Insights into asphaltene aggregate structure using ultrafast MAS solid-state $^1$H NMR spectroscopy

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HIGHLIGHTS

- First ultrafast MAS solid-state $^1$H NMR study of asphaltenes.
- High spin-rate allows detection of otherwise obscure signals.
- Double Quantum correlation and $T_2$ relaxation experiments help elucidate asphaltene aggregate structure.
- Asphaltenes mostly consist of large single-core PAHs.
- Nanoaggregation occurs through $\pi-\pi$ interactions, and clusters consist of a rigid central core and a mobile periphery.

ABSTRACT

Solid-state $^1$H NMR spectroscopy under ultrafast magic angle spinning (60 kHz) is used for the first time to investigate the solid phase aggregate structure of a petroleum asphaltene. The fast spinning speed, combined with high-magnetic field (16.4 T, 700 MHz $^1$H) spectral filtering techniques facilitate the observation of signals that generally remain obscured even in solution-state NMR techniques. Signals shielded by aromatic ring currents were observed in both the aromatic and aliphatic regions of the spectrum, indicating a stacked geometry. A homonuclear double quantum correlation experiment reveals molecular interactions, which suggest that asphaltene molecules aggregate through skewed $\pi-\pi$ stacking. These nanoaggregates further cluster among themselves through alkyl-alkyl and alkyl-aromatic interactions. Based on the range of chemical shifts and molecular interactions, it is proposed that asphaltenes predominantly consist of large PAHs (≥7 or more). Transverse relaxation times ($T_2$) and dipolar filter experiments reveal two domains in a solid asphaltene cluster: a rigid central core composed of stacked aggregates and a much smaller fraction of mobile peripheral alkyl sidechains. Additionally, the relaxation results are consistent with the presence of small fraction of small PAHs as substituents attached to large central PAHs.

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1. Introduction

Asphaltene structure remains a subject of contention among researchers in the field [1,2]. While the question of asphaltene molecular weight has been largely settled [3,4], considerable controversy persists regarding their true structure and mode of aggregation [5]. Recently, the presence of very large polyaromatic hydrocarbon (PAH) ring systems, consisting of up to 15–20 condensed rings was unambiguously demonstrated using atomic force microscopy (AFM) [6]. The same AFM study also showed that “single aromatic core with peripheral alkanes is the dominant asphaltene molecular architecture” [6]. A few instances where the central core is divided into “several distinct PAHs” joined by a single aryl (sp²–sp²) bond were also observed, which confirmed the presence of archipelago type structures [6]. Nevertheless, not one molecule of the traditional archipelago structure was reported with two PAHs connected by an alkane linkage [4]. The presence of very large PAHs, with 5–10 fused rings being the most abundant PAH size, were also postulated previously using theoretical calculations [7]. Predominantly large PAHs have also been reported by NMR spectroscopy [8–10] and molecular orbital calculations [11], along with the presence of a nanoaggregate-cluster hierarchy [8]. Small angle neutron and X-ray scattering studies from different groups [12,13] have described asphaltene nanoaggregates as disk-shaped core-shell structures, where the core consists of densely packed aromatic structures and the shell consists of alkyl sidechains. The larger ‘clusters’ form by fractal organization of these nanoaggregates [12,13]. These studies show excellent agreement with the so-called ‘Yen-Mullins’ model [14], and indicate that aggregation among individual asphaltene molecules is primarily driven by π–π interactions. However, they do not support the dominance of so-called ‘archipelago’ structures and the related ‘supramolecular assembly’ model [5,15].

Previously, we have demonstrated novel ways in which nuclear magnetic resonance (NMR) spectroscopy can be used to study asphaltenes both in solution- and solid-state [8,9]. Specifically, we have shown how 1H solid-state NMR spectroscopy can be utilized to make important observations, something which has been largely overlooked in asphaltene research [9]. It was observed that a peak at a negative chemical shift appears in the solid-state 1H spectrum of Athabasca oil-sands asphaltenes, and was interpreted as evidence for intercalation of alkyl sidechains between aromatic sheets, which causes shielding of the alkyl protons due to the aromatic ring current effect [9,16]. Subsequent relaxation measurements supported this observation. These results demonstrated the potential for further use of solid-state 1H NMR spectroscopy in the study of asphaltenes.

