Adsorption/Occlusion Characteristics of Asphaltenes: Some Implication for Asphaltene Structural Features

Zewen Liao,*,‡,§ Honggang Zhou,‖ Alain Graciaa,‡ Anna Chrostowska,⊥
Patrice Creux,‡ and Ansong Geng§

*Laboratoire des Fluides Complexes, UMR 5150 TOTAL-CNRS-UPPA, BP 1155,
64013 Pau Cedex, France, State Key Laboratory of Organic Geochemistry, Guangzhou Institute
of Geochemistry, Chinese Academy of Sciences, Guangzhou, 510640, People's Republic of
China, TOTAL S.A., CSTJF, Avenue Larribau, 64018 Pau Cedex, France, and Laboratoire de
Chimie Théorique et Physico-Chimie Moléculaire, UMR CNRS 5624, University of Pau,
BP 1155, 64013 Pau Cedex, France*

In the crude oil, the other fractions such as hydrocarbons could be adsorbed and/or occluded inside asphaltene structures. In this work, the deuterated compound $n\text{-}C_{20}D_{42}$ has been used to simulate the adsorption/occlusion characteristics of asphaltene in toluene solution. Based on the highly polydispersed structures of asphaltenes, the experimental results indicate that the adsorbed hydrocarbons could be exchanged with the outside bulk phase, whereas the occluded ones inside the core of asphaltenes could not be exchanged. These results suggest that substantial microporous units exist inside asphaltene structures, and these structural units are suitable to adsorb and occlude the other fractions in the crude oil. The carbon number of the occluded hydrocarbons could be up to C_{40}, and the weight could be more than 0.5%, based on the initial asphaltene weight. The adsorption should occur at the periphery of asphaltene aggregates (the loosely packed ones), and then they are liable to be exchanged with the outside bulk phase. If the asphaltene molecule is large enough, the occlusion could occur at the asphaltene molecular level. However, this type of occlusion perhaps just occurs inside asphaltene aggregates (the close aggregating ones); if this is the case, this type of asphaltene aggregate should be considered to be the stable unit in toluene solution, and then the occluded hydrocarbons could not be exchanged with the bulk phase. Regarding the adsorption/occlusion properties of asphaltenes, the aforementioned results should be valid, even extrapolated into the crude oil reservoir system.

Introduction

Asphaltene is an operational concept, namely in the crude oil system, that is soluble in an aromatic solvent (such as toluene) while insoluble in a saturated hydrocarbon solvent (such as *n*-heptane). In addition, this is also the simple principle to prepare asphaltenes from crude oils. However, asphaltenes represent a class of compounds that are highly polydispersed,[1,2] with respect to their basic physicochemical properties such as molecular weight, molecular size, solubility, polarity, elemental composition, and so on.

Recently, some authors reported that asphaltene molecules were much smaller than previously believed: for example, the molecular weight is very likely to be ∼700−1000 amu for petroleum asphaltenes, and even smaller (∼500 amu) for coal-derived asphaltenes.[3−6]

However, the molecular weight is not necessarily a good parameter to characterize asphaltene,[7] simply because asphaltene is defined through the operational concept and it should include a wide scope of compounds that are associated with a high polydispersity. The aforementioned low molecular weight is based on the fluorescence measurement; however, this method is thought to be unsuitable for the asphaltene molecular weight (Mw) measurement, and the reasons have been discussed in details by Strausz et al.[1] If the fact that asphaltenes could be considered to be the soluble fractions of kerogens in the crude oil reservoirs is taken into consideration, the highly polydispersed properties of asphaltenes are reasonable, and then they should be constituted by the small ones (e.g., molecular weights of well below 1000) up to the very big ones (with Mw values maybe as large as tens of thousands).[1] For example, from different crude oils, the molecular weight

* Author to whom correspondence should be addressed. Fax: +86-20-85 29 07 06. E-mail: zw_liao@hotmail.com.
‡ Laboratoire des Fluides Complexes.
§ State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences.
‖ TOTAL S.A., CSTJF.-
⊥ Laboratoire de Chimie Théorique et Physico-Chimie Moléculaire.
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of asphaltenes has been reported ranging from Mw = 1000 to Mw > 5000.[8]

It has been well-known that, even at a very low concentration, the asphaltenes exist as aggregates, even in a good solvent such as toluene.[1,9–11] In the toluene solution, with a very low concentration of asphaltenes (tens of parts per million (ppm)), they still exist as aggregates,[9,10] and these types of aggregates seem to behave as stable independent entities.[10] This is possibly due to the strong intermolecular forces inside asphaltene aggregates, because strong specific forces such as hydrogen bonding drive the aggregation, whereas weaker nonspecific dispersion forces determine asphaltene precipitation.[9,12,13] The molecular structure of asphaltene is governed by the balance between the propensity of fused aromatic ring systems to stack via π-bonding versus the steric disruption of stacking due to alkane groups.[11,14–16] These types of polar intermolecular forces (such as hydrogen bonding/π-bonding) could allow the aggregates to have a stable existence in the crude oils or even in the toluene solution.

