{M_1}\right)^\alpha \quad (8)$$

where D_1 and D_2 are sample A and toluene diffusion coefficients at infinite dilution, respectively, M_1 is the sample A average

(46) Ostlund, J. A.; Nyden, M.; Auflem, I. H.; Sjoblom, J. *Energy Fuels* **2003**, 17, 113–119.

(47) Biswas, R.; Bhattacharyya, S.; Bagchi, B. *J. Phys. Chem. B* **1998**, 102, 3252–3256.

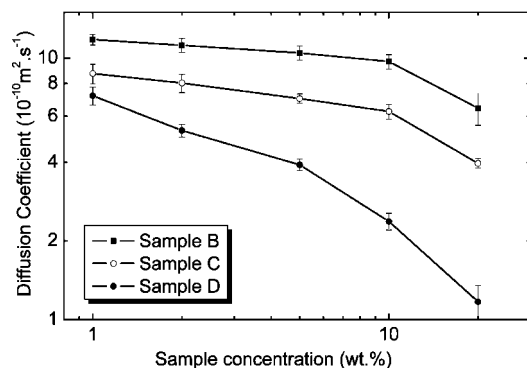


Figure 3. Self-diffusion coefficients of samples B–D in solution in toluene- d_8 as a function of the solute concentration.

molecular weight, and M_2 is the toluene molecular weight. α is supposed to be 0.33 for a spherical particle, whereas a value of 0.5 for α would reflect either a random coil oligomer in a θ solvent or a flat disk. In the case of a good solvent, α should be equal to 0.6.⁵¹

Knowing the nature of sample A and thus a range of molecular weights would help us in determining the value of α for petroleum mixtures in toluene. According to the boiling point range of sample A (summarized in Table 1), this sample is a fraction composed of hydrocarbon molecules with 12–25 carbon atoms. Hence, the average molecular weight is expected to be around 200–300 g mol⁻¹. The experimental molecular weight calculated for a spherical particle ($\alpha = 0.33$) is equal to around 488 g mol⁻¹, which is therefore not in agreement with the expected value. This demonstrates that DOSY also provides information on the shape of the molecules, because the measurements show that the hypothesis of a spherical particle is not acceptable. However, if $\alpha = 0.5$ is assumed, M_A should be approximately 345 g mol⁻¹, which is better than the molecular weight obtained for a spherical particle but still too high. In the case of $\alpha = 0.6$, M_A is assumed to be about 280 g mol⁻¹, which corresponds more to the nature of the sample. For the following petroleum samples analyzed in toluene, α will be fixed as 0.6.

4.2. Influence of the Sample Nature on the Diffusion Coefficient. The diffusion coefficients of samples B–D measured at different concentrations in toluene- d_8 at 20 °C are displayed in Figure 3. Diffusion coefficients have been measured on aliphatic peaks (0.7–1.5 ppm) for the solutes and at 7.15 ppm for the solvent. The physical properties of the samples, including boiling point range and density, are summarized in Table 1.

The three fractions B–D were obtained from the same feedstock by distillation. For a given concentration, the diffusion coefficients decrease with increasing boiling points. This is consistent with the theory, because boiling points are linked to the number of carbon atoms and, as a result, to the molecular weight. However, for each sample, the observed diffusion coefficient decreases when increasing its concentration. Samples B and C present the same behavior. In the 0–10 wt % region, the diffusion coefficients only vary slightly. The interactions involved are more or less constant in this range of concentrations and mainly because of solute–solvent interactions. The solute is not concentrated enough to induce significant interactions between its molecules. This region can be considered as a dilute

