Surface Chemistry and Spectroscopy of UG8 Asphaltene

Langmuir film, Part 1

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Supporting Information

Figure S1. Amplitude versus frequency showing the resonant frequency at 159.85 kHz (peak maximum) and the working frequency of 159.75 kHz in repulsive dominant regime.

Figure S2. Surface pressure-area isotherms for UG8 asphaltene spread from a distilled toluene solution showing slightly a different apparent molecular area.

Figure S3. Compression-decompression cycles for UG8 asphaltene Langmuir film spread from freshly distilled toluene solution.

Figure S4. UV-vis absorption spectrum of 10^{-4} M UG8 asphaltene in toluene measured in solution using a 0.2 cm optical path quartz cuvette.

Figure S5. Comparison between the *in situ* UV-vis absorption spectra of UG8 asphaltene with a waiting time period of 15 min before compression using toluene (**A**) and benzene (**B**) as spreading solvents.

Figure S6. Stability for asphaltene Langmuir film spread from freshly distilled toluene at constant surface pressure (30 mN/m, —) and measured area (—●—) vs. time (A); Relaxation surface pressure after target (32 mN/m) is reached: constant area (15 $\text{\AA}^2/\text{molecule}$, —●—), and surface pressure relaxation (—) vs. time (B).

Surface pressure relaxation measurements as the one shown above in Figure S6B are not unusual. Similar results are reported in the literature many Langmuir film forming molecules. For stearic acid and Zn stearate which are known to be very stable monolayers two graphs are shown below:

Graph 1. Surface-pressure relaxation isotherm of Langmuir monolayer of zinc stearate compressed to a surface area of 0.20 nm^2 per molecule [from H. Sakai and J. Umemura, Evaluation of structural change during surface pressure relaxation in Langmuir monolayer of zinc stearate by infrared external reflection spectroscopy, *Colloid Polym. Sci.* **2008**, 286, 1637–1641].

Graph 2. Decrease in initial surface pressure for stearic acid versus time for preselected surface pressures. Compression rate $4.4 \text{ Å}^2/\text{molecule}/\text{min}$. [from J. W. Munden, D. W. Blois and J. Swarbrick, Surface Pressure Relaxation and Hysteresis in Stearic Acid Monolayers at the Air-Water Interface, *J. Pharm. Sci.*, **1969**, 58, 1308-1312].

This effect can be reduced, but not eliminated, by reducing the compression rate or the target surface pressure. Since this effect is always present an assessment of the Langmuir film stability is to monitor the decrease in the surface area as a function of time for a given surface pressure to assure that no molecules are lost in the subphase or that no multilayers are formed.

Figure S7. Surface pressure-area isotherms for UG8 asphaltene spread from benzene at the air-water interface.

Figure S8. Compression-decompression isotherm cycles of UG8 asphaltene Langmuir film spread from benzene, run 1 (**A**) and at run 2 (**B**).

All measurements at the air-water interface were performed with 1 mg/mL solutions of UG8 asphaltene in toluene or benzene using spreading volumes of 45 – 50 μL .