Traditionally, solid-state NMR spectroscopy of asphaltenes has been performed at low to moderate magic angle spinning (MAS) rates (<20 kHz) [9,17–27]. Working at lower speeds is advantageous when performing cross-polarization (CP)-based experiments, since higher speeds reduce the effective 1H–13C dipolar coupling. Also, experiments on complex naturally occurring materials such as asphaltenes require a fairly large sample volume in order to obtain spectra within reasonable time-frames, since isotopic labeling is not possible, which necessitates the use of larger rotors, limiting the highest spinning speeds that can be achieved. Larger volumes are required mostly for the experiments observing natural abundance 13C, which take much longer to provide a good signal-to-noise ratio if the sample volume is insufficient. In contrast, 1H observed experiments which are orders of magnitude more sensitive, do not require large sample volumes, hence smaller rotors can be used at significantly higher spinning speeds. The spectral lines in 1H solid-state NMR spectra are inherently broad due to strong homonuclear dipolar coupling [9], hence the spectra typically lack sufficient resolution to reliably obtain detailed chemical shift information. Only when very high MAS speeds and/or spectral filtering techniques [9] are used, finer details in the spectrum are more likely to be observed. Moreover, using a stronger magnetic field, such as the 16.4 T (700.4 MHz 1H) field further reduces line broadening since the chemical shift dispersion is increased and spin diffusion is suppressed to a greater extent, offering better resolution. To the best of our knowledge, such studies using a combination of ultrafast MAS rates and a high static magnetic field strength have not yet been employed for asphaltenes, and thus provide a compelling opportunity to reveal more detailed information.

Herein is reported the first solid-state 1H NMR spectroscopic study of asphaltenes under ultrafast (60.0 kHz) MAS. Proton dipolar filtering experiments reveal underlying signals in an otherwise broad 1H spectrum, with unprecedented detail. Homonuclear 1H double-quantum (DQ) correlation experiments were employed to investigate the molecular interactions among asphaltenes, which provides insight into the structure of the asphaltene aggregates, which are complemented by T2 relaxation analysis to distinguish between signal associated with rigid and mobile components. The results presented here provide significant insight into how asphaltene monomers exist in an aggregated state, and to a lesser extent into the structure of the monomers themselves.

2. Theoretical background

2.1. 1H dipolar filter

The dipolar filter (DF) pulse sequence [28] shown in Fig. 1A is a well-known domain selective technique based on refocusing the homonuclear dipolar coupling and chemical shift anisotropy (CSA) interactions. It is generally used to segregate signals from rigid and mobile domains in a polymer [29–31]. In the case of proton, the selection is based mostly on refocusing the homonuclear dipolar coupling due to the CSA being small.

It consists of a train of twelve 90° pulses of length p, separated by a variable inter-pulse delay τ, phase cycled such that chemical shift evolution is suppressed, followed by a final pulse for observation. The total filtering period is given by: $n(2\pi + p)$, n being the number of times the pulse-train is repeated. The total filtering period determines the effective refocusing timescale defining the upper limit of the effective coupling strength that is refocused. For a given inter-pulse delay, the sequence selects for the weak 1H—1H dipolar coupling interactions that have relatively longer transverse relaxation times (mobile domains) compared to those with strong 1H—13C dipolar coupling interactions relax much faster (rigid domains), consequently removing the magnetizations from the rigid domains. The final spectrum consists of signals mostly from the mobile domains of the sample.

2.2. 1H Back-to-Back (BABA) recoupling Double Quantum correlation under MAS (DQ-MAS)

The dipolar coupling that is averaged out by magic angle spinning (MAS) can be reintroduced using a recoupling sequence [32]. This reintroduction is necessary in certain cases for the purpose of establishing connectivities within the molecule or to measure internuclear distances. This is particularly true under fast MAS conditions, where the averaging of dipolar coupling is more effective. Recoupling sequences can be used for both homonuclear and heteronuclear cases, but only the homonuclear 1H–1H recoupling is relevant to this work.

In the case of 1H, which has strong homonuclear dipolar coupling, double quantum (DQ) coherences can be created, which arise...
from the nuclei that are coupled to each other. Since DQ coher-ences cannot be detected directly, they have to be converted to single quantum (SQ) coherences for observation. A commonly used pulse sequence for creating DQ coherences is the Back-to-back (BABA) \([33]\) recoupling sequence. The name is derived from the back-to-back \(\pi/2\) pulses that are used to excite the homonuclear DQ coherences. The pairs of back-to-back \(\pi/2\) pulses are rotor synchronized, such that there is half a rotor period (\(\tau_1/2\)) between each pair, and the DQ coherences are created by phase cycling the pulse pairs in 90\(^\circ\) steps \([33]\). A rotor period is the inverse of the MAS frequency \(v_r\). Multiple such pairs of pulses can be used in a BABA sequence, depending on the time, called the mixing time, for which recoupling is desired. Fig. 1B shows the BABA sequence where recoupling, or DQ excitation, is allowed for at least two rotor periods. This mixing period can be extended if required by looping the block of pulses by integer multiples. Once the DQ coherences are created, they are allowed to evolve for a period \(t_1\), which is incremented in steps that are integer multiples of the rotor period. Fourier transform of this period provides the indirect dimension of the final 2D plot. Since DQ coherences cannot be detected directly, the final observation is done by converting them to SQ coherences using another pair rotor synchronized \(\pi/2\) pulses and a final detection pulse, which provides the direct dimension for the 2D plot. A schematic of a typical DQ-SQ correlation plot is shown in Fig. 2. The SQ dimension contains the normal one-dimensional spectrum with signals at their characteristic chemical shifts, while the DQ dimension has chemical shifts that are double that of the SQ dimension. If dipolar coupling exists between two nuclei, say with SQ chemical shifts of \(\delta_1\) and \(\delta_3\), it will give rise to two cross peaks at \((\delta_1, \delta_1 + \delta_3)\) and \((\delta_3, \delta_1 + \delta_3)\), the first term being the SQ chemical shift of one of the nuclei and the second term being the sum of the SQ shifts in the DQ dimension. A correlation peak between two signals indicates that the moieties from which the signals arise are close to each other and interact via dipolar coupling. To choose the optimum mixing time, the experiment is often initially performed in one dimension at different mixing times, without incrementing the \(t_1\) evolution period. The intensity is then plotted against the mixing time to construct a build-up curve, where the maximum intensity is chosen as the optimum mixing period.

