

Supporting Information

Temperature-Triggered Rearrangement of Asphaltene Aggregates as Revealed by Pulsed-Field Gradient NMR

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1. Proton NMR spectra of the asphaltene solution in CHCl_3

The proton spectrum of an asphaltene solution normally comprises a lot of overlapping signals that originates from the diversity of proton positions within the asphaltene molecules. Nevertheless two characteristic regions can be distinguished in the proton spectrum at 7.0 – 9.0 ppm and 0.0 – 3.0 ppm (**Figure S1**) which correspond to aromatic ring hydrogens and aliphatic hydrogens respectively. As can be seen, the solvent signal at 7.3 ppm overlaps significantly the signal of aromatics.

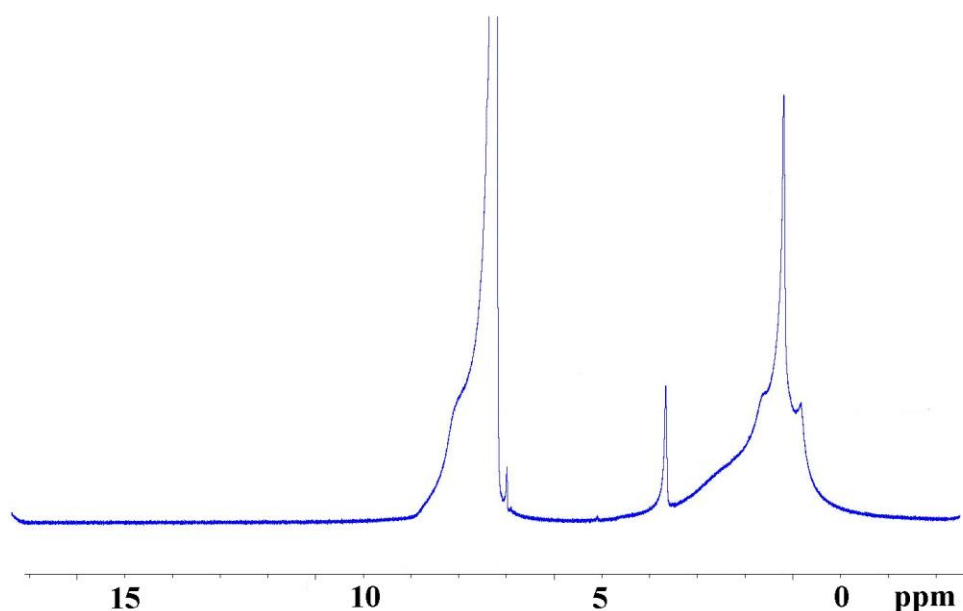


Figure S1. Proton NMR spectrum of asphaltene solution in CHCl_3 . Sample concentration is 76 g/L, temperature is 20°C.

The majority of hydrogen atoms which give a signal in proton spectra belong to the branched aliphatic part of the asphaltene molecules since the hydrogen atoms of polycondensed aromatics are mostly present on periphery of highly substituted aromatic core. As the chloroform line overlaps significantly the signal of aromatic protons, the diffusion measurements were

carried out using 0.0 – 3.0 ppm region in the spectra. This spectra part can be subdivided into few components (**Figure S2**) related to the hydrogen atoms localized in different positions: alkyl groups that are at the α position to aromatic rings, broad shoulder at 2.0–4.0 ppm (H_α); naphthenic hydrogens (CH and CH₂) + CH and CH₂ in paraffinic chains + methylene and methine groups that are at β position to aromatic rings, 1.0–2.0 ppm (H_β); and hydrogen in terminal or isolated CH₃ and CH₃ at the γ position or furthermore to aromatic rings, 0.5–1.0 ppm (H_γ).