As mentioned in the Introduction, based on asphaltene structural features such as the polydispersity and the aggregates concepts, the adsorption/occlusion characteristics of asphaltenes should be interesting and important. In turn, the adsorption/occlusion results could also shed some light onto the study of asphaltene structures. In the asphaltene structures, besides the aromatic ring units, an abundance of aliphatic-chain units also exists.[17–19] Asphaltenes have the capacity, because of the presence of long polymethylene bridges, to fold upon themselves into a complex, three-dimensional globular conformer with internal structures.[20,21] This type of structural feature enables asphaltenes to form substantial microporous units,[21,22] and then allow them to adsorb and occlude the other fractions in the crude oil. Because of this type of structural feature, free radical ions[2] (monitored using the zeta potential[23,24]) could steadily exist inside of asphaltenes. The other fractions in crude oils, even such as resins, could penetrate into the asphaltene microporous structures.[22] The asphaltene aggregates are constituted by a well-

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Table 1. Group Compositions of the Crude Oil Samples

sample	SARA Analysis (wt %)			
	saturated hydrocarbon	aromatic hydrocarbon	resin	asphaltene
Con1	39.60	30.70	26.40	3.30
Con2	58.34	27.78	12.98	0.90
Ven1	14.35	41.36	34.79	10.50
Ven2	45.28	30.92	17.00	6.80

packed and insoluble core, which is even impervious to solvents (such as toluene), and by a loose-packed periphery, which keep the aggregates dispersed in solution by allowing solvent penetration.[2,25] Keeping in mind the high polydispersity and the aggregate structural features of asphaltenes, as stated previously, the adsorption and occlusion properties of asphaltenes should be considered as progressing from the loosely adsorption to the close occlusion.

In this work, the deuterated compound n-$C_{20}D_{42}$ was used to simulate the adsorption/occlusion characteristics of asphaltenes in toluene solution. This compound was selected because our previous work has indicated that, among the adsorbed/occluded hydrocarbons inside of asphaltenes, n-$C_{20}H_{42}$ is an abundant compound.[26] The deuterated compound could be easily differentiated from the nondeuterated ones using gas chromatography–mass spectroscopy (GC–MS), and then the n-$C_{20}D_{42}$ is a suitable choice for simulating our experimental work. Also, the oxidative reagents 30% H_2O_2/CH_3COOH were used to release the occluded fractions inside the asphaltene structures. The experimental results have been discussed, and some insights into asphaltene structural features have been presented.

Samples and Experimentals

Samples and Chemicals. In this work, four crude oils were collected from the Congo (Con1 and Con2) and Venezuela (Ven1 and Ven2). Table 1 shows the group compositions (saturated hydrocarbons, aromatic hydrocarbons, resins, and asphaltenes (SARA) analysis) of all the crude oil samples; these results were determined using Iatroscan thin-layer chromatography with a flame ionization detector (TLC–FID). The Congo samples were derived from Type I kerogen, whereas the Venezuela crude oils were derived from Type II kerogen. During the secondary evolving processes of oil reservoirs, Con1 and Ven1 have been subjected to biodegradation, whereas Con2 and Ven2 have not. Sample Ven1 was very viscous; it almost lost its fluidity.

Toluene, n-heptane, and chloroform (high-performance liquid chromatography (HPLC) grade) was obtained from Fluka. The deuterated compound n-$C_{20}D_{42}$ was obtained from CDN Isotopes Company, Canada (99.22%-d_{42} and 98.7% purity). SiO_2 was obtained from Fluka (35–70 mesh), and Al_2O_3 was obtained from Aldrich (99% purity, 100 mesh). SiO_2/Al_2O_3 was used for column chromatography and was extracted by chloroform prior to use. CH_3COOH ($\geq$99.7% purity) and 30% H_2O_2 (each from Aldrich) also were used.