3. Materials and methods

3.1. Asphaltene extraction

The petroleum asphaltenes were extracted from crude oil (UG8, Kuwaiti crude) by standard n-heptane precipitation. In short, a n-heptane:crude oil (40:1) mixture was stirred overnight to allow the asphaltenes to precipitate. Precipitates were then extracted by vacuum filtration over a Teflon membrane with 0.47-\(\mu\)m pores. Co-precipitates were removed by Soxhlet extraction with n-heptane for three days. The elemental analysis of this asphaltene is available elsewhere \([10]\).

3.2. NMR spectroscopy

All solid-state NMR experiments were performed on a 16.4 T Bruker Avance III HD NMR spectrometer, operating at 700.4 MHz \(^1\)H Larmor frequency, using a quadruple resonance \((^1\text{H}-^{19}\text{F}-^{13}\text{C}-^{31}\text{P})\) 1.3-mm Bruker solid-state MAS probe. The UG8 petroleum asphaltene sample was packed into a 1.7 \(\mu\)L (1.3-mm
O.D.) rotor, which was spun at 60.0 kHz. The temperature was controlled at 22 °C for all experiments and all $^1$H 90° pulses were of 2.5 μs duration. A relaxation delay of 4 s was used for all the solid-state experiments. The solution-state $^1$H NMR spectrum in Fig. 3 was obtained on the same magnet using a 5-mm Bruker solution-state TBO ($^1$H-$^{31}$P-X) probe, with a 2 s recycle delay, 128 scans, and 17.5 μs $^1$H 90° pulse. The sample concentration was 30.0 g/L (in CDCl$_3$).

3.2.1. Solid-state $^1$H dipolar filter

The inter-pulse delay was varied from 10 to 200 μs, the dipolar filter pulse train was looped five times and 256 scans were recorded for each experiment. The 90° pulses in the 12-pulse train were each of 2.5 μs duration. The total filtering time corresponding to an inter-pulse delay $\tau$ can be calculated as: $5 \times 12 \times (2.5 + \tau) \times 10^{-3}$ ms.

3.2.2. Solid-state $^1$H $T_2$ relaxation

A standard rotor-synchronized Hahn-echo sequence was used for the $T_2$ relaxation-filtering experiments, the echo period being varied from 0.03 ms to 40.10 ms in 15 increments, 512 scans each. Both the aliphatic and aromatic signals were completely dephased by 30 ms. The $T_2$ relaxation times and associated standard errors were measured by fitting the decay curves to either mono- or bi-exponential decay equations using a non-linear least square regression algorithm on the statistical software R [34].

3.2.3. Solid-state $^1$H Back-to-Back (BABA) recoupling DQ-MAS

The two rotor-period BABA recoupling sequence described in Fig. 1B was employed, with the DQ excitation loop repeated two times for each experiment, making the total recoupling period equal to four rotor-periods, i.e., 66.7 μs (for 60 kHz MAS). A total of 128 transients were collected for the indirect dimension with 32 scans each and the delay being incremented in rotor-synchronized steps of 33.3 μs. In the one-dimensional $^1$H NMR spectrum, spinning sidebands of equal intensity occurred at around 60 kHz from the isotropic peaks, on both sides. Therefore, the DQ dimension is required to be at least double the spectral width used in the SQ dimension, which itself should be at least greater than 120 kHz when centred at the isotropic peaks, to avoid folding of the sidebands. Using a large spectral width in the indirect dimension reduces digital resolution, but this problem can be circumvented by using a DQ spectral width that is $\frac{1}{2}$n of the SQ, where n is a positive integer. It folds back the sidebands exactly on to the centre band of the isotropic signals, enhancing its intensity. A spectral width of 30 kHz in the indirect dimension was used in this study.