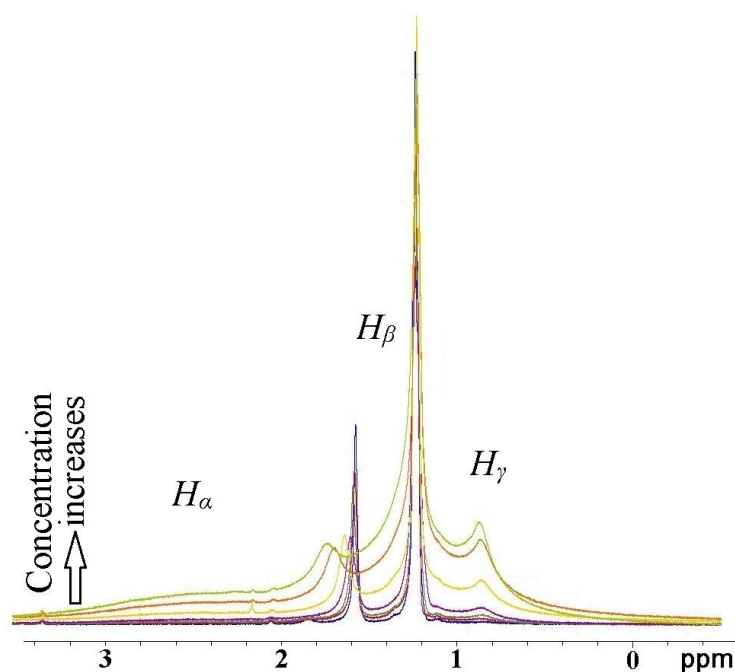


Figure S2. Aliphatic region of ¹H NMR spectra of the asphaltenes dissolved in CHCl₃ at 20°C in concentration range of 120 – 1.9 g/L.

The variation of the asphaltene concentration results in the changes of the spectra. As the concentration of the asphaltenes decreases the width of the lines decreases also that can be related to the growth the reorientation rate of the asphaltene molecules that determines the spin-spin relaxation time T_2 and consequently the line width, **Figure S2**. It was found that the most

noticeable line narrowing happens within 10 – 20 g/L concentration range. The position of the lines though behaves differently: while the peaks at 0.9 ppm and 1.2 ppm are not affected, the peak at 1.6 ppm slightly shifts toward H_α protons peak (the biggest $\Delta\delta \sim 0.2$ ppm) as the asphaltene concentration increases. Since this peak is attributed to the naphthenic hydrogens, its slight drift could have been explained by stronger interaction of aromatic core planes in asphaltene aggregated structures upon their formation via π - π stacking: the naphthenic cycles generally lie within the same plane as polycondensed aromatic rings so the protons may begin to “feel” an aromatic environment in aggregated structure. The crowded nature of the proton 1D NMR spectra along with an overlapping of the broad signals makes the structural analysis very complicated when solely based on 1H spectroscopy. We could not find in the literature the spectra of asphaltene solution in $CHCl_3$ recorded for the whole measured concentration range (120 – 0.5 g/L) to make a direct comparison; however our spectra are generally consistent with those reported previously in respect to such features as chemical shift of the lines, number of the components, and the line narrowing effect.

2. Concentration dependencies of the partial weights of the diffusion components

The partial weights (p) of the different diffusion components were inferred from the multi-exponential analysis of the signal attenuation decays according to equation:

$$I=I_0\{p_1\exp[-\gamma^2G^2D_1\delta^2(\Delta-\delta/3)] + p_2\exp[-\gamma^2G^2D_2\delta^2(\Delta-\delta/3)] + p_3\exp[-\gamma^2G^2D_3\delta^2(\Delta-\delta/3)]\}. \quad (S1)$$

The results are presented in **Figure S3** where the partial weights of the nano (red triangles) and macroaggregates (blue diamonds) were extracted from three-component processing (eq.S1)

whereas the two-component processing obviously gives an average sum (green circles) of them. For comparison the sum of partial weights of nano and macroaggregates (eq.S1) is also presented (red line in **Figure S3**).