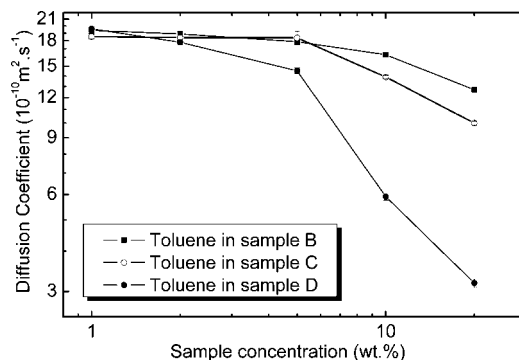


Figure 4. Comparison of the self-diffusion coefficients of toluene in samples B–D as a function of the sample concentration.

regime as established for sample A. Beyond 10 wt %, the decrease is amplified, which indicates an increase of the contribution of intermolecular interactions, such as solute–solute interactions, attractive solvent–solute interactions in concentrated solutions, and also obstruction effects. This range of concentrations stands for the semi-dilute regime. Having the same decreasing behavior implies that samples B and C have similar chemical structures and involve similar types of interactions. However, for the heaviest fraction (sample D), the decrease of diffusion coefficients starts at very low concentrations. In fact, the aggregation process seems to begin at 1 wt %. This suggests that the size and shape of the molecules and especially the interactions involved in sample D are different from the ones involved in samples B and C.

Figure 4 shows the self-diffusion of toluene in samples B–D as a function of the concentration of samples B–D.

The toluene diffusion constants decrease with an increase of the sample concentration. The trend is the same as the one observed in Figure 3. Its diffusion coefficients tend to a unique value for the three samples, which stands for the pure toluene diffusion coefficient when analyzed alone: $19.6 \pm 0.2 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$.

Samples B and C have mostly the same behavior until the concentration reaches 5 wt %. Whereas beyond this point, interactions (attractive solute–solvent interactions, attractive solute–solute interactions, and obstruction effects)³³ have major influence in sample C compared to sample B. Thus, in the high concentration region, the diffusion coefficient of the toluene is smaller in C than in B. However, for sample D, there is a much larger drop of the toluene diffusion coefficients starting for lower concentrations. The obstruction effect is also dependent upon the molecular size of the solutes analyzed. Thus, for sample D whose boiling point is higher than 560 °C and is the heaviest fraction, the obstruction effect starts at a lower concentration, leading to a hindrance of the motion of toluene molecules and consequently to a lower diffusion coefficient of toluene and probably the beginning of an aggregation process more pronounced in sample D than in samples B or C.

According to what has been established for sample A ($\alpha = 0.6$), molecular weights have been calculated for each sample and are summarized in Table 2. The calculated values for samples B and C are in agreement with what should be expected for such samples. It appears that the hypothesis made ($\alpha = 0.6$) based on sample A results is valid for the lighter fractions and especially for sample B because they mostly belong to the same boiling point range, whereas for sample D, the molecular weight calculated was underestimated, with $\alpha = 0.6$. This shows the importance of obtaining an appropriate α factor for each type of sample.

(48) Macchioni, A.; Ciancaleoni, G.; Zuccaccia, C.; Zuccaccia, D. *Chem. Soc. Rev.* **2008**, 37, 479–489.

(49) Chen, H. C.; Chen, S. H. *J. Phys. Chem.* **1984**, 88, 5118–5121.

(50) Perrin, F. *J. Phys. Radium* **1936**, 7, 1–11.

(51) Cosgrove, T.; Griffiths, P. C. *Polymer* **1995**, 36, 3335–3342.

Table 2. Samples B–D Molecular Weights Calculated According to Their Diffusion Coefficients at Infinite Dilution and $\alpha = 0.6$