4. Results and discussion

4.1. $^1$H dipolar filter at 60 kHz MAS

In Fig. 3A, the 8 kHz MAS $^1$H NMR spectrum for UG8 asphaltenes obtained at 11.7 T (500.3 MHz) is compared with the same spectrum at 60 kHz MAS and 16.4 T (700.4 MHz). A significant improvement in resolution is observed, the aromatic and aliphatic protons are clearly resolved due to the reduction of broadening caused by homonuclear dipolar coupling, influenced by the ultrafast-MAS and greater chemical shift dispersion at the higher field strength. The narrower linewidths allow for the observation of underlying signals with even greater detail when filtering techniques are applied and deconvolution analysis can be performed on the $^1$H NMR spectrum with greater accuracy.
The $^1$H dipolar filtered spectra at different filtering times, corresponding to inter-pulse delays of 100, 110, 160 and 180 $\mu$s, are compared against the unfiltered spectrum at 60 kHz MAS in Fig. 3B. The filtered spectra have been magnified in intensity for easy investigation. Notice that the filtered spectra constitute only ~1–2% of the overall $^1$H signal. Since the dipolar filter sequence removes rigid component signals, this suggests that the majority of the asphaltene molecules are in a rigid environment, with only a small mobile fraction. This mobile fraction likely constitutes alkyl sidechains not partaking in aggregation, small PAHs and possibly the smaller nanoaggregates which are not part of a bigger cluster. These filtered spectra show unprecedented detail, especially in the 5–8 ppm region, where multiple distinct aromatic proton environments can be observed. The aliphatic region of the dipolar filtered $^1$H spectra also shows the presence of multiple narrow components, possibly from protons on mobile aliphatic chains overlapping much broader signals. A clear signal is also observed at a slightly negative chemical shift, which is consistent with a previous study on Athabasca bitumen asphaltene [9]. It is assigned to alkyl groups that lie in the aromatic shielding region. To the best of our knowledge, this is the first time in asphaltene literature that a solid-state $^1$H NMR spectrum with such high degree of detail is reported. The component signals of the aromatic region are not resolved even in a solution-state NMR spectrum due to high degree of inhomogeneous broadening, proving the efficiency and applicability of this technique. Since these signals constitute only a small fraction of the overall spectrum, major conclusions cannot be drawn from them with sufficient confidence. However, they do provide hints for further investigation, such as the diversity of PAH sizes and the presence of shielding effects due to π-stacking.

4.2. Solid-state $^1$H $T_2$ filter

A $^1$H Hahn-echo experiment acquired at 60.0 kHz MAS reveals the underlying narrow components of the aliphatic region, and also permits the determination of their respective $T_2$ relaxation times. Fig. 4 shows the $^1$H NMR spectrum obtained after 6.68 ms of $T_2$ filtering or Hahn-echo. Based on the underlying peaks observed in the $T_2$ filtered spectra, and the dipolar filtered spectra shown earlier, a peak-fitting (deconvolution) model was constructed which enables the identification of the major components of the $^1$H NMR spectrum. The presence of a prominent signal at the chemical shift of ~0.1 ppm unambiguously confirms that shielded protons with negative chemical shifts are indeed present which is likely associated with π-stacking of asphaltene molecules. The distinct aromatic proton environments as seen previously in the dipolar filter spectra were also observed. These distinct aromatic proton environments can likely be explained by factors including very diverse PAHs as observed in molecular imaging [4] and ‘aromatic ring current’ effect, which we have previously explained elsewhere [9]. In brief, depending on the position of a moiety relative to the aromatic ring system, it will either be shielded or deshielded from the static magnetic field by the currents generated due to the circulating π-electrons. The shielding region lies directly on top or bottom of the ring system, which essentially decreases the chemical shift of any nuclei lying within it. Here, the aromatic proton signals span a range from below 6 ppm to more than 8 ppm. A similar situation has been reported in literature with respect to the solid-state $^1$H NMR spectrum of hexabenzocoronene (HBC) and its derivatives [35,36]. These disc-like polyaromatic molecules form skewed π–π stacks (for instance, see Fig. 5B) in the solid phase that shields the aromatic protons lying directly on top of the aromatic rings, and hence resonate at a lower chemical shift (~6 ppm), while those in the deshielding region resonate at higher chemical shifts (~8 ppm), compared to other aromatic protons. Therefore, it is reasonable to assume that asphaltene PAH cores exhibit a similar skewed- or staggered-stacking motif, resulting in distinct aromatic proton environments, some more shielded by the aromatic ring currents than others. Moreover, theoretical calculations support these motifs [37], and also postulate other stacking geometries that can give rise to shielded aromatic protons, such as the “twisted hexagonal” motif (see Figure 15 in Ref. [37]). However, for brevity and illustrative purposes, we show the skewed stacking (parallel displaced) motif, while recognizing the probable existence of the other packing motifs. The $^1$H chemical shifts higher than 8.5 ppm are also generally assigned to aromatic protons in the ‘bay’ and ‘fjord’ regions of PAHs [38] (Fig. 5A). These motifs (‘bay’ and ‘fjord’) are only possible in PAHs with at least three (‘for bay’) or four (‘for fjord’) condensed rings, phenanthrene being the smallest such molecule with ‘bay’ aromatic protons, their occurrence becoming more probable with larger PAHs. Moreover, smaller PAHs (3 or less rings) represent only a very limited number of aromatic proton environments, and thus a smaller range of chemical shifts, even when π-stacked. The results here suggest that large PAH cores are predominant, consistent with recent molecular imaging observations [6] and solid-state NMR results [39], which show > 7 ring PAHs as dominating.