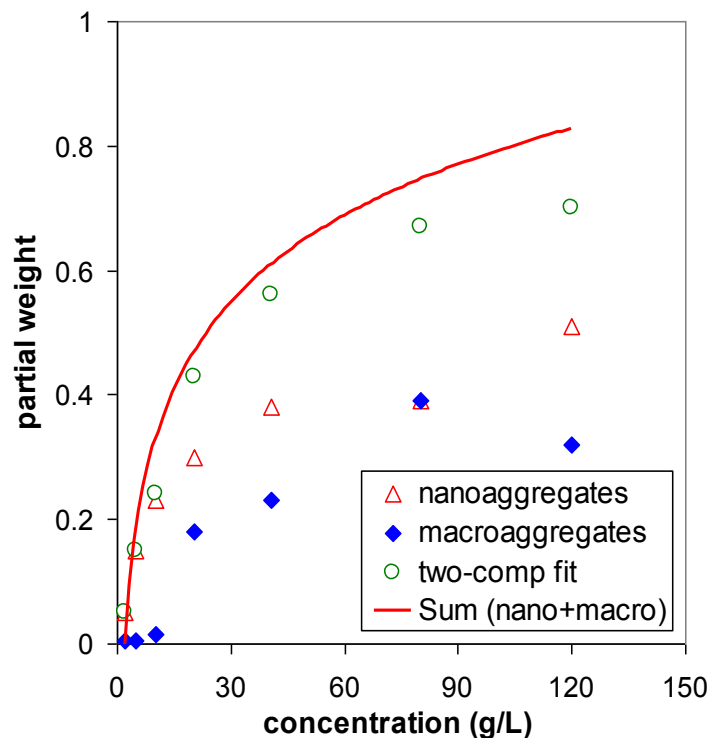


Figure S3. Concentration dependences of the partial weights of the components extracted from the multi-component fitting.

3. Concentration dependencies of the hydrodynamic radius of asphaltene aggregates

The Stokes-Einstein equation relates the diffusion coefficient D with hydrodynamic radius R_h of moving particle:

$$D = kT / 6\pi\eta R_h, \quad (S2)$$

where k is the Boltzman constant, T is the absolute temperature, η is the fluid viscosity. Neglecting the change of fluid viscosity with increase of asphaltenes concentration, the hydrodynamic radii were calculated at 293 K and are presented in **Figure S4**.

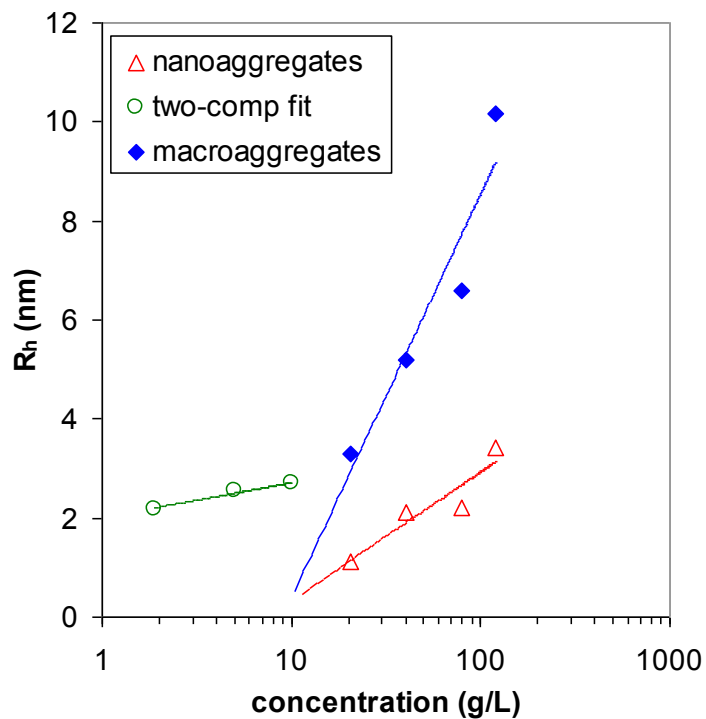
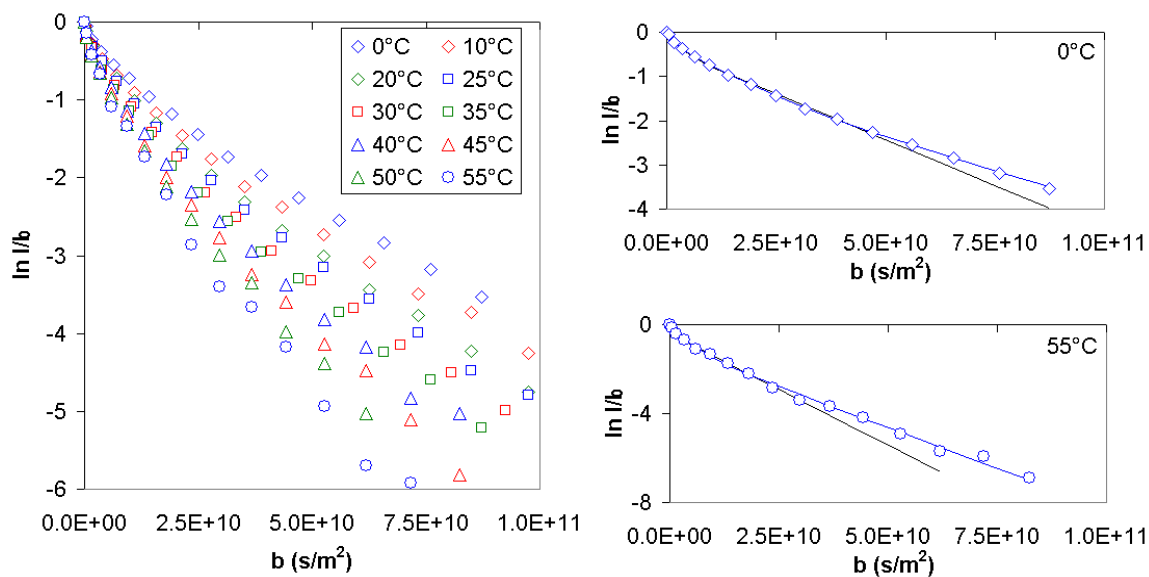