Preparation of Asphaltenes. The preparation method of asphaltenes has been described in our previous report.[26] In short, a 1:1 (v/v) mixture of crude oil/toluene was precipitated by n-heptane. The obtained asphaltene solids appear brittle and have a metallic luster for all the four samples. The asphaltenes obtained in this work were called Asphaltene-0.

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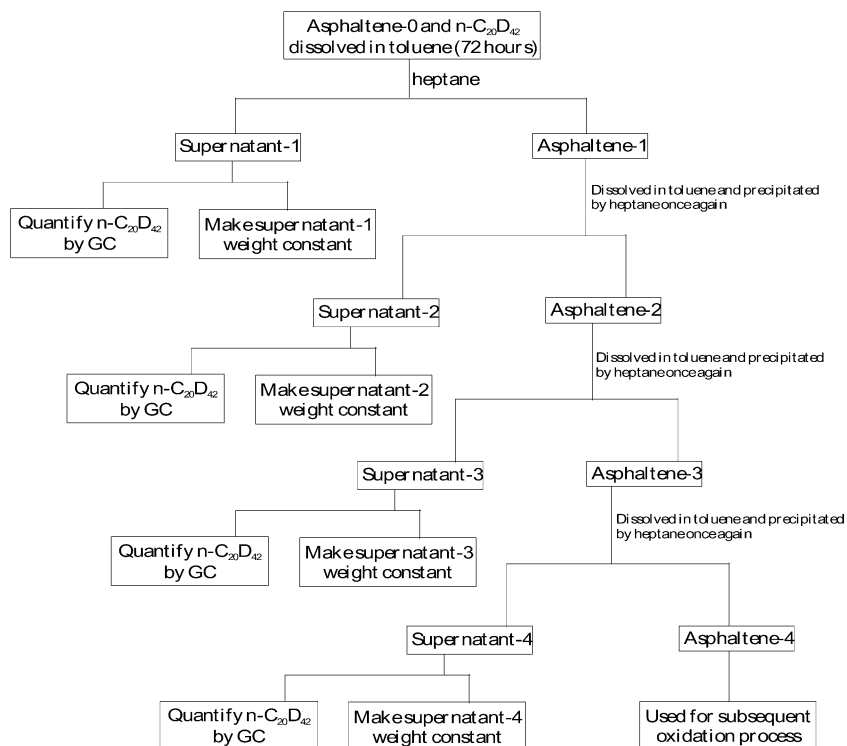(26) Liao, Z.; Geng, A. *Org. Geochem.* **2002**, *33*, 1477–1486.

Figure 1. Flowchart of the simulative experiment.

Simulation of the Adsorption/Occlusion Properties of Asphaltenes in Toluene Solution. Figure 1 shows a flowchart of the simulative experiment. Under room temperature (~25 °C), inside a 250-mL flask, ~200 mg of Asphaltene-0 (see the previous paragraph) and 100 mg of n-$C_{20}D_{42}$ were dissolved into 20 mL of toluene, stirred for 4 h with a magnetic stirrer, and then put aside for 72 h. Two hundred milliliters of n-heptane was then added into the flask to precipitate the asphaltene once again. The mixture is stirred for 4 h and then put aside for 24 h. After centrifugation, the supernatant (hereafter called Supernatant-1) was concentrated by rotary evaporation, brought to a constant volume of 100 mL by adding toluene, and subjected to quantitative analysis for the n-$C_{20}D_{42}$ by GC. This solution was then rotary-evaporated and brought to a constant weight. The precipitated asphaltene obtained by centrifugation was called Asphaltene-1.

Again, the Asphaltene-1 was dissolved in 10 mL of toluene, stirred for 4 h, and then put aside for 72 h. One hundred fifty milliliters of n-heptane was added into this mixture, to precipitate the asphaltene. After centrifugation, the supernatant (hereafter called Supernatant-2) was concentrated by rotary evaporation and brought to a constant volume of 50 mL by adding toluene, and its concentration of n-$C_{20}D_{42}$ determined by GC. Supernatant-2 was then evaporated and brought to a constant weight. The re-obtained asphaltene was called Asphaltene-2. The aforementioned procedure was repeated two more times, and then the concentration of n-$C_{20}D_{42}$ in Supernatant-3 and Supernatant-4 were obtained by GC. Finally, Asphaltene-4 was obtained, which was subsequently subjected to chemical degradation by oxidative reagents.

To measure the marked compound n-$C_{20}D_{42}$ quantitatively from the supernatant liquid, the standard curve of GC intensity versus n-$C_{20}D_{42}$ concentration has been made. Then, seven solutions with different concentrations of n-$C_{20}D_{42}$ in heptane have been prepared, and the GC results indicate that the correlation between GC intensity and n-$C_{20}D_{42}$ concentration is good (Figure 2).