In addition to skewed or staggered π-stacking, the aromatic protons can also be shielded by T-shaped interactions. These T-shaped stacking geometries are a common motif in the crystal structure of PAHs [35,36,40] and have been shown to be energetically favourable using molecular dynamics simulations [41–43]. It has been noted that asphaltene monomers that possess a lower number of alkyl substitutions, or those where substitutions are limited to only one side of the central aromatic core, show a greater propensity for such T-shaped aromatic stacking geometries due to reduced steric interference from the sidechains [43].
However, a T-shaped stacking geometry between individual asphaltenes would preclude the formation of tightly packed nanoaggregate cores, which are expected based on SANS and SAXS studies [12,13]. \(\pi\)-Stacking is also consistent with the known small aggregation numbers of asphaltene nanoaggregates [44] and also seen in X-ray structures of large PAHs with symmetric substitution [40]; hence, it is more probable that the skewed \(\pi\)-stacking geometry dominates in the case of nanoaggregates. The T-shaped interactions likely play only a small role and are shown for illustration. Please note that the stacked molecules in B represent sp2-hybridized aromatic cores, not sp3 carbons. The unsaturations in the rings have been removed for clarity of the illustration. Also note that the skewed stacking conformation is one of the three possible motifs amenable to shielding of aromatic protons, the others being staggered and twisted hexagonal [37].

Earlier theoretical work also predicted a direct face-to-face packing motif between asphaltene monomers, calling it “hexagonal stacking” [37], but that is only possible in the case of identical molecules, which is highly unlikely in asphaltenes, where the core sizes and sidechain lengths are highly variable [39]. Such conformations are hence precluded.

In Table 1, the assignments for the deconvolved peaks are shown, along with their corresponding transverse relaxation times. Mono- or bi-exponential fitting functions were used to fit the relaxation data, depending on the nature of the signal decay. To make the assignments, the relaxation times, linewidths, and chemical shifts were all considered.

Fig. 5. Schematic showing the possible modes of aggregation and molecular interactions among asphaltene monomers. All hexagonal rings are to be considered aromatic. (A) Alkyl-aromatic interactions in ‘bay’ or ‘fjord’ type regions, (B) possible interactions and shielding regions in a skewed \(\pi\)-stacking conformation, (C) shielding of alkyl groups through intercalation between aromatic sheets, (D) an asphaltene cluster, composed of nanoaggregates. The T-shaped interactions likely play only a small role and are shown for illustration. Please note that the stacked molecules in B represent sp2-hybridized aromatic cores, not sp3 carbons. The unsaturations in the rings have been removed for clarity of the illustration. Also note that the skewed stacking conformation is one of the three possible motifs amenable to shielding of aromatic protons, the others being staggered and twisted hexagonal [37].
A bi-exponential relaxation behavior suggests that the moiety in concern exists in two distinct domains of mobility. More rigorously speaking, the behavior is likely multi-exponential, but the bi-exponential model provides the two extremes of $T_2$ relaxation time. Typically, longer $T_2$ values infer higher mobility component, while shorter values are indicative of rigidity. At first glance the overall picture that emerges from the relaxation times is that much of the asphaltenes are rigid with short $T_2$ values. Furthermore, a small mobile fraction exists most notably associated with signals corresponding to the aliphatic sidechains which have much longer $T_2$ which clearly would belong to the periphery of the clusters. Looking more closely, the aromatic protons assigned to fused ring systems ($\delta_{1H} = 8.0$ and 7.5 ppm) are found to be mostly rigid, evident from the larger fraction of the shorter $T_2$ components (75.8% and 60.3%, respectively), and the rigidity can be ascribed to nanoaggregation, which restricts movement of the individual molecules. The $\delta_{1H} = 8.0$ ppm protons show the shortest $T_2$ among these (0.24 ± 0.08 ms), which justifies its assignment to larger, more rigid PAHs. The $\delta_{1H} = 6.5$ ppm signal exhibits a single, moderately short $T_2$ (1.08 ± 0.04 ms). Even though this peak has the largest deconvolved linewidth, it does not have the shortest $T_2$, which is counter-intuitive. However, the inverse relationship between the linewidth and $T_2$ assumes homogeneous broadening. Due to the complex nature of asphaltenes there is significant structural variation, and it is probable that the broadness of this fitted peak is due to a distribution of shielding environments, or heterogeneous broadening, with a wide range of aromatic moieties resonating around a similar chemical shift. This holds true for most of the broad peaks. Moreover, the $\delta_{1H} = 6.5$ ppm signal has no mobile component, and has dephsed almost completely after 6.68 ms filtering. Whereas, the narrower peaks (compared to the 6.5 ppm peak) that possess a $T_2$ component shorter than that of the 6.5 ppm peak, also have a mobile component, which may explain the reduced linewidth. The more mobile aromatic components (the longer $T_2$ values) corresponding to the aromatic signals at $\delta_{1H} = 8.0$ and 7.5 ppm likely exist in a less restrictive environment, on the periphery of the clusters (Fig. 5D), or in aggregates that are significantly smaller than the bulk of the clusters. The aromatic signal at $\delta_{1H} = 6.9$ ppm deserves more consideration. It arises from aromatic protons that are mostly mobile, 82.2% of them having the higher $T_2$ of 1.24 ± 0.04 ms, while the lower $T_2$ component of 0.06 ± 0.02 ms constitutes only 17.8% of the signal. Compared to it, all the other aromatic protons ($\delta_{1H} = 8.0, 7.5$ and 6.5 ppm) are mostly rigid, as discussed earlier. Therefore, the $\delta_{1H} = 6.9$ ppm protons likely belong to small aromatic and heteroaromatic rings that are not condensed with the larger PAH cores, making them less structurally constrained. These PAHs are possibly "pandant" aromatic rings, attached to the central core via a direct bond between sp² aromatic carbons, similar to model hexabenzocoronene derivatives reported by Fechtenkotter et al. [45] and Fischbach et al. [40], even in their $^1H$ chemical shift. These moieties are likely <3 rings in size, since the large PAHs are >3. Similar motifs have been reported for UG8 asphaltenes in a recent AFM imaging study [6]. In addition, these smaller PAHs could be the central PAH of smaller island compounds indicated by smaller molecules within the molecular weight profile of asphaltenes [3]. This possibility is consistent with a quantitative analysis of asphaltene optical spectra [11]. It is, however, not possible to calculate the number of pendant rings using any of the techniques presented in this paper. The signal at $\delta_{1H} = 5.6$ ppm can be assigned to shielded aromatic protons and phenolic –OH moieties. These protons are largely rigid, with 78.4% of them possessing the shorter $T_2$ of 0.19 ± 0.03 ms, supports the hypothesis that they are shielded through skewed π-stacking or T-shaped interactions, as illustrated in Fig. 5.

