

Effect of *n*-Alkanes on Asphaltene Structuring in Petroleum Oils

Christian Stachowiak,[†] Jean-Romain Viguié,[‡] Jean-Pierre E. Grolier,^{*,†} and Marek Rogalski^{*,‡}

Laboratoire de Thermodynamique des Solutions et des Polymères UMR 6003, Université Blaise Pascal, 24, Avenue des Landais, 63177 Aubière Cedex, France, and Laboratoire de Chimie et Applications, Université de Metz, 1, Boulevard Arago, CP 87811, 57078 Metz Cedex 3, France

Received November 23, 2004. In Final Form: March 10, 2005

The interactions between asphaltenes and short- to medium-chain *n*-alkanes were studied using titration microcalorimetry and inverse chromatography. The exothermic heat effects observed upon mixing of asphaltenes and *n*-alkanes were interpreted in terms of assembling of the two types of compounds into mixed structures. We show that the energy of the interactions between *n*-alkanes and the asphaltene hydrocarbon chains is close to the energy of the interactions between the asphaltene chains. We propose that the latter interactions are responsible for the formation of the asphaltene aggregates and are the driving force of the aggregate assembly into higher structures.

1. Introduction

The asphaltene fraction of the petroleum crude oil is defined relative to its solubility in hydrocarbon solvents. Asphaltenes are the least soluble fraction in petroleum that precipitates in light alkanes such as *n*-pentane, *n*-hexane, or *n*-heptane. While this definition allows for identifying the fraction containing a wide variety of heaviest and most polar molecules of the crude oil, it reveals little about the asphaltene properties. A better understanding of asphaltene properties, important for technological applications, may be obtained by investigating their interactions with alkanes. The latter solvents allow isolating asphaltenes from the crude oil. The molecular weight of asphaltene monomers, as determined with experiments carried out in diluted solutions,^{1–3} is estimated to be around 700–1000 g/mol. Asphaltene monomers consist of 2–6 polynuclear aromatics and contain small amounts of sulfur, nitrogen, and oxygen, as well as trace amounts of nickel and vanadium. The aromatic core is surrounded by alkyl side chains of an average length of 5–6 carbon atoms.⁴ Such molecular structures favor stacking of polyaromatic moieties. This effect may induce formation of discotic liquid crystals such as those encountered in pitch mesophases.⁵ However, in organic solvents and in crude petroleum oils as well, the entropic penalty lowers the number of stacked asphaltene monomers. Thus, the asphaltene aggregates present in crude petroleum are formed with a limited number of monomers.^{6–12}

Estimation of the shape and size of asphaltene aggregates using small-angle neutron scattering (SANS) measurements in good solvents, such as, e.g., toluene, were reported recently. In diluted solutions of asphaltenes, thin disks,^{13,14} prolate ellipsoids, and spheres¹⁵ were observed depending on the solvent used, the temperature, and the nature of asphaltenes. At higher concentrations, asphaltenes self-assemble into flat sheets resembling those formed with classical surfactants¹⁶ and certain small aromatic molecules¹⁷ in water. A high propensity of the sheet structures to bending and twisting leads to formation of vesicles¹⁶ and coils.¹⁷ It was proposed recently that analogous phenomena take place in crude petroleum-containing asphaltenes.¹⁸ While the hypothesis of spontaneous formation of asphaltene vesicles is consistent with physical properties of petroleum fluids,¹⁸ the mechanism of vesicle formation is not known.

Some insights into the behavior of asphaltenes in different solvents were obtained recently from calorimetric titration.^{19,20} The conspicuous break points observed in the heats evolved upon the dilution of asphaltene solutions were ascribed to asphaltene micellization.²⁰ However, since the asphaltenes do not exist as monomers even in very diluted solutions,¹⁸ the effects observed could correspond rather to the aggregation of dimers and trimers into larger aggregates. While these large aggregates are stable in good solvents, such as toluene and pyridine, they form clusters and flocs in poor solvents, such as *n*-alkanes.⁶

We propose that the aggregation of asphaltenes could be considered as a phase transition process and, consequently, described quantitatively using phase-transition thermodynamics. Indeed, formation of large asphaltene aggregates may be assimilated to liquid–liquid crystal or liquid–gel first-order phase transitions, with the asphaltene-rich phase forming a dispersion. While the dispersed

* Authors to whom correspondence should be addressed. E-mail: rogalski@sciences.univ-metz.fr (M.R.); j-pierre.grolier@univ-bpclermont.fr (J.-P.E.G.).

[†] Université Blaise Pascal.

[‡] Université de Metz.

- (1) Groenzin, H.; Mullins, O. C. *J. Phys. Chem. A* **1999**, *103*, 11237.
- (2) Groenzin, H.; Mullins, O. C. *Energy Fuels* **2000**, *14*, 677.
- (3) Boduszynski, M. M. *Energy Fuels* **1988**, *2*, 597.
- (4) Speight, J. G. *J. Pet. Sci. Eng.* **1999**, *22*, 3.
- (5) Hurt, R. H.; Hu, Y. *Carbon* **1999**, *37*, 281.
- (6) Rogel, E.; Leon, O.; Torres, G.; Espidel, J. *Fuel* **2000**, *79*, 1389.
- (7) Andersen, S. I.; Speight, J. G. *Fuel* **1993**, *72*, 1343.
- (8) Sheu, E. Y.; Tar, M. M. D.; Storm, D. A.; DeCanio, S. J. *Fuel* **1992**, *71*, 299.
- (9) Mohamed, R. S.; Ramos, A. C. S.; Loh, W. *Energy Fuels* **1999**, *323*.
- (10) Andersen, S. I.; Christensen, S. D. *Energy Fuels* **2000**, *14*, 38.
- (11) Storm, D. A.; Barresi, R. J.; DeCanio, S. J. *Fuel* **1991**, *70*, 779.
- (12) Murgich, J.; Rodriguez, M. J.; Aray, Y. *Energy Fuels* **1996**, *10*, 68.