Oxidation of Asphaltene-4. The choice of 30% H_2O_2/CH_3COOH as the oxidative system has been detailed in a previous paper.[26] Basically, this method can guarantee that any hydrocarbons, obtained from the oxidation products of asphalt-
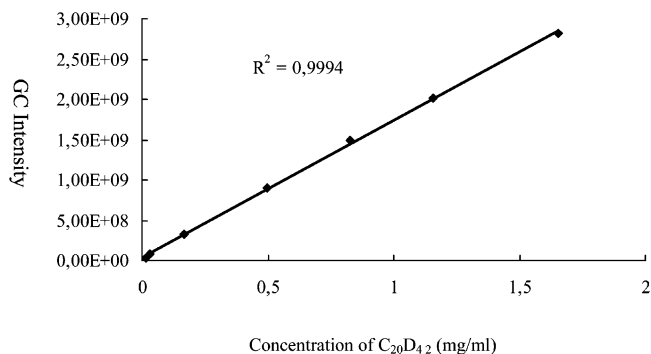

Figure 2. Standard curve for gas chromatography (GC) intensity versus concentration of $C_{20}D_{42}$.
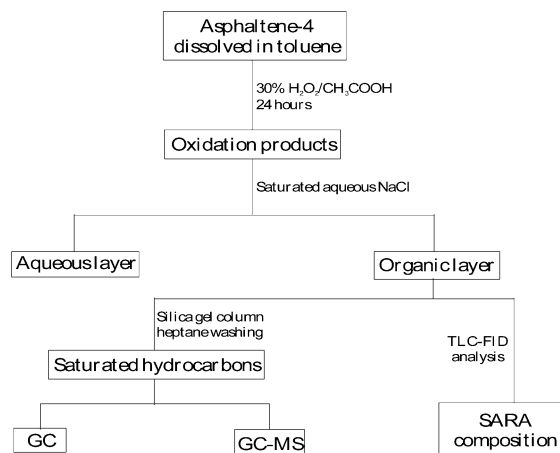

Figure 3. Flowchart of the oxidation for Asphaltene 4.

enes, should belong to the occluded compounds inside asphaltene structures, but not the segments chemically bonded to the asphaltene molecule. This method then allows direct study of the occluded compounds.

Table 2. n-$C_{20}D_{42}$ and the Other Fractions from the Supernatants[a]

	Amount (mg)				amount of total extracts (mg)	initial amount of n-$C_{20}D_{42}$ (mg)	loss of n-$C_{20}D_{42}$ (mg)
sample	Supernatant 1	Supernatant 2	Supernatant 3	Supernatant 4			
Con1	124.25 (53.35)	2.48 (11.02)	0.39 (3.61)	0.02 (1.38)	127.14 (69.36)	128.1	1.0
Con2	111.24 (71.16)	1.90 (9.6)	0.34 (6.66)	0.02 (3.48)	113.5 (90.9)	114.6	1.1
Ven1	112.08 (22.1)	2.39 (4.1)	0.08 (1.0)	0.02 (0.5)	114.57 (27.7)	116.1	1.5
Ven2	119.15 (57.64)	2.52 (6.2)	0.12 (2.8)	0.02 (0.5)	121.81 (67.14)	122.6	0.8

[a] The data without parentheses represent the amount of n-$C_{20}D_{42}$ and the data within parentheses represent the amount of other fractions (maybe the highly soluble asphaltenes in toluene (HSA) fractions) from the supernatants.

Figure 3 shows the oxidation processes for Asphaltene-4. Twenty milliliters of toluene was used to transfer the Asphaltene-4 into a 250-mL flask. Four milliliters of 30% H_2O_2 was mixed with 15 mL of CH_3COOH in a 50-mL beaker, and the oxidative reagent was then slowly transferred into the flask containing the Asphaltene-4. The reactant liquids were stirred during this operation. The reaction was conducted at ambient temperature (at ~25°C) and under agitation for 24 h. At the end of the reaction, the oxidation products were transferred into a 250-mL separatory funnel, using another 50 mL of toluene, into which 40 mL of saturated aqueous NaCl was added. The organic layer was collected and dried using Na_2SO_4. Finally, the organic phase was condensed by rotary evaporation and brought to constant weight. The obtained product was subsequently used to analyze its SARA composition by TLC−FID. Also, from the oxidation product, the nC_7-soluble fractions were further separated using SiO_2/Al_2O_3 column chromatography. The saturated hydrocarbons fraction was washed down by n-heptane, which was subjected afterward to GC and GC−MS analyses.