The aliphatic $\delta_{1H} = 2.6$ ppm signal are assigned to –CH₂ and –CH₃ groups directly attached to the aromatic ring [25]. As a result, they are almost exclusively rigid in nature, with ~97% having a shorter $T_2$ of 0.27 ± 0.01 ms. The broad aliphatic signal at 1.6 ppm is partly assigned to the cycloalkyl groups, with a shorter $T_2$ of 0.32 ± 0.05 ms. Their largely rigid (72.3%) nature suggests that they are condensed with the aromatic core. The second component of this signal, with the slightly longer $T_2$ of 0.92 ± 0.26 ms, is likely the chain –CH₂ moieties that are located inside the bulk of the clusters, which restricts their mobility. These are the groups that facilitate cluster formation through alkyl-alkyl interactions between nanoaggregates. In contrast, the chain –CH₂ groups resonating at $\delta_{1H} = 1.2$ and 1.1 ppm are significantly more mobile, with the longest $T_2$ values of 27.65 ± 1.39 and 13.50 ± 0.96 ms, respectively. These likely belong to the alkyl sidechains on the periphery of the clusters, which makes them significantly more mobile than those in the bulk. Among these, the $\delta_{1H} = 1.2$ ppm peak has the longer $T_2$ (27.65 ± 1.39 ms), which is likely on account of

<table>
<thead>
<tr>
<th>ppm</th>
<th>Linewidth (Hz)</th>
<th>Relative abundance (%)</th>
<th>Assignment</th>
<th>$T_{21}$ (ms)</th>
<th>$T_{22}$ (ms)</th>
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<tr>
<td>8.0</td>
<td>959</td>
<td>4.9</td>
<td>Pyrolytic –NH, arom. H on larger fused ring systems (&gt;3 rings)</td>
<td>2.63 ± 1.61 (24.2%)³</td>
<td>0.24 ± 0.08 (75.8%)</td>
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<tr>
<td>7.5</td>
<td>1162</td>
<td>3.5</td>
<td>Arom. H on smaller fused ring systems (&lt;3)</td>
<td>1.57 ± 0.15 (39.7%)</td>
<td>0.49 ± 0.04 (60.3%)</td>
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<tr>
<td>6.9</td>
<td>1046</td>
<td>8.8</td>
<td>Small pendant aromatics, small heteroaromatic rings</td>
<td>1.24 ± 0.04 (82.2%)</td>
<td>0.06 ± 0.02 (17.8%)</td>
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<td>6.5</td>
<td>1598</td>
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<td>Arom. H ortho/para to –O/–NH substituted arom. C, shielded arom. H</td>
<td>1.0 ± 0.04 (100%)</td>
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<td>5.6</td>
<td>1474</td>
<td>11.8</td>
<td>Shielded arom. H, phenolic –OH</td>
<td>2.55 ± 0.84 (21.6%)</td>
<td>0.19 ± 0.03 (78.4%)</td>
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<td>2.6</td>
<td>1070</td>
<td>6.6</td>
<td>–CH₃/–CH₂  from aryl ring</td>
<td>2.55 ± 1.70 (3.4%)</td>
<td>0.27 ± 0.01 (96.6%)</td>
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<td>1.6</td>
<td>1137</td>
<td>2.5</td>
<td>Cyclic or chain –CH₃ inside the bulk of the clusters</td>
<td>0.92 ± 0.26 (27.7%)</td>
<td>0.32 ± 0.05 (72.3%)</td>
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<td>1.2</td>
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<td>3.6</td>
<td>Chain –CH₂ more than 6 from aryl ring on longer chains on the cluster periphery</td>
<td>27.65 ± 1.39 (100%)</td>
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<td>48</td>
<td>1.7</td>
<td>Chain –CH₂ more than 6 from aryl ring on shorter chains on the cluster periphery</td>
<td>13.50 ± 0.96 (100%)</td>
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<td>1.0</td>
<td>955</td>
<td>41.6</td>
<td>Rigid –CH₂</td>
<td>1.37 ± 0.35 (35.2%)</td>
<td>0.50 ± 0.08 (64.8%)</td>
</tr>
<tr>
<td>0.7</td>
<td>67</td>
<td>2.0</td>
<td>–CH₃ on the periphery of clusters</td>
<td>25.31 ± 1.11 (100%)</td>
<td>–</td>
</tr>
<tr>
<td>0.6</td>
<td>405</td>
<td>1.8</td>
<td>–CH₃ on the bulk interior of clusters</td>
<td>1.08 ± 0.22 (32.9%)</td>
<td>0.35 ± 0.05 (67.1%)</td>
</tr>
<tr>
<td>-0.1</td>
<td>529</td>
<td>9.3</td>
<td>Shielded terminal =CH₃</td>
<td>1.78 ± 2.09 (13.4%)</td>
<td>0.44 ± 0.10 (86.6%)</td>
</tr>
</tbody>
</table>