- (13) Herzog, P.; Tchoubar, D.; Espinat, D. *Fuel* **1988**, *67*, 245.
- (14) Ravey, J. C.; Ducouret, G.; Espinat, D. *Fuel* **1988**, *67*, 1560.
- (15) Tanaka, R.; Hunt, J. E.; Winans, R. E.; Thiagarajan, P.; Sato, S.; Takanohashi, T. *Energy Fuels* **2003**, *17*, 127.
- (16) Israelachvili, J. N. In *Intermolecular and Surface Forces*, 2nd ed.; Academic Press: San Diego, 1994.
- (17) Rogalski, E.; Rogalski, M.; Krzywicki-Gulik, T.; Chipot, C. *Proc. Natl. Acad. Sci.* **1996**, *96*, 6577.
- (18) Porte, G.; Zhou, H.; Lazzeri, V. *Langmuir* **2003**, *19*, 40.
- (19) Andersen, S. I.; Birdi, K. S. *J. Colloid Interface Sci.* **1991**, *142*, 497.
- (20) Andersen, S. I.; Christensen, S. D. *Energy Fuels* **2000**, *14*, 38.

phase is stable in good solvents, it is unstable in the {crude oil + *n*-alkane} systems and gives rise to the formation of a bulk phase of flocculated asphaltenes. Recent NMR²¹ and SANS^{22,23} results obtained for asphaltene concentrations close to the flocculation onset demonstrate that the asphaltene aggregation can be considered as a phase transition. Indeed, both techniques revealed local inhomogeneities in the macroscopically homogeneous mixture, characteristic for approaching a phase separation.²⁴ One more argument for the phase transition-based description of the asphaltene flocculation is the successful modeling of this phenomenon using Hildebrand²⁵ and Flory–Huggins theory.^{26–28}

For a better understanding of the onset of the asphaltene flocculation, the properties of the asphaltene-rich phase should be analyzed. According to the recent molecular dynamic calculations²¹ and SANS results,^{29–31} the aggregates of asphaltenes hold together by a set of cooperative, noncovalent polar, π – π and van der Waals interactions. It seems that the van der Waals interactions between the aliphatic lateral chains of asphaltenes are particularly important for the aggregate formation.

In the present work, we have elucidated the mechanism by which the asphaltene aggregates are formed in the presence of *n*-alkanes, leading to flocculation. The exothermic heat effect observed upon mixing *n*-heptane with a crude oil^{32,33} was interpreted in terms of the decrease of the mobility of *n*-alkane molecules engaged in the interactions with the asphaltene alkyl chains. The latter effect was used to probe the interactions between the alkyl chains of the asphaltenes. On the basis of the results obtained, we propose that the van der Waals interactions, as well as induced conformational changes and molecular orientations, between adjacent chains of both *n*-alkanes and asphaltenes are the main driving force responsible for the self-assembling of asphaltenes into flat sheets.

2. Experimental Section

2.1. Materials. Crude oils 1 and 2 (for composition see Table 1) were used in calorimetric experiments. The factor of stability with respect to flocculation of these two oils was calculated as (aromatics + resins)/(saturated + asphaltenes). Oil 2, having a higher content of the asphaltenes, has a higher stability factor compared to oil 1.

De-asphalted oils were prepared by precipitating asphaltenes with five volumes of *n*-pentane per one volume of the crude oil. The asphaltenes were filtered off, and the *n*-pentane was evaporated at 40 °C. As the crude oils used in this study were gas-free (they were submitted to the evaporation procedure at 40 °C), it was assumed that the de-asphaltation did not change significantly their composition.

The asphaltenes used in chromatographic experiments were obtained by precipitation from oil 2 with 40 mL of *n*-heptane per 1 g of oil. After 16 h, the asphaltenes were filtered under vacuum on sintered glass and subsequently eluted from the precipitate

Table 1. Compositional Characterization of the Two Crude Oils Studied

fraction analysis (molar %)	crude oil 1	crude oil 2
C1–C5	3.05	2.31
C6–C10	22.13	26.03
C11–C19	31.77	37.88
C20+	43.05	33.78
SARA analysis (weight %)		
saturated	52.3	40.07
aromatics	27.2	30.2
resins	18.4	24.0
asphaltenes	2.0	5.0
C20+	45.2	55.0

with toluene. After evaporation of toluene and drying at 60 °C, the asphaltenes were further washed with *n*-heptane to remove the residual, non-asphaltene components.

2.2. Titration Calorimetry. Calorimetric measurements were performed using the titration microcalorimeter Titrys (Setaram, France).³³ This calorimeter, built according to the Calvet principle, includes two calorimetric cells placed in the calorimetric block and maintained at constant temperature to within ± 0.02 K. The high sensitivity of this device makes it possible to measure heat effects as low as 5 mJ. When a difference of temperature between the measuring and the reference cell is detected, the controlling system generates an electrical signal proportional to the heat effect in the measuring cell. A PC-controlled sample injection system equipped with two syringe pumps permits the introduction into the cells of a precisely known amount of the solvent. Before each measurement, 2 mL of the crude oil and of *n*-alkane were placed in the measuring and in the reference cell, respectively, and the injection syringes were filled with *n*-alkane. All experiments were carried out at $T = 302.93 \pm 0.02$ K. At this temperature, the thermal stability of the system was reached after 4 h. The volume of 0.500 mL of *n*-alkane was progressively injected with the flow rate of 0.250 mL·min^{−1}. The global heat effect of dilution obtained by integration of the calorimetric signal recorded during the injection cycle was used to calculate the enthalpy of mixing per gram of the crude oil.