Elemental Analysis. The carbon, hydrogen, and nitrogen contents were obtained by combustion at 1050 °C on a Nitromatic 500 analyzer. The sulfur content was measured by combustion at 1320 °C on a sulfur coulometric analyzer.

The oxygen content was determined by a coulometric analyzer. At 1120 °C, through reaction with amorphous carbon, the oxygen was initially transformed to CO, and then, with CuO, transformed to CO_2, the content of which was determined by a coulometric analysis method.

GC and GC−MS Analyses. GC−FID analyses were performed using a Hewlett−Packard model HP6890 apparatus with a split/splitless injector and an HP Ultra-5 fused silica column (30 m × 0.32 mm × 0.25 μm). Helium was used as the carrier gas (2.0 mL/min). The oven temperature was initially set at 80 °C for 4 min and programmed to 290 °C at a rate of 2 °C/min, then isothermally held for 30 min. Full-scan GC−MS was performed using a Hewlett−Packard model HP6890 gas chromatograph combined with an HP6890 mass-selective detector. GC was performed under conditions that were the same as those for GC−FID, and the MS was operated at an ionization energy of 70 eV and a source temperature of 155 °C, with an electron multiplier voltage of 1765 V and a mass range of 19−500 amu.

Results and Discussion

Results from the n-$C_{20}D_{42}$ Simulation Experiment. Table 2 shows the results from the simulation experiment. From the supernatants, besides the marked compound n-$C_{20}D_{42}$, the other fractions perhaps represent the more-soluble asphaltenes and/or the coprecipitated compounds. Here, these fractions are simply called the HSA compounds (highly soluble asphaltenes in toluene). Most of the n-$C_{20}D_{42}$ has been extracted from Supernatant-1, whereas a substantial portion of it has also been measured from Supernatant-2, Supernatant-3, and Supernatant-4. The marked compound n-$C_{20}D_{42}$ from Supernatant-2, Supernatant-3, and Supernatant-4 could represent the adsorbed ones during the first step

Table 3. Weight Percentage of Adsorbed n-$C_{20}D_{42}$ in the Asphaltene Structures and the Highly Soluble Asphaltenes in Toluene (HSA) Fractions from the Supernatants, Based on the Initial Asphaltene Mass

component	Con1	Con2	Ven1	Ven2
n-$C_{20}D_{42}$[a]	1.30	1.04	1.10	0.95
HSA[b]	31.24	42.06	12.34	23.98

[a] n-$C_{20}D_{42}$ from the Supernatants 2, 3, and 4. [b] HSA denotes the highly soluble asphaltenes in the toluene, and, here, it indicates, besides the n-$C_{20}D_{42}$, all the other fractions extracted from all the supernatants.

Table 4. Results of the Elemental Analyses of the n-C_7 Precipitated Asphaltenes

	Content (wt %)					
sample	carbon	hydrogen	nitrogen	oxygen	sulfur	total
Con1	84.48	8.45	1.56	2.45	2.86	99.80
Con2	86.35	11.10	0.99	0.84	0.26	99.54
Ven1	80.60	7.90	2.04	1.86	5.65	98.05
Ven2	87.30	7.17	1.62	1.07	2.37	99.53

of the simulation experiments, which have been subsequently released into the supernatants. This result suggests that some of the n-$C_{20}D_{42}$ has been adsorbed by asphaltene structures but not occluded into the structures, because it has been released during the subsequent experimental processes. From Supernatant-4, only a trace amount of n-$C_{20}D_{42}$ has been measured (see Table 2). Therefore, the Asphaltene-4 has been subjected to the oxidation handling, to investigate the occlusion characteristics of asphaltenes, which will be discussed in the following sections. During all the simulation experimental processes, the loss of n-$C_{20}D_{42}$ is ~1 mg, which is in a reasonable scope.

Similarly, Table 2 shows that most of the HSA fraction has been extracted from Supernatant-1, and only a slight HSA fraction was observed from Supernatant-4. Based on the initial asphaltene weight, Table 3 shows the weight percentage of n-$C_{20}D_{42}$ adsorbed in asphaltene structures, and the HSA fraction from the supernatants. Compared to the asphaltenes from normal oils (Con2 and Ven2), those from the biodegraded oils (Con1 and Ven1) could adsorb more n-$C_{20}D_{42}$. However, with respect to the HSA fraction, the asphaltenes from the normal oils could release significantly more compounds than those from the biodegraded oils. This is possible because, among the asphaltenes from the normal oils, there are more of the smaller ones, whereas among the asphaltenes from the biodegraded oils, there are more of the bigger ones. Therefore, asphaltenes from the normal oils could release more compounds as the HSA fraction but adsorb less of n-$C_{20}D_{42}$, compared to those from the biodegraded oils.