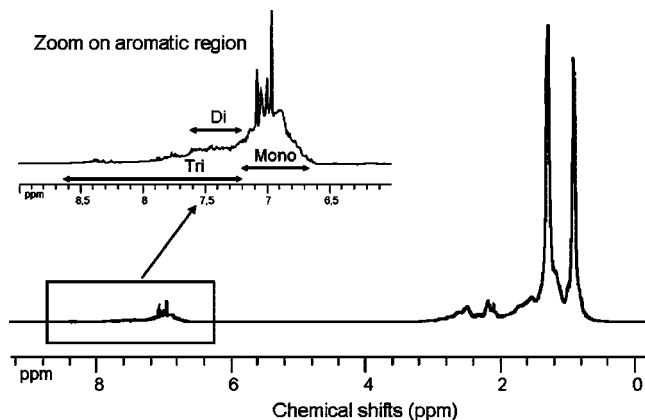
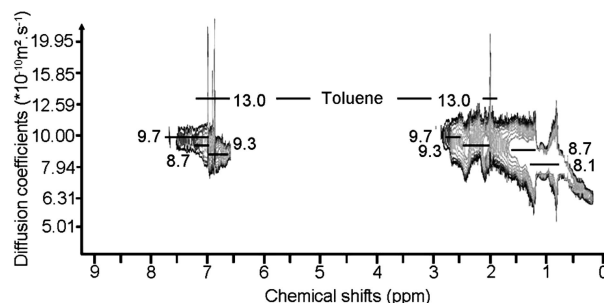
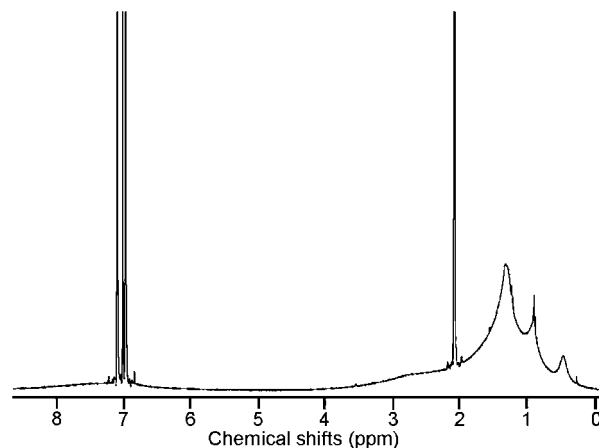
	sample B	sample C	sample D
$D_{\text{solute}} (\times 10^{-10} \text{ m}^2 \text{ s}^{-1})$	12 ± 0.2	9.0 ± 0.2	7.4 ± 0.9
$D_{\text{solvent}} (\times 10^{-10} \text{ m}^2 \text{ s}^{-1})$	19.7 ± 0.1	18.5 ± 0.1	20.6 ± 0.4
range of molecular weights expected (g mol^{-1})	200–300	300–600	>600
molecular weight calculated with $\alpha = 0.6$ (g mol^{-1})	~230	~335	~550

4.3. ¹H DOSY Spectrum of a Diesel Sample. A diesel sample with a cetane number of 41.3 has been analyzed, and both proton and ¹H DOSY spectra are presented in this section. First of all, the proton spectrum presented in Figure 5 is composed of two main parts: an aromatic and an aliphatic region. Signals from toluene and the sample are overlapped, which makes the identification difficult.

The four sharp peaks at 2.09, 6.96, 7.00, and 7.08 ppm belong to the toluene. On the basis of a simulation of model molecules including substituted and unsubstituted mono-, di-, tri-, and tetra-aromatics with 18–20 carbon atoms, a better explanation of the proton spectrum could be achieved. In the aromatic region, the peaks at 6.6–7.2 ppm stand for monoaromatics, while those between 7.2 and 7.6 ppm pertain to diaromatic molecules. Peaks appear at 7.2–8 ppm, and peaks above 8 ppm are due to the presence of tri- and possibly tetra-aromatic species. In the aliphatic zone, things are different. There are two main peaks at 1.3 and 0.9 ppm, which belong to CH₂ and CH₃, respectively, in long alkyl chains. Their strong intensities prove that there are a lot of long side chains. A similar shifted shape is observed at 2.1 and 2.6 ppm. They stand for CH₃ (2.1 ppm) and CH₂ (2.6 ppm) that are directly linked to aromatic rings. The shift between CH₂ (1.3 ppm) and CH₃ (0.9 ppm) and those at 2.6 and 2.1 ppm observed are due to the deshielding induced by the proximity of the aromatic rings.