Crude oils, de-asphalted oils, and mixtures {crude oil + behenic acid} were titrated using *n*-alkanes from *n*-pentane to *n*-tetradecane. Behenic acid, C₂₂H₄₄O₂, was used as a model compound of acid components of crude oils.

2.3. Inverse Gas Chromatography. We have used the gas-phase inverse chromatography to determine infinite dilution activity coefficients of *n*-alkanes dissolved in pure asphaltenes or in mixtures containing asphaltenes. Measurements were carried out using a Shimadzu GC8A chromatograph equipped with a catharometric detector. The stability of the gas mass flow was controlled with an Alborg GFC17 device to within $\pm 0.1\%$. The temperature of the oven was measured with a Pt 100 probe and controlled to within ± 0.1 K. The stainless steel columns (2 mL $\times$ 2 mm i.d.) were packed with the stationary phase prepared by soaking the Chromosorb W HP (0.125–0.14 mm) with 10% (w/w) of the stationary phase. The composition of the chromatographic stationary phases which played the role of solvents were, respectively, as follows. {asphaltenes (30% (w/w)) + C₂₃H₄₅O₂ (70% (w/w))}, {asphaltenes (70% (w/w)) + C₂₃H₄₅O₂ (30% (w/w))} and {asphaltenes (90% (w/w)) + C₂₃H₄₅O₂ (10% (w/w))}. Retention volumes of *n*-alkanes from *n*-heptane up to *n*-tetradecane determined in the temperature range between 340 and 520 K give access to infinite dilution activity coefficient.

The fundamental equation³⁴ that relates chromatographic retention data with the dissolution thermodynamics is as follows

$$K_L = \frac{c_2^L}{c_2} = \frac{V_N}{V_L} \quad (1)$$

where the partition coefficient, K_L , of the solute, 2, between the

(21) Evdokimov, I. N.; Eliseev, N. Y.; Akhmetov, B. R. *Fuel* **2003**, *82*, 817.

(22) Roux, J.-N.; Broseta, D.; Demé, B. *Langmuir* **2001**, *17*, 5085.

(23) Takanoashi, T.; Sato, S.; Saito, I.; Tanaka, R. *Energy Fuels* **2003**, *17*, 135.

(24) Almásy, L.; Scer, L.; Jancsó, G. *Physica B* **2000**, *276–278*, 446.

(25) Hirschberg, A.; de Jong, L. N. J.; Schipper, B. A.; Meijer, J. G. *SPE J.* **1984**, *XX*, 283.

(26) Buckley, J. S.; Hirasaki, G. J.; Liu, Y.; Von Drasek, S.; Wang, X.; Gill, B. S. *Pet. Sci. Technol.* **1998**, *16*, 251.

(27) Buckley, J. S. *Energy Fuels* **1999**, *13*, 328.

(28) Andersen, S. I.; Speight, J. G. *J. Pet. Sci. Eng.* **1999**, *22*, 53.

(29) Herzog, P.; Tchoubar, D.; Espinat, D. *Fuel* **1988**, *67*, 245.

(30) Ravey, J. C.; Ducouret, G.; Espinat, D. *Fuel* **1988**, *67*, 1560.

(31) Fenistein, D.; Barré, L.; Brosseta, D.; Espinat, D.; Livet, A.; Roux, J.-N.; Scarsella, M. *Langmuir* **1998**, *14*, 1013.

(32) Mahmoud, R., Ph.D. Thesis, ENSIC INPL, Nancy, 1999.

(33) Stachowiak, C., Ph.D. Thesis, Université Blaise Pascal, Aubière, 2001.

(34) Conder, J. R.; Young, G. L. *Physicochemical Measurement by Gas Chromatography*; John Wiley and Sons Ltd.: New York, Toronto; 1979.

gas and liquid phase is defined as the ratio of the concentration of the solute in gas, c_2^G and liquid, c_2^L , phases and can be obtained as the ratio of the retention volume, V_N , and the volume of the stationary phase, V_L . Equilibrium thermodynamic properties are usually obtained from the specific retention volume ν_g° , that is characteristic for a particular solute, stationary phase, and carrier gas.

$$\nu_g^\circ = \frac{273V_N}{W_L T} \quad (2)$$

W_L is the mass of the stationary phase (solvent).