The elemental composition of asphaltenes is indicated in Table 4. The asphaltenes (Con1 and Ven1) from biodegraded oils have a much higher content of het-

Table 5. Weight Percentage of the Occluded Saturated Hydrocarbons Inside of Asphaltene Structures, Based on the Initial Asphaltene Mass

component	close occluded saturated hydrocarbons (wt %)
Con1	0.62
Con2	0.72
Ven1	0.34
Ven2	0.71

eroatoms (N, O, and S), and then maybe have a better ability for adsorption and less solubility in toluene. This also could account for the results in Table 3.

Hydrocarbons from the Oxidation Products of Asphaltene-4. As mentioned from the previous section, hydrocarbons from the oxidation products of Asphaltene-4 should represent the occluded compounds, but not those cracked from the molecule through bond cleavage.[26] Among the oxidation products, no n-$C_{20}D_{42}$ has been detected anymore, but some of the other saturated hydrocarbons have been observed. For the four samples studied in this work, based on the initial asphaltene weight, the weight percentage of the occluded saturated hydrocarbons inside asphaltene structures is 0.34%–0.72% (Table 5). Under the simulation experimental conditions, these saturated hydrocarbons cannot be exchanged into the supernatants, and the marked compound n-$C_{20}D_{42}$ cannot be inserted into the asphaltene structures as an occluded fraction either. In other words, these occluded hydrocarbons have been protected fairly well by asphaltene structures, and even in the toluene solution, they cannot be released into the bulk phase.

Some Information from the GC–MS Analyses. The details concerning the geochemical aspects of this work will be discussed elsewhere.[27] Here, we just take one sample—Con2, for example—to determine what type of information could be obtained from the GC–MS analyses, with respect to the adsorption/occlusion characteristics of asphaltenes. Figure 4 shows the GC chromatograms of saturated hydrocarbons for Con2-S (directly from the maltene), Con2-1 (from Supernatant-1), and Con2-D-S (from the oxidation products of asphaltene-4). From Supernatant-1 of the Con2 sample, besides the marked compound n-$C_{20}D_{42}$, some other saturated hydrocarbons have also been detected by GC–MS (Con2-1 in Figure 4). However, from Supernatant-2, Supernatant-3, and Supernatant-4, no such saturated hydrocarbons have been observed anymore. Hydrocarbons from Con2-1 may represent the coprecipitated and/or adsorbed compounds from the crude oil, which have been released into the toluene solution during the first step of the simulation experiment.

The three GC chromatograms in Figure 4 are distinctly different from each other. Con2-S has a light bimodal distribution for n-alkanes, with Pr/Ph > 1, whereas Con2-D-S shows a distinct bimodal distribution for n-alkanes, with Pr/Ph < 1, and also there are more abundant of mid-methyl alkanes in Con2-D-S. This is because Con2-S is from the maltene, which has been subjected to the secondary alteration processes occurred in the reservoir oil, whereas Con2-D-S belongs to the occluded fraction inside asphaltene structures, which

has been well-protected from the secondary alteration. This fraction could be considered as the original oil and, therefore, has a special meaning in the aspect of organic geochemistry.[26–29] Con2-1 just shows the distribution for n-alkanes, and the concentration of other types of saturated hydrocarbons may be too low to be measured by GC–MS.

The saturated hydrocarbons occluded inside asphaltene structures could be up to C_{40} (Con2-D-S in Figure 4), and their weight could be >0.5%, based on the initial asphaltene weight. These results indicate that, in the asphaltene structures, there exists an abundance of microporous structural units, which should be even impervious to solvents such as toluene.[2,25] These types of structural units could stably exist in the crude oil system, because the GC–MS results have indicated that the distribution of the occluded hydrocarbons (Con2-D-S) is characteristically different from those of Con2-S and Con2-1, because they have been little affected by the secondary alteration processes occurred in the oil reservoir. However, the hydrocarbons from Supernatant-1 of the Con2 sample have been affected by the secondary evolving processes. In the crude oil system, these hydrocarbons belong to the adsorbed ones by the asphaltene structures and could be exchanged with the bulk maltene (and, in the simulation experiment, could be exchanged with the marked compound n-$C_{20}D_{42}$ from the toluene solution), at least to a certain extent; therefore, the distribution of Con2-1 in Figure 4 is distinctly different from those of both Con2-S and Con2-D-S.