Table 1
Assignments for the deconvolved peaks of the T₂ filtered $^1H$ NMR spectrum, along with their corresponding calculated $T_2$ values at 60 kHz MAS and the relative abundances after 6.68 ms $T_2$ filter.

Footnotes:

³ After 6.68 ms filter.

² The values in brackets represent the relative abundance of the long and short $T_2$ components.

⁴ Large fitting uncertainty, disregarded.
them belonging to longer chains. It indicates that a distribution of short and long alkyl sidechains exists in UG8 asphaltenes. The $\delta_{1H} = 1.0$ ppm signal is mostly rigid, with 64.8% corresponding to a short $0.50 \pm 0.08$ ms $T_2$, and is assigned to rigid $-CH_3$ groups, possibly in the cluster interior. The signal at $\delta_{1H} = 0.7$ ppm, with a single component of $T_2$ at 25.31 ± 1.11 ms, belongs to the mobile terminal $-CH_3$ groups on the periphery of the clusters, while those at 0.6 ppm probably arise mostly from those on the interior, since they have a large rigid fraction (67.1%) with a $T_2$ of 0.35 ± 0.05 ms. The $-0.1$ -ppm peak is assigned to $-CH_2$ groups that are shielded either by intercalating between $\pi$-stacked aromatic cores or participating in a T-shaped interaction. These groups are largely rigid in nature, evinced by the majority fraction (86.6%) having a short $T_2$ of 0.44 ± 0.10 ms, suggesting that these interactions occur mostly on the interior of the clusters. The longer $T_2$ for this peak has a large error associated with its measurement, but it has only a minor contribution, and hence is disregarded. Note that the mobile sidechains constitute only small fraction of the overall aliphatic signal, which suggests that the majority of the alkyl groups are in rigid environments. Additionally, the $-0.1$ -ppm peak has a substantial contribution to the overall spectrum, indicating the presence of a significant degree of $\pi$-stacking.

4.3. $^1H$ Back-to-Back recoupling DQ-MAS homonuclear correlation

The homonuclear BABA recoupling experiment enables the identification of protons that are spatially proximate to each other and interact via dipole-dipole coupling. Therefore, it is well suited for investigating aggregate structure, by probing molecular interactions. As described earlier, if two protons via dipole-dipole coupling, they will exhibit two cross peaks, each at the SQ chemical shift of the respective signals and the DQ chemical shift given by the sum of the SQ shifts (Fig. 2). There will be only one cross-peak (autocorrelation peak) for chemical shift equivalent protons. The $^1H$ DQ-MAS NMR spectrum of UG8 P-asphaltenes obtained at 60 kHz MAS using BABA recoupling is shown in Fig. 6a, while Fig. 6b shows the slices extracted at specific double quantum resonances of interest. Note that due to the highly heterogeneous nature of asphaltenes, a single DQ resonance can arise from the combination of several different SQ resonances.