The dissolution of the solute in the chromatographic column occurs in infinite dilution conditions. Therefore, eqs 1 and 2 can be combined with an expression that describes the phase equilibrium between the solute in the vector gas at p_2 pressure and its part dissolved in stationary phase that is supposed to be liquid to give the following³⁴

$$f_2^\infty = \frac{273.15R}{M_L \nu_g^\circ p_2^*} \quad (3)$$

with p_2^* being the vapor pressure of pure liquid 2 and M_L the molar mass of the stationary phase that was assumed being 1000 Da. This value is widely accepted in the literature.^{1–3}

The infinite dilution excess enthalpy of n -alkanes was calculated using the dependency in temperature of the activity coefficient:

$$h_2^E = R \frac{\partial \ln f_2^\infty}{\partial (1/T)} \quad (4)$$

The infinite dilution excess entropy was determined using a fundamental thermodynamic relationship:

$$s_2^E = \frac{h_2^E}{T} - R \ln f_2^\infty \quad (5)$$

3. Results and Discussion

Sheetlike asphaltene aggregates present in crude oils assemble into multilayered structures¹⁸ during the precipitation process. Titration calorimetry and inverse chromatography were used to probe the interactions between n -alkanes and, respectively, the dispersed and the precipitated asphaltenes as the two types of aggregates have the same elementary structure¹⁸ and are in the same energetic state, independently of the size.

3.1. Probing of n -Alkane–Asphaltene Interactions via Heat of Mixing Measurements. To get some insight into the nature of the interactions between n -alkanes and asphaltenes present in crude oils, three series of independent calorimetric experiments were performed yielding enthalpies of mixing of { n -alkane + crude oil}, { n -alkane + de-asphalted crude oil}, and { n -alkane + crude oil + behenic acid}.

Enthalpies of mixing obtained with n -hexane, n -heptane, n -octane, and n -hexadecane and crude oils 1 and 2 are given in parts a and b of Figure 1, respectively. The heat effect is strongly endothermic with n -hexane but becomes increasingly exothermic for n -heptane and n -octane. The heat effect for n -hexadecane is close to that obtained for n -octane, indicating that the dependency of enthalpy of mixing with the n -alkane chain length levels off. On the basis of these results, rather unexpected for a homologous series of nonpolar compounds, we conclude that the global heat effect is composed of two opposite contributions, namely an endothermic contribution prevailing with lower n -alkanes, and an exothermic contribution, dominating with n -heptane and higher n -alkanes. Most likely, the endothermic enthalpy of mixing is due to

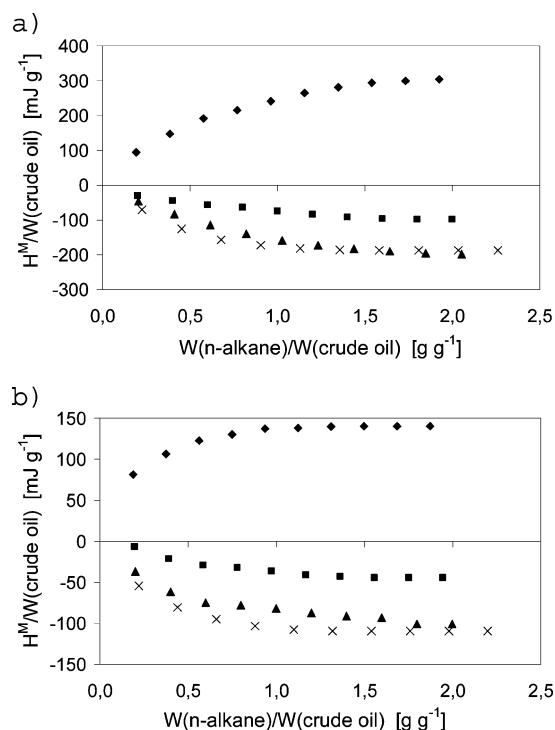


Figure 1. Enthalpy of mixing of (a) crude oil 1 with $\blacklozenge$, n -hexane; $\blacksquare$, n -heptane; $\blacktriangle$, n -octane; and $\times$, n -hexadecane and (b) crude oil 2 with $\blacklozenge$, n -hexane; $\blacksquare$, n -heptane; $\blacktriangle$, n -octane; and $\times$, n -hexadecane.

van der Waals dispersion interactions between the n -alkanes and the crude oil while the exothermic effect would result from physical interactions between long aliphatic chains and strongly organized asphaltene structures. The type of such interactions would result from induced conformational changes on the n -alkane aliphatic chains, as it was observed with n -alkanes in mixture with substituted naphthalene molecules, e.g., 1-chloronaphthalene.³⁵

To elucidate the origin of the heat effects observed on mixing of n -alkanes with crude oil, the enthalpy of mixing of the de-asphalted oils 1 and 2 with n -heptane has been determined. This effect was shown to be endothermic (Figure 2a and b) and of the same order as the enthalpy of mixing of {toluene + n -heptane}³⁶ taken as a model system of van der Waals interactions between the components of crude oils. This result supports the hypothesis that the endothermic part of the heat effect obtained with the crude oil stems from the van der Waals dispersion interactions between the aromatic and saturated hydrocarbons. The fact that the exothermic effect was not observed with n -alkanes lower than n -heptane indicates that it is not directly related either to the asphaltene aggregation, to the flocculation process, or to the n -alkane chain length. This observation allows the conclusion that the exothermic effects can be explained by n -alkane–asphaltene interactions, particularly induced conformational changes of the long-chain n -alkanes by the rigid platelike asphaltene structure. Indeed, recent results of the modeling of the asphaltene structure²³ using molecular dynamics indicate that van der Waals interactions between aliphatic lateral chains of asphaltenes are responsible for the formation of the asphaltene aggregates. On the basis of our results, we propose that only n -alkanes

(35) Grolier, J.-P. E.; Inglese, A.; Roux, A. H.; Wilhelm, E. *Ber. Bunsenges. Phys. Chem.* **1981**, *85*, 768.

(36) Sorai, M.; Saito, K. *Chem. Rec.* **2003**, *3*, 29.