Figure 6 shows the ¹H DOSY spectrum of sample B at 30 wt % in toluene.

In the proton spectrum, there were two main signals defined as the aromatic and aliphatic signals. The more crowded the signals (because of the overlapped signals from the solvent and product), the more difficult the processing. However, in the DOSY spectrum, a better resolution is achieved in the diffusion dimension, enabling the separation between the solvent and the petroleum molecules. A molecular-weight dispersion can be observed for the solute. It illustrates that the petroleum sample is a polydispersed mixture. Although it should be theoretically

**Figure 5.** Proton spectrum of sample B in toluene with a zoom of the aromatic part. Mono, Di, and Tri stand for mono-, di-, and triaromatic regions, respectively.**Figure 6.** ¹H DOSY spectrum of sample B in toluene.**Figure 7.** Asphaltene ¹H spectrum at 1 wt % in toluene at 20 °C.

possible to separate all of the components according to their molecular weight and their chemical shifts, this is not the case in practice. In fact, there is not enough difference between the diffusion coefficients of the compounds, which does not enable the separation of the mixture into individual components. Despite a better spectrum, overlapping signals are still present and restrict the information.

Nevertheless, it is first of all possible to separate the signals of toluene from those of the petroleum fraction. Three aromatic and one aliphatic peaks were attributed to the toluene, with an average diffusion coefficient of $13.0 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$. Moreover, the determination of the presence of various types of molecules is possible, because monoaromatics can be differentiated from di- to tri-ring aromatics. The row at $8.7 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ stands for mono-ring aromatics with very long carbon chains, whereas the row at $9.3 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ represents di-ring aromatics linked to shorter alkyl chains. Some tri-ring aromatics connected to very short chains are also present to a lesser extent and have an average diffusion coefficient of $9.7 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$. Because mono-ring aromatics are linked to long aliphatic chains, they diffuse more slowly compared to di- or tri-ring aromatics with short methyl substitutions. This is in agreement with Kapur's work.³² These observations illustrate the advantage of ¹H DOSY compared to PFGSE: it has been possible to isolate the different families of aromatics (mono-, di-, or tri-aromatics) and to link them to long or short alkyl chains. Such information can not be obtained by simple PFGSE NMR.

4.4. Asphaltene ¹H DOSY Spectrum. Similar to Gawrys et al.,¹³ asphaltene was dissolved in toluene-*d*₈, so that their concentration was 1 wt %. This sample was analyzed at 20 °C. Figure 7 shows the proton spectrum.

The sharp peaks at 2.09, 6.98, 7.02, and 7.10 ppm in Figure 7 belong to the toluene signal. There are few aromatic protons as expected for asphaltene molecules whose aromatic cores are highly substituted. It can be noticed that asphaltene peaks are

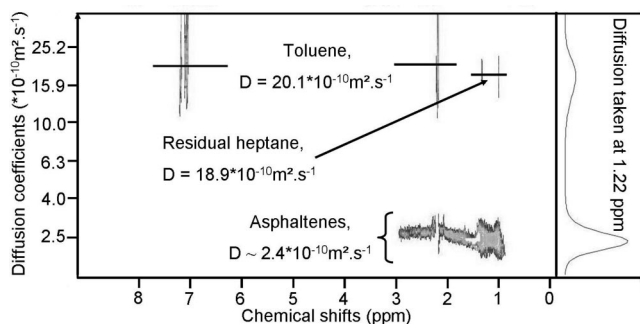


Figure 8. Asphaltene ^1H DOSY spectrum in toluene and, in the right panel, the projection of a diffusion spectrum taken at 1.22 ppm.

very broad, leading to a reduction of their intensities and especially for aromatic signals. This interpretation is in agreement with the continental¹⁸ model proposed for asphaltenes.