Some Structural Features of Asphaltene Aggregates. In the toluene solution, results from the simulation experiments indicate that much of the HSA fractions have been released into the solution, which suggests the highly polydispersed distribution properties of asphaltenes, and they should be constituted from the small ones to the big ones, probably with a wide variability.[1,2] In the simulation experiment, some of n-$C_{20}D_{42}$ has been adsorbed by asphaltene structures, which has been subsequently released into Supernatant-2, Supernatant-3, and Supernatant-4. This type of adsorption should occur at the periphery of asphaltene aggregates, and these asphaltene aggregates should be loosely packed; therefore, the adsorbed compounds are liable to be released. However, from the oxidation products of Asphaltene-4, no n-$C_{20}D_{42}$ was observed anymore, but some other saturated hydrocarbons have been detected. These saturated hydrocarbons should belong to the occluded fraction inside asphaltene structures and probably have been derived from the original oil when asphaltenes were generated from kerogen.[27] The experimental results indicate that an abundance of microporous structural units exists in asphaltenes, which are still stable in toluene solution. If the asphaltenes are large enough, this type of occlusion could occur at the molecular level; nevertheless, maybe it just occurs inside asphaltene aggregates. If this is the case, these aggregates should stably exist in toluene solution, maybe as the independent entities,[10] and then the occluded compounds inside these entities have been

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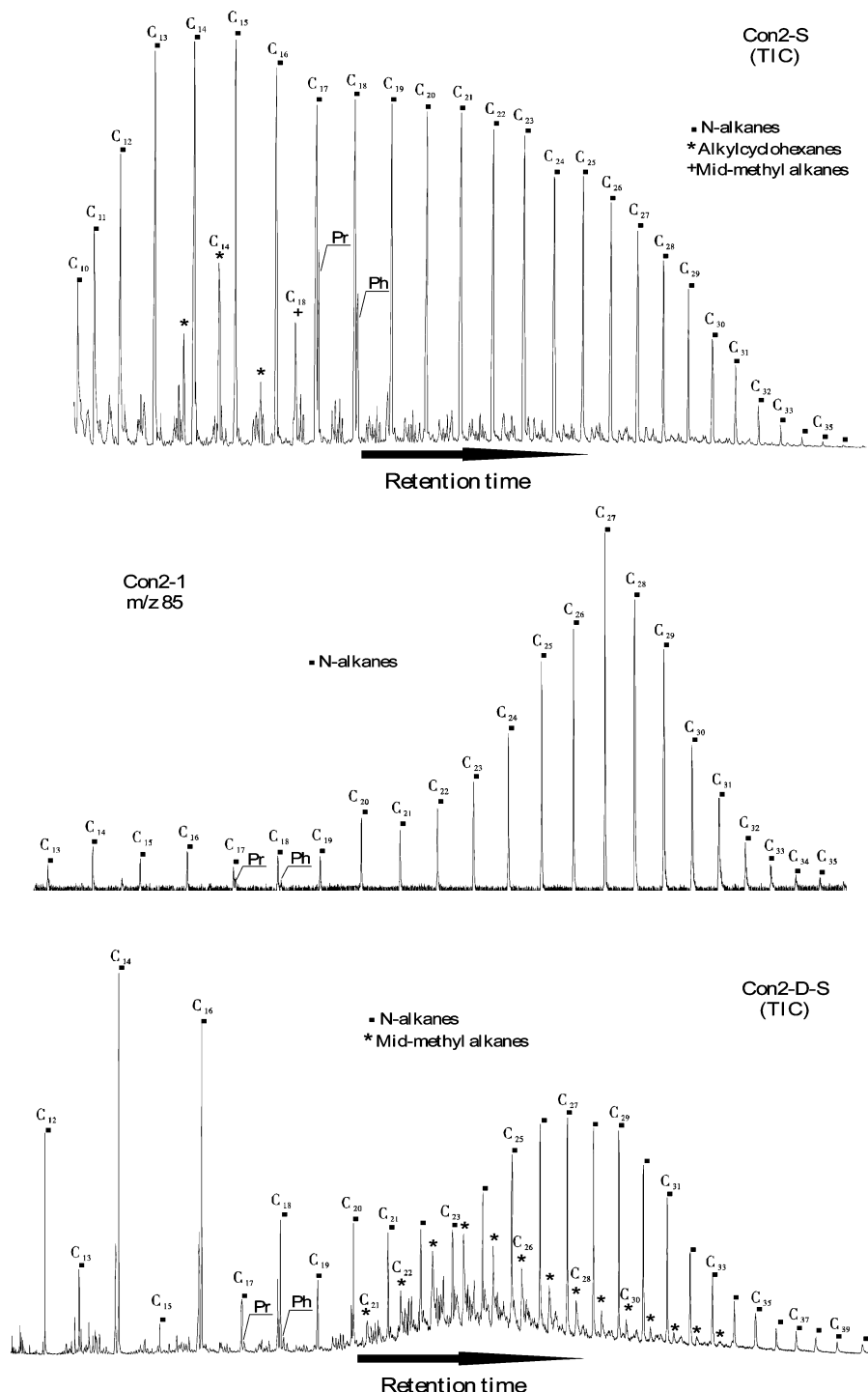
Figure 4. Chromatograms for Con2-S (directly from the maltene), Con2-1 (from Supernatant 1), and Con2-D-S (from the oxidized products of Asphaltene-4).