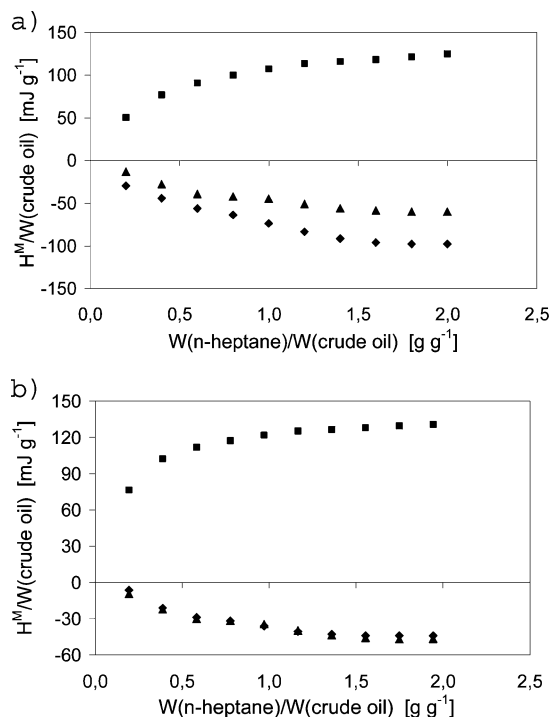


Figure 2. Enthalpy of mixing of *n*-heptane with (a) $\blacklozenge$, crude oil 1; $\blacksquare$, de-asphalted crude oil 1; $\blacktriangle$, crude oil 1 + behenic acid and (b) $\blacklozenge$, crude oil 2; $\blacksquare$, de-asphalted crude oil 2; $\blacktriangle$, crude oil 2 + behenic acid.

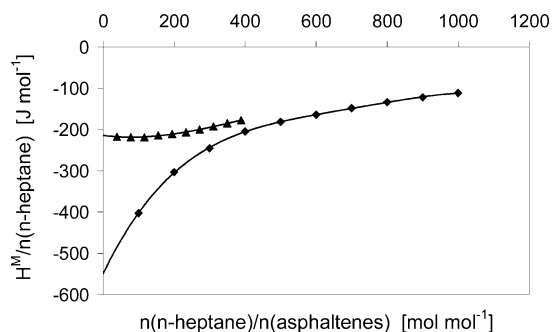


Figure 3. The net exothermic effect per mole of the added *n*-heptane calculated as a difference between the heat effects measured with the crude oil and the corresponding de-asphalted crude oil in function of the molar ratio of *n*-heptane and asphaltenes: $\blacklozenge$, crude oil 1; $\blacktriangle$, crude oil 2.

longer than *n*-hexane can contribute to these interactions through molecular orientation correlation between aliphatic chains in the presence of rigid structures.^{35,37} The resulting loss of the mobility of the *n*-alkanes stuck in the asphaltene aggregates gives rise to the observed exothermic effect. Figure 3 shows the net exothermic effect per gram of the added *n*-heptane calculated as a difference between the heat effect measured with the asphaltene-rich oil and the corresponding asphaltene-free oil. At high concentrations of *n*-heptane, the net heat effect evolves in a similar way for both oils and is nearly independent from the *n*-heptane concentration; its limiting value obtained with oil 2 for the *n*-heptane concentration tending to zero is $-220 \text{ J} \cdot \text{mol}^{-1}$. At low *n*-heptane concentrations, the net heat effect for the oil 1 decreases sharply and attains a limiting value of $-550 \text{ J} \cdot \text{mol}^{-1}$. In other words, at the low *n*-heptane concentrations, the calorimetric experiments reveal the differences between the oil prop-