The dominant correlations at the centre (Fig. 6) represent all the dipolar interactions between aliphatic protons, which is expected since they represent the majority of the protons in the system. These interactions can be both intra- and inter-molecular. The intermolecular interactions may be largely due to interacting adjacent nanoaggregates in a cluster, which suggest the alkyl sidechains playing a role in cluster formation. Interestingly, correlations between aromatic protons and highly shielded alkyl protons with negative chemical shifts are also observed, although somewhat weak (Fig. 6, slice at 3.0 ppm). A similar interaction is also observed between the normal alkyl protons and the highly shielded protons (slice at $-0.6$ ppm DQ). Since one of the interacting groups have a negative chemical shift, the corresponding DQ chemical shift is less than the sum of the SQ chemical shifts. Similar interactions between shielded alkyl groups and aromatic protons have been reported for HBC derivatives, where the $\pi$-stacked aromatic cores occur in a T-shaped configuration [36]. Another route through which the shielded alkyl groups can interact with aromatic protons is if they intercalate between $\pi$-stacked aromatic cores, as illustrated in Fig. 5C, and also demonstrated in previous work [9]. Therefore, it is probable that asphaltene clusters are formed both through alkyl-alkyl interactions or T-shaped interactions between nanoaggregates. In nanoaggregates where the steric interference from the sidechains is negligible, allowing them to approach each other, the T-shaped interactions can be aromatic-aromatic [43]. In other cases, this interaction can be alkyl-aromatic (Fig. 5D). However, if T-shaped interactions were a significant factor for intra-nanoaggregate binding, aggregation numbers could potentially grow indefinitely and gel formation could occur, which is not typically seen. It is also important to note that the range of negative chemical shifts as seen from the slices suggests that shielding effects are strong and significant, which is likely a consequence of the predominance of large pericondensed PAHs. A wide variety of correlations is observed between alkyl$-CH_3$ groups and aromatic protons (slices at 9.0, 8.4 and 6.0 ppm DQ), some of those interactions shown in Fig. 5A.

The broadness of the SQ-DQ correlations in asphaltenes, when compared to the SQ-DQ correlations of certain model systems, make for important observations. Recent works on graphene nanoribbons synthesis [46,47] show that the DQ-MAS spectra of the polyphenylene-type precursors contain narrow, fairly well defined SQ-DQ correlations due to the fairly mobile aromatic rings. However, on the formation of the graphene nanoribbons the correlations become broad and stretched out, because of the high

![Fig. 6. $^1H$ DQ-MAS NMR spectrum of UG8 asphaltenes obtained at 60 kHz MAS using the BABA recoupling sequence. The black bars connect the SQ chemical shifts that correspond to interacting protons, description in text. Interactions between protons at negative chemical shifts and other protons, both alkyl and aromatic, clearly demonstrate the presence of $\pi$-stacking.](image-url)
rigidity of the graphene sheet and the shifting of $^1$H signals caused by ring-current effects from heterogeneous stacking. On the same note, the broadness of asphaltene SQ-DQ correlations suggest large, rigid and stacked PAHs, rather than small flexible systems. The negative chemical shifts as seen in asphaltenes also appear in these graphene nanoribbon systems [46,47], further reinforcing the above observations.

5. Conclusions

The dipolar filter and DQ-MAS results provide a number of important insights regarding asphaltene monomer and aggregate structure. Based on the observed interactions and shielding effects, it can be said that skewed π-stacking occurs between the aromatic cores in a nanoaggregate, and that the nanoaggregates form clusters both through alkyl-alkyl interactions and T-shaped interactions. A wide variety of aromatic proton environments, shielded and deshielded by ring currents, including definite bay and fjord type regions, are observed, suggesting that the asphaltene monomers participating in aggregate formation are generally larger than simple 3–4 ring PAHs. DQ-MAS studies using alkyl substituted polycyclic aromatic molecules (hexabenzocoronene derivatives) support the observations made in this work, with respect to the stacking of the monomers [35,36].

The relaxation results, combined with those from the dipolar filter and DQ-MAS experiments, allow the description of a solid-state aggregation model of petroleum asphaltenes, as presented schematically in Fig. 5. Petroleum asphaltene monomers are dominated by large pericondensed PAHs (7 or more rings) [6,39], and they aggregate with other monomers through skewed π–π stacking to form nanoaggregates. This results in the shielding of certain aromatic and aliphatic proton nuclei, resulting in chemical shifts lower than expected. The $T_2$ relaxation experiments imply that in the solid phase, asphaltenes exist as clusters of ‘nanoaggregates’, consisting of a rigid central bulk and a small fraction of mobile alkyl chains on the periphery. This observation is supported by the dipolar filter experiments, which shows that majority of the asphaltene molecules reside in a highly rigid environment. The clusters are formed by alkyl-alkyl and alkyl-aryl interactions between the nanoaggregates. It is similar to the clusters posited by the ‘Yen-Mullins’ model, but instead of only alkyl-aryl interactions forming the clusters, T-shaped interactions may also play a role. However, if T-interactions were important for intra-nanoaggregate binding then aggregation numbers could grow indefinitely and gel formation could occur – this has not been observed. The relaxation results are consistent with a small fraction of smaller PAHs bonded to larger PAHs, as observed in direct molecular imaging [8] and the modes of aggregation proposed here are supported by existing theoretical simulations [41,43,48], and other experimental techniques [12,13]. Recently published molecular dynamics simulations [48] suggest that the ‘size of the conjugated aromatic core’, and the length and nature of the alkyl sidechains are more strongly correlated with the aggregation mechanism, rather than the presence of particular heteroatoms. The experimental results presented here support this hypothesis.

Conflict of interest

The authors declare no financial conflicts of interest.

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References


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