As mentioned before, no DOSY spectrum of asphaltenes has been found in the literature. Hence, Figure 8 presents the first ^1H DOSY spectrum of asphaltenes.

First of all, in this spectrum, the main asphaltene signals are aliphatic. Even though there are some aromatic protons, they are not detected because the signal-to-noise ratio is too low compared to the toluene signals. In the two-dimensional spectrum, it is also possible to isolate the solvent signals from the asphaltene signals, as shown in Figure 8. The diffusion coefficients of the solute and solvent are completely different: around $2.4 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ for the asphaltenes and $20.1 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ for the toluene. Moreover, although they were overlapped in the proton spectrum, it was also possible to extract residual *n*-heptane signals from the solute signals in the ^1H DOSY spectrum. The right panel is an example of a diffusion spectrum taken at 1.22 ppm to show the good separation in the diffusion dimension between residual *n*-heptane and asphaltenes at this precise chemical shift. The presence of *n*-heptane is due to the sample preparation because asphaltenes were extracted from crude oil by the addition of *n*-heptane. Furthermore, some structural information can be extracted from the main species signals. Peaks between 2.1 and 3 ppm stand for CH , CH_2 , and CH_3 connected to polycyclic aromatic hydrocarbons. In fact, the proximity of the aromatic rings induces a deshielding of the signals. Even if the signals are not very intense, there are some short chains connected to aromatic rings. However, the most intense peaks ranging from 1 to 2 ppm belong to the CH_2 signals, and those at 0.9 ppm belong to the final CH_3 in long alkyl chains.

Besides chemical information, asphaltene molecular weight can be estimated. According to $\alpha = 0.6$, an average molecular weight calculated is equal to approximately 3450 g mol^{-1} , which is higher to what has been recently published^{12,18} and is supposed to be underestimated (on the basis of sample D results). Finally,

according to the extension of Stokes–Einstein equation (eq 3), an average hydrodynamic radius is estimated, equal to about 15 Å.

5. Conclusions

DOSY is a promising global approach for the physicochemical characterization of complex samples. This technique provides information on size, aggregation state, and composition of the mixture. The influence of the concentration of the fraction in solution in toluene has been demonstrated. At low concentrations, the diffusion coefficients remain constant because only solute–solvent interactions limit the translational self-diffusion. However, more intermolecular interactions are involved in concentrated samples (beyond 10 wt % in toluene): attractive solute–solute interactions leading to the aggregation process, attractive solvent–solute interactions, and also obstruction effects. It leads to a drop of the diffusion coefficients of both the solvent and solute. This stands for a semi-dilute regime as defined for polymers,⁵² whereas a dilute regime could be established for concentrations lower than 10 wt % in toluene. The behavior of the diffusion coefficients while increasing the sample concentration provides some information on the nature of the mixture entities. Some structural parallels or oppositions between three fractions extracted from the same feedstock were established on the basis of the profile of the decrease of the solute and solvent diffusion coefficients. A spectrum of a diesel sample fraction has been presented as an example of the potential of DOSY technique to analyze heterogeneous petroleum samples. Several types of molecules have been highlighted: some mono-ring aromatics connected to long alkyl chains, some di-ring aromatics linked to smaller chains, and also some tri-ring aromatics in lower proportions connected to shorter chains. The key advantage of ^1H DOSY compared to PFGSE sequences is to obtain in just one shot both physical and chemical information. The first ^1H DOSY spectrum of an asphaltene sample is shown in this study. It appears that aromatic species in this sample are highly substituted and that polycyclic aromatic hydrocarbons are connected to long alkyl chains. This is consistent with a continental model of asphaltenes. Further work on diesel and asphaltene samples is still in progress and will be presented in a subsequent paper.

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(52) De Gennes, P. G. Polymer solutions in good solvents. In *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979; pp 69–97.