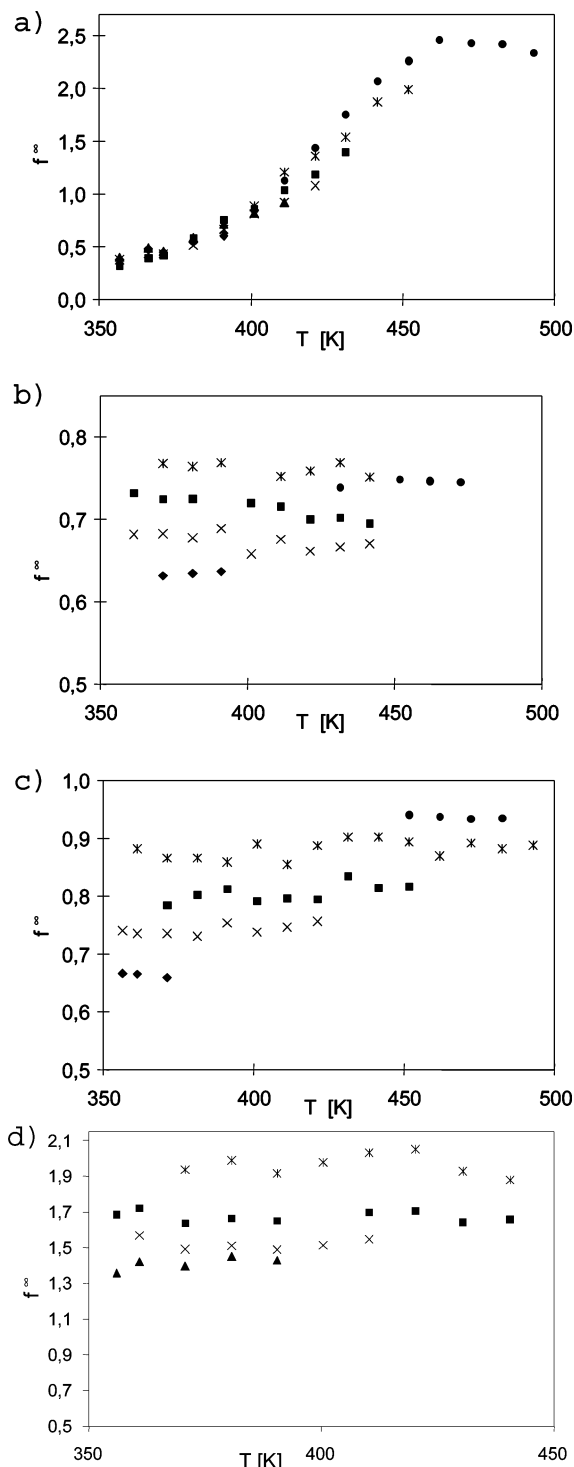


Figure 4. Infinite dilution activity coefficients of $\blacklozenge$, *n*-heptane; $\blacksquare$, *n*-octane; $\blacktriangle$, *n*-nonane; $\times$, *n*-decane; $*$, *n*-dodecane; $\bullet$, *n*-tetradecane dissolved in (a) asphaltenes, (b) 30% $\text{C}_{36}\text{H}_{74}$ + 70% asphaltenes, (c) 70% $\text{C}_{36}\text{H}_{74}$ + 30% asphaltenes, and (d) 10% behenic acid + 90% asphaltenes.

erties via titrating of the *n*-alkane–asphaltene interactions. The overall calorimetric results confirm the hypothesis that small amounts of *n*-alkanes longer than *n*-hexane may be entangled in the asphaltene lateral chains.

To have a better understanding of interactions between asphaltenes and *n*-alkanes, calorimetric experiments were performed with oils 1 and 2 enriched in behenic acid. As mentioned previously, the presence of naphtenic acid in the oil delays the onset of the flocculation of the as-

(37) Tamura, K.; Murakami, S.; Fujihiro, R. *J. Chem. Thermodyn.* **1975**, *7*, 1089.

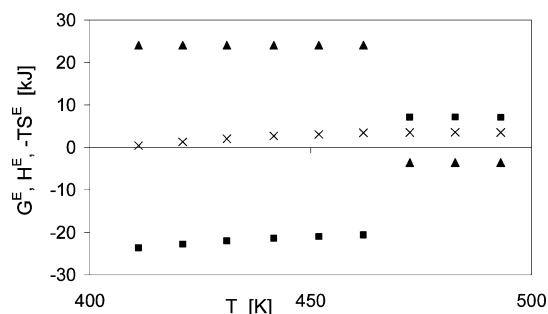


Figure 5. Thermodynamic excess functions at infinite dilution as a function of temperature of *n*-tetradecane dissolved in asphaltene: $\times$, infinite dilution excess Gibbs energy; $\blacksquare$, infinite dilution excess enthalpy; $\blacktriangle$, infinite dilution excess entropy.

phthalenes.³⁸ The calorimetric experiments performed by titrating with *n*-heptane the samples of crude oils containing 20% (w/w) of behenic acid show that the exothermic heat effects in the crude oil 1 are significantly lowered (Figure 2a and b). However, in the case of crude oil 2, the influence of the behenic acid on the heat effect is much smaller. It has to be noticed that oil 2 contains a significantly higher amount of resins compared to oil 1 (Table 1). The results obtained with the two oils indicate that the interactions between the *n*-heptane and the asphaltene aggregates stabilized with the behenic acid in the case of oil 1, or with the resins in the case of oil 2, are hampered. Obviously, the *n*-heptane added to the behenic acid- or resin-rich oils does not interact with the asphaltene, which is shielded with a protective molecular layer. In the absence of such a protective layer, the *n*-heptane could, indeed, interdigitate with the lateral chains of the asphaltene.

3.2. Influence of Temperature on *n*-Alkane–Asphaltene Interactions Probed with Inverse Gas Chromatography Measurements. The inverse chromatography was used to get access to the activity coefficients of *n*-alkanes from *n*-heptane to *n*-tetradecane in solvents containing asphaltene. Partial excess enthalpies and entropies of *n*-alkanes were calculated from the temperature dependence of the activity coefficients.

The fact that the activity coefficients of *n*-alkanes dissolved in asphaltene increase sharply with temperature up to 450 K and level off above this temperature (Figure 4a) implies that the partial excess enthalpy of mixing of *n*-alkanes is negative at low temperatures and becomes close to zero at 450 K. Figure 5 shows changes with temperature of $G_i^{E,\infty}$, $S_i^{E,\infty}$, and $H_i^{E,\infty}$ of *n*-tetradecane dissolved in asphaltene. The highly negative values of both enthalpy and entropy imply the compensation effect and, consequently, indicate that the *n*-alkanes present in the solvent are not liquid. In light of experimental data, the solute in equilibrium is distributed between the gas phase, and the “solid-like state” attained in the asphaltene matrix and noted with index “c”. As this state is unknown for a part, it is more astute to use an unsymmetrical reference system. If the infinitely diluted solute is taken as a reference state and noted $G_2^{\circ,c}$, then, chemical potentials of the solute in equilibrium between stationary phase and vector gas at pressure *p* are written as

$$G_2^{\circ,c} + RT \ln f_2^c x_2^c = G_2^{\circ,v} + RT \ln p_2 \quad (6)$$

where p_2 is the partial pressure of the solute in the mixture, i.e., the pressure of 2-flow in the chromatograph.

