USE OF LASER TECHNIQUES FOR THE STUDY OF ASPHALTENE AGGREGATION AND ADSORPTION.

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Introduction.

The adsorption of asphaltenes on mineral surfaces is an important phenomena related to many process in crude oil processing such as changes in humectability of oil well, asphaltene precipitation during production, transportation and storage, pore well clogging, catalysis fouling, etc. This has promoted some studies of asphaltene adsorption in the past[1,2]. Most of these studies, performed with very diluted solutions, afforded L-type isotherms, suggesting the saturation of the interface without further adsorption of sample. However, as shown below, using several laser techniques, we found that adsorption of asphaltenes on silica and glass surfaces could lead to step-wise adsorption and to the formation of thick multilayers which in some cases amount to grams of sample per gram of adsorbent. In this communication we review our previous work in this area and some new results are presented.

Methods.

Furrial crude oil (20° API, and 10% asphaltene) was used. This crude is from Monagas State in the east part of Venezuela and was selected due to the severe asphaltene precipitation problems it presents. Asphaltenes were obtained by precipitation, by the addition of 40 volumes of n-heptane to the crude as described elsewhere[3]. Commercial samples of silica gel for chromatography were used as the adsorbent. Using the dye method (methylen blue-water), an area of about 35 m^2/g was obtained for this solid when an area of 120 A^2 per molecule was used for the dye[4]. For kinetic runs, small silica plates (2.5x1 cm^2, 24 mg of silica) were introduced in small glass vials containing 8 mL of asphaltene-toluene solution. These vials were well sttopered to avoid solvent evaporation. Changes in absorbance with time was continuously monitored by passing a He-Ne laser beam (632.8 nm) throught the vials and the intensity registered by using a photodiodc. In one experiment (asphaltene concentration equal to 200 mgL^{-1}) the solution was stirred by using a small magnetic stirrer. Since no difference in rate was observed with and without stirring all experiment were carried out without stirring. A desorption experiment was performed as follows: Asphaltenes were adsorbed on a silica plate from a 200 mgL^{-1} solution as described above. After 72 h, the quantity of sample adsorbed was equivalent to 133 mgL^{-1}. The plate was withdrawn, dried and embedded in pure toluene. The absorbance increase was monitored as usual and after 50 h no further change was observed. The amount desorbed was equivalent to 4 mgL^{-1}.

Isotherms were measured using the photothermal surface deformation (PSD) method described earlier[3]. Briefly, in this method the amount of solute adsorbed on the surface is determined directly. That is, by using a procedure similar to the one described for the kinetic runs (see above) the sample was adsorbed on the silica plate. After the required time, the plate was withdrawn, dried and set for analysis. This was performed by using two lasers, one for pumping and the other as the probe. The pumping beam heat the sample and produces a dilatation that is proportional to the sample mass. This is measured by the probe beam. Signal calibration was performed by comparing with the adsorption measured by tramitance measured as described in the kinetic runs.

In another experiment a silica plate was contacted with a toluene solution of asphaltene (5000 mgL^{-1}) during 24 h in the same way as described above for the kinetic studies. After this time, the plate was withdrawn from this solution, allowed to dry and the sample adsorbed was determined by weight difference. After this, the same plate was contacted with a fresh solution of the same concentration and the procedure was repeated for one day periods during 21 days.

Number average molecular weight (M$_n$) and molecular weight distribution (MWD) were measured by GPC in THF as described earlier[5]. The samples were analyzed as follows: Toluene solution of asphaltenes were contacted with silica for periods of 1, 4, 8 and 24 hours. After these times, an aliquot was withdrawn, the toluene was evaporated, the residue dissolved in THF and the above M$_n$ and MWD of Furrial asphaltenes were determined in

each case.

When required the area per asphaltene molecule A_a was estimated from equation 1:

$$A_a = 0.166(MA_s/v) \qquad\qquad 1$$

Here A_s is the area of the silica in m^2/g, v the sample adsorbed is in mg/g, A_a is in A^2 per molecule and M is the molecular weight.