Figure S4. Concentration dependencies of the hydrodynamic radius of asphaltene aggregates.

4. Temperature dependences of the signal attenuation decays

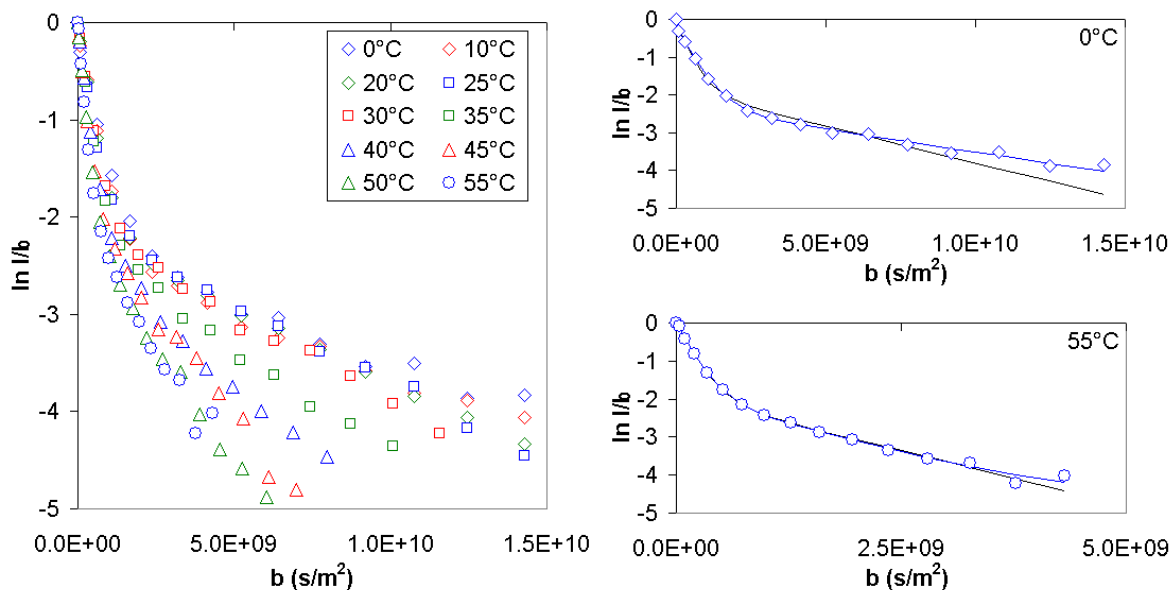
The signal attenuation decays of the samples with concentration of 120 g/L and 7 g/L for temperature range of 0 – 55°C are presented in **Figure S5** and **Figure S6**, respectively. For clarity the difference between two- and three-component fittings is also presented.



(a)

(b)

Figure S5. (a) The decays of the signal related to aliphatic hydrogens of asphaltene dissolved in CHCl_3 at concentration of 120 g/L within the temperature range of 0 – 55°C. (b) The examples of two- (black line) and three-component (color line) fittings applied for the analysis of the data obtained at low and high temperatures.



(a)

(b)

Figure S6. (a) The decays of the signal related to aliphatic hydrogens of asphaltene dissolved in CHCl_3 at concentration of 7 g/L within the temperature range of 0 – 55°C. (b) The examples of two- (black line) and three-component (color line) fittings applied for the analysis of the data obtained at low and high temperatures.