(38) Östlund, J. A.; Nydén, M.; Auflem, I. H.; Sjöblom, J. *Energy Fuels* **2003**, *17*, 113.

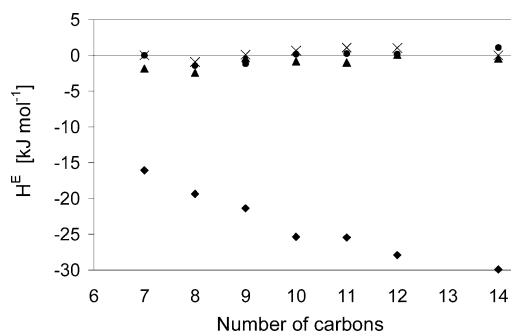


Figure 6. $H_i^{E,\infty}$, infinite dilution excess enthalpy of *n*-alkanes C_nH_{2n+2} at 370 K as a function of *n*. Solution of *n*-alkanes in $\blacklozenge$, asphaltene; $\blacktriangle$, 30% $C_{36}H_{74}$ + 70% asphaltene; $\times$, 70% $C_{36}H_{74}$ + 30% asphaltene; $\bullet$, 10% behenic acid + 90% asphaltene.

In dilute solutions, f_2^c tends to 1, then

$$G_{i,x}^{\circ,c} + RT \ln x_i^c = G_i^{\circ,v} + RT \ln p_2 \quad (7)$$

If the solute dissolved in asphaltene was in the liquid state as was initially supposed then eq 7 is written as

$$G_2^{\circ,v} + RT \ln p_2 = G_2^{\circ,1} + RT \ln(p_2/p_2^*) \quad (8)$$

Using eqs 7 and 3 gives

$$G_{2,x}^{\circ,c} + RT \ln(x/y) = G_2^{\circ,c} + RT \ln[(\nu_g^0 p M_L)/(273.15R)] = G_2^{\circ,v} + RT \ln p \quad (9)$$

$$G_2^{\circ,1} + RT \ln(p/p_2^*) = G_2^{\circ,v} + RT \ln p \quad (10)$$

Subtracting eq 10 from eq 9 gives an expression identical to eq 3.

$$G_2^{\circ,c} - G_2^{\circ,1} = RT \ln[(273.15R)/(\nu_g^0 p_2^* M_L)] \quad (11)$$

This result indicates that the chromatographic retention data may be used to have a direct insight into the physical state of the solute dissolved in the stationary phase.

The changes of activity coefficients with increasing temperature are due to the difference of entropy between two reference states:

$$\Delta S_i = \partial(G_{2,x}^{\circ,c} - G_2^{\circ,1})/\partial T \quad (12)$$

The excess enthalpy of *n*-alkanes, $H_i^{E,\infty}$, calculated using chromatographic data was compared with their enthalpies of fusion and of adsorption on graphite³⁹ for a chosen temperature of 370 K (Figure 7). It can be seen that the values of the $H_i^{E,\infty}$ are close to the enthalpy of fusion and follow the same characteristic pattern for the odd versus even carbon number. It can be concluded accordingly that the hypothetical state of the pure *n*-alkanes, $G_2^{\circ,c}$, in the asphaltene network is close to the solid-state i.e., in a more condensed morphology. The *n*-alkanes incorporated into the asphaltene aggregate would exist in a frozen state, and the low mobility of their aliphatic chains would be responsible for the loss of entropy and enthalpy compared to the liquid state. As shown in Figure 6, the $H_i^{E,\infty}$ values are nearly constant for *n*-alkanes higher than *n*-decane. The calorimetric results reported in Figure 1 show that no heat effect was observed with the low *n*-alkanes and the heat effect observed with the higher *n*-alkanes was independent from the chain length. The comparison of

(39) Groszek, A. J. *Carbon* **1987**, *25*, 717.

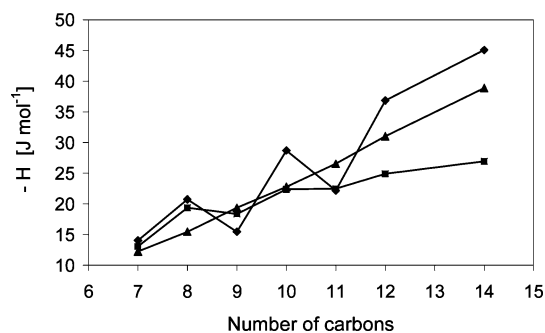


Figure 7. Enthalpic effects of state changes of *n*-alkanes: ■, $H_i^{E,\infty}$, infinite dilution excess enthalpy in asphaltenes at 370 K; ♦, enthalpy of crystallization; ▲, enthalpy of adsorption on the basal plane of the graphite.³⁶

the two sets of experiments leads to the conclusion that only the chains 7–10 carbons long are incorporated and immobilized in the asphaltene aggregates.

A dramatic decrease of the entropy, $S_i^{E,\infty}$, and of the enthalpy, $H_i^{E,\infty}$, was observed at 450 K, as illustrated with *n*-tetradecane in Figure 5. These changes may indicate a phase transition of the asphaltene aggregates. The fact that the value of the bonding energy of one $-\text{CH}_2$ group calculated for the asphaltene-*n*-alkane system from $H_i^{E,\infty}$ (3400 J·mol⁻¹ in the case of *n*-octane) is close to the value of the thermal energy (RT) at 450 K (3700 J·mol⁻¹) indicates that the latter represents the gain in mobility of one $-\text{CH}_2$ group in the aliphatic chains during the phase-transition. The asphaltene-*n*-alkane interactions and asphaltene-asphaltene interactions involving lateral chains are thus quantitatively very similar. The gain in chain mobility leads to the melting of the asphaltene hydrocarbon chains, a phenomenon analogous to that observed in phospholipid bilayers.⁴⁰ In the conditions of the global increase of the mobility of the hydrocarbon chains, neither the asphaltene aggregates can be stabilized by the lateral chains interactions, nor the *n*-alkanes can be stably immobilized in the asphaltene aggregates.