Results.

On Table 1 the values for the apparent first order constants k, obtained for the studied solutions are shown. These were obtained by fitting the results to a first order kinetics. The fittings were quite good for the 5-50 mgL^{-1} runs. However, for the 200 and 400 mgL^{-1} runs the results suggested that the readings at long times should correspond to a slower rate (see Figure 1). Results from the desorption experiment (see above) showed that desorption from the surface could be neglected in the concentration range examined. The adsorption isotherms obtained are shown in the Figure 2. Note that for 18 and 48 h, the isotherms are L-type whereas the one measured at 96 h shows a tendency towards H-type. In other words, the isotherm slope increases with time and moves to smaller c_s values in the more diluted region. Using the procedure described above, no significative changes in M_n or MWD were detected as a function of the contact time between the asphaltene solution and the silica. M_n values remained constant around 1000 and the MWD measured was in the range from 12000 to 200 in all cases.

In order to have an approximated idea of the amount of asphaltenes that could be adsorbed when the surface is in permanent contact with a liquid with a constant asphaltene concentration, such as the the surfaces in the crude oil well, the experiment above, where the surface is contacted with fresh toluene solutions after 24 h periods was carried out. After 21 days we found that the equivalent of 10g of asphaltene adsorbed on one gram of silica.

Discussion.

Since adsorption rates were not changed significantly by stirring (see above), diffusion to the outer surface of the solid is not rate determining. Also neither average molecular weight nor molecular weight distribution were affected by adsorption (see Methods), suggesting that diffusion into solid pores is not kinetically important. Thus it appears that diffusion along the surface to find a site for adsorption is rate determining, since desorption in this concentration range is unimportant. Using a Langmiur treatment for the dye we found that only 14.4 mg/g of this compound were needed to saturate the silica surface. By using any reasonable value of A_a for asphaltene lying on the surface, one should expect saturation values much smaller than this. However, according to Figure 2, these "saturation" values are higher than 20 mg/g and show a slow increase with time. These results and the first order found, suggest that when asphaltenes are adsorbed they create new adsorption sites were other asphaltene molecules could be adsorbed. In this way the sample could pile up at different places in the surface and by the time the silica surface is completely covered an asphaltene multilayer is already present. This would explain the somewhat slower adsorption rate found at long times with the more concentrated solutions (see above and Figure 1). Also, adsorption of small aggregates, such as dimmers, trimmers, etc is likely in this concentration range. Using a thermal lens technique it was suggested that aggregation of asphaltenes in toluene could begin at very low concentrations, probably around 50 mgL$^{-1, 6}$.

When the adsorption of toluene solutions of asphaltene on glass plates was studied by the above PSD technique in a wider concentration range (0- 6000 mgL^{-1}) step-wise adsorption isotherms were found for several asphaltene samples (Furrial, Hamaca, Jobo)[3]. The occurrence of such steps as a result of the adsorption of large aggregates is an interesting possibility. In any case, thick multilayers were apparent from these adsorption measurements.

According to the results above, under appropriated conditions, very large quantities of asphaltenes could be adsorbed on silica (up to 10 g/g or more). This suggest that adsorption alone could easily leads to plugging of pore wells and other problems related to solid formation during oil production.

Conclusions.

Use of lasers, either in the usual tramitance mode or in the PSD mode allows the quantitative study of asphaltene adsorption. Also, reasonable inferences about aggregate formation in solution could be made from these studies. The first order adsorption rates measured in this work were found consistent with multilayer formation and aggregate

adsorption. The L-type isotherm found after 18 h is probably due to saturation of the surface by a multilayer of asphaltene formed either as usual, or by the adsorption of aggregates. Change of these isotherms with time after long periods are due to the adsorption of asphaltene or asphaltene aggregates on the multilayer. Since adsorption alone could lead to plugging of pores and the formation of organic solid deposits, treatment with surfactants and solvents should consider, as a very important consideration, the displacement of asphaltenes from the surface.