protected very well, without being released into the bulk toluene solution. Recently, small-angle neutron scattering (SANS) has been used to examine the various topological features of asphaltenes in different solvents.[30] Asphaltene aggregates were observed to exist in the form of a prolate ellipsoid at a low temperature of 25 °C and became a compact sphere with a radius size of ~25 Å at 350 °C. This finding indicates that asphaltene aggregates should exist in an irregular three-dimensional structural form,[31] and then inside

these aggregates, the adsorption/occlusion could be steadily occurring.

The previously stated structural features of asphaltenes could be extrapolated into the crude oil system. For example, under the conditions of an oil reservoir, asphaltene aggregates should stably exist as one of the basic structural units, and then the occluded fraction has been well-protected from the secondary alteration processes occurred in the oil reservoir system. The outskirts of asphaltene aggregates could adsorb the other fractions from crude oil; however, this type of fraction has not been well-protected from the secondary alteration processes, and they could be exchanged with

(30) Tanaka, R.; Hunt, J. E.; Winans, R. E.; Thiyagarajan, P.; Sato, S.; Takanohashi, T. *Energy Fuels* **2003**, *17*, 127−134.
(31) Gray, M. R. *Energy Fuels* **2003**, *17*, 1566−1569.

compounds from the bulk crude oil phase, at least to a certain extent.[27] In this work, results from the GC−MS analyses have verified such structural features of asphaltenes in crude oils well. For example, the saturated hydrocarbons from the oxidation products of Asphaltene-4 should originate from the occluded fractions, which have been protected very well and could be considered as the original oil, whereas those from Supernatant-1 of the Con2 sample should belong to the adsorbed fraction, which has been subjected to some alteration occurred in the crude oil system. Therefore, the three chromatograms in Figure 4 are characteristically different from each other. Recently, the results from a molecular mechanics/molecular dynamics (MM/MD) simulation have indicated that asphaltene structures aggregated through several noncovalent interactions (aromatic−aromatic, electrostatic, and van der Waals forces) are the most stable,[32] which are still stable, even at a high temperature up to 523 K. Therefore, these types of structural units could stably exist, even under the conditions of a crude oil system.

Conclusions

Results from the simulation experiments indicate that an abundance of microporous structural units exists inside asphaltene structures, which allow asphaltenes to adsorbe/occlude the other fractions. The occluded compounds have been protected well by the asphaltene structures and could not be exchanged with the bulk phase. The occlusion should occur inside the core of asphaltene aggregates, which could stably exist as the independent structural units, even in the toluene solution, while the adsorption occurs at the outskirts of asphaltene aggregates. Therefore, the adsorbed compounds could be exchanged with the bulk phase, at least to a certain degree.

In association with the results from gas chromatography−mass spectroscopy (GC−MS) analyses, the asphaltene structural features stated previously could be well-extrapolated into the crude oil system. Under the conditions of a crude oil reservoir, the occluded compounds have been well-protected from the secondary alteration processes that occurred in the oil reservoir and could be considered to be the original oil, whereas the adsorbed compounds have been affected by the secondary evolving processes. The asphaltene aggregates should belong to one of the basic structural units in the crude oil system.

(32) Takanohashi, T.; Sato, S.; Saito, I.; Tanaka, R. *Energy Fuels* **2003**, *17*, 135−139.