Activity coefficients of *n*-alkanes dissolved in asphaltene-*n*-C₃₆H₇₄ mixtures are presented in Figure 4b and c. The dissolution process differs from the previously reported dissolution in pure asphaltenes. Due to the nonhomogeneous structure of the asphaltene-*n*-hexatriacontane mixture forming a two-phase system, the activity coefficients reflect global interactions of *n*-alkanes with the components of the asphaltene and *n*-hexatriacontane phases. In the case of the mixture {30% C₃₆H₇₄ + 70% asphaltenes}, the activity coefficients are much less sensitive to the temperature changes but depend on the chain length of the *n*-alkane. The lowest value of activity coefficients (0.67) was obtained with *n*-octane, and the highest value (0.93) with *n*-tetradecane. The absence of the exothermic enthalpic effect, Figure 6, suggests that asphaltene-*n*-alkanes structures are already formed at the point when the alkane is added. Activity coefficients obtained with the second mixture, {70% C₃₆H₇₄ + 30% asphaltenes}, are nearly constant with temperature and do not change significantly with the length of *n*-alkane. Moreover, they are close to the activity coefficients obtained with pure *n*-C₃₆H₇₄. Indeed, the activity coefficients of *n*-heptane and *n*-nonane in C₃₆H₇₄ at 357 K are 0.66 and 0.72,⁴¹ respectively. The corresponding values

obtained with {70% C₃₆H₇₄ + 30% asphaltenes} mixture are 0.79 and 0.77, indicating that, in the case of this mixture, the global activity coefficient is dominated by the interactions of the *n*-alkane with *n*-hexatriacontane. In the case of the mixtures containing the behenic acid {asphaltenes (90% (w/w)) + C₂₃H₄₅O₂ (10% (w/w))} the activity coefficients of all *n*-alkanes are nearly independent from temperature and increase with the increasing chain length of the *n*-alkane (Figure 4d). The activity coefficient of *n*-tetradecane is 2.3 at temperatures ranging from 410 to 450 K. It is interesting to note that the activity coefficient of *n*-tetradecane measured in pure asphaltenes is nearly the same at high-temperature ranges, $T > 450$ K (Figure 4a). This result suggests that the transition observed with asphaltenes at 450 K leads to the aggregation state that have similar thermodynamic properties as asphaltene aggregates stabilized by behenic acid or by resins.

Conclusions

Asphaltene aggregation followed by flocculation is of a great technological significance for the petroleum industry. These complex processes have not been well understood until now despite numerous experimental and theoretical studies.⁴² In the present work, we have studied the asphaltene-*n*-alkane interactions used as simplified models of the asphaltene-asphaltene interactions. Titration microcalorimetry and inverse gas chromatography were used to study the asphaltene-*n*-alkane interactions.

Chromatographic measurements showed that the asphaltene aggregates stabilized by the lateral chain interactions exist up to 450 K. At this temperature, a phase transition involving the change of the aggregate structure takes place. We suggest that the phase transition is due to the melting of the asphaltene lateral chains. During this process, the hydrocarbon chains recover their mobility. For *n*-CH₂ frozen groups, the phase transition involves the energy corresponding to nRT . The fact that this value is similar to the excess enthalpy of *n*-alkanes, $H_i^{E,\infty}$, found using inverse chromatography, shows that the energy of the interactions between *n*-alkanes and the asphaltene lateral chains is close to the energy of the interactions between the asphaltene lateral chains. We propose that these interactions are responsible for the formation of the low-temperature structure of asphaltene aggregates. The energy of interactions between the asphaltene lateral chains (nRT) may be sufficient to initiate formation of sheetlike structures described in the literature,¹⁶ the molecular basis of which was not explained until now in the case of asphaltenes.¹⁸ Accordingly, the exothermic heat effect observed with microcalorimetry upon mixing of asphaltenes with *n*-alkanes was attributed to the interactions through induced conformational changes and molecular orientation correlation between the *n*-alkanes and the asphaltene aliphatic chains. This effect depends on the solvation of the asphaltenes with the oil components and is different for different oils. The chromatography and calorimetry experiments performed with different oils containing behenic acid used as a model resin indicate that resins favor assembling of the asphaltene aggregates into micelle-like structures, compared to sheetlike structures formed in their absence.

Acknowledgment. We thank the Centre National de Recherche Scientifique and Total for financing this research. C.S. acknowledges the Ministère de la Recherche et la Technologie for the fellowship.

LA047126K

(40) Heimburg, T. In *Planar Lipid Bilayers (BLMs) and their Applications*; Tien, H. T., Ottova-Leitmannova, A., Eds.; Elsevier: Amsterdam, 2003; Chapter 8, p 269.

(41) Parcher, J. F.; Weiner, P. H.; Hussey, C. L.; Westlake, C. N. J. *Chem. Eng. Data* **1975**, *20*, 145.

(42) Szewczyk, V.; Béhar, E. *Fluid Phase Equilibria* **1999**, *158–160*, 459.