References.
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Table I. Apparent first order rate constant k, for the adsorption of Toluene Solution of Furrial Asphaltenes on Silica[a].

Initial concentration (mg L^{-1})	k x 10^3 (min^{-1})[a]	R^{2,b}
5	1.09 ± 0.8	0.991
20	1.24 ± 0.3	0.993
50	1.12 ± 0.3	0.996
200[c]	1.62 ± 0.3	0.992
400[c]	0.79 ± 0.3	0.994

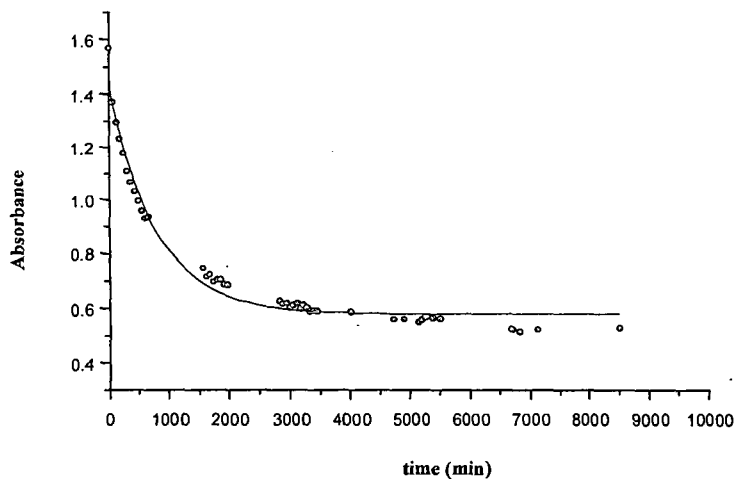a: At Room temperature. b: Correlation coefficient for first order fitting. C: see text.

Figure 1.   Adsorption kinetics for a toluene solution of Furrial asphaltenes (200 mg L^{-1}) obtained on silica at room temperature. Points are experimental and the curve is the fitting to a first order.
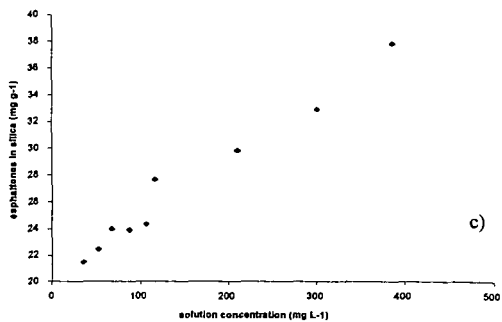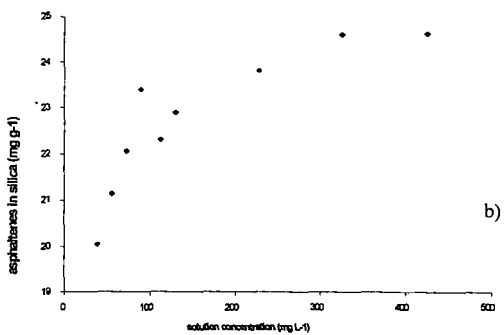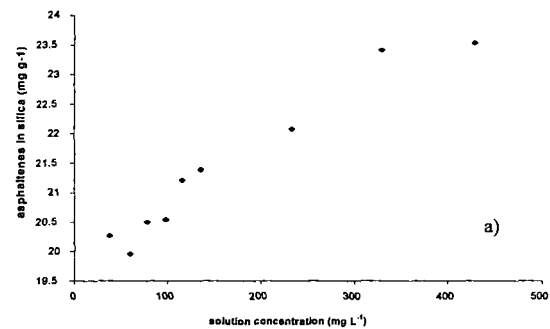
Figure 2.   Adsorption isotherm of toluene solutions of Furrial asphaltenes on silica measured by PSD at room temperature. a) after 18 hours, b) after 48 hours, c) after 96 hours.