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Importance of asphaltene aggregation in solution in determining the adsorption of this sample on mineral surfaces

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Abstract

Adsorption rate constants and adsorption isotherms on silica have been obtained for toluene solutions of Furrial asphaltenes. For initial solution concentrations of 5, 20 and 50 mg l^{-1} an adsorption rate proportional to solute concentration was observed with an average first order rate constant of $(1.17 \pm 0.3)\ 10^{-3}\ min^{-1}$. For more concentrated solutions (200 and 400 mg l^{-1}), we found the same initial rate constant. However, at long times significant lower rates were apparent. We found that desorption of asphaltenes from the surface was very slow and could be neglected. Also, we found that the adsorption isotherms, measured for solution concentrations (c_s) below 500 mg l^{-1}, changed with time over a period of days where adsorption on the surface (v) grows slowly with time. A slow tendency from L-type to H-type was observed for the adsorption isotherms measured at 18, 48 and 96 h. Under the conditions of concentration and time examined, these results are consistent with the formation of asphaltene multilayer at the silica surface and with the adsorption of aggregates (dimers, trimers, etc.) as well as single asphaltene molecules. In view of these results we suggest that for solutions concentration below 50 mg l^{-1}, small aggregates are adsorbed on the surface at a rate similar to the single molecules until the silica surface is covered or saturated. After this 'saturation' adsorption continues on the asphaltene layer at a much smaller rate.

Keywords: Asphaltenes; Kinetics; Adsorption; Aggregation

1. Introduction

Due to its impact on petroleum production, phenomena such as asphaltene aggregation, floc-

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culation and precipitation have been the subject of many studies [1–8]. The emphasis in these investigations have been on asphaltene dispersion by the solvent or by surfactants which, no doubt, are very important aspects. However, it should be realized that along with dispersion, adsorption of the sample on the different surfaces contacted by the crude, is a very important factor to be considered.

Adsorption of asphaltene on minerals studies have been reported earlier in the literature for very diluted solution. Langmiur type isotherms were found in most cases [9–11]. However phenomena such as the importance of multilayer formation, aggregate formation, impact of the adsorption on flocculation among others have been neglected, possibly due to the lack of adequate methods for dealing with more concentrated solutions.

On account of these considerations, we began studies in this area some time ago [12–14]. Due to the high optical density of asphaltene solutions, and since asphaltene aggregation and flocculation are most important in concentrated solution, some optical methods were developed to conduct studies under these conditions [14]. Among other aspects, it was found that thick multilayers could be formed on sand, organic and glass surfaces. This sample aggregation in solution could compete with adsorption; that both these phenomena change with time and that, asphaltene adsorption could grow with time to the equivalent of grams per gram of solid.

Thus, it is reveled that at moderate and higher concentrations, asphaltene adsorption is a very complex matter, far from the apparently simple Langmiur type adsorption found in some cases at high-diluted solutions.

In this paper we report adsorption kinetic and adsorption isotherms for Furrial asphaltenes in toluene and silica gel. As suggested below, any proper account of asphaltene adsorption should consider the formation of multilayers, the adsorption of aggregates and the change of adsorption with time.

2. Experimental and methods

2.1. Materials

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 oil as described elsewhere [14]. Resins were removed from the precipitated asphaltenes by extraction with boiling *n*-heptane in a Soxhlet apparatus as described earlier [14].

Commercial samples of silica gel for chromatography were used as the adsorbent. Using the dye method (methylen blue-water), an area of about 35 $m^2\ g^{-1}$ was obtained for this solid using an area of 120 $Å^2$ per molecule for the dye [15] (see Eq. (3) below). A somewhat smaller area have been reported for a similar material (21.8 $m^2\ g^{-1}$) [16].

2.2. Methods

Asphaltene–toluene solutions were prepared by toluene dilution of a stock solution (500 mg l^{-1}). The stock solution was prepared by weighting the appropriated amount of dried asphaltene and them dissolved in toluene using ultrasonic bath. The solution was allowed to stand for two days before using it.

For kinetic runs, small silica plates (2.5×1 cm^2, 24 mg of silica) were introduced in small glass vials containing 8 ml of asphaltene–toluene solution. These vials were well capped to avoid solvent evaporation. Absorbance was continuously monitored by passing through vials a He–Ne laser beam (632.8 nm) and changes in intensity registered by a photodetector. In previous experiment 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.

Kinetics plots are obtaining by plotting the solution absorbance as a function of the time. From these kinetic plots, the amount of adsorbed solute at any time in each case v_t (mg g^{-1}), as

well as the corresponding solution concentration C_t (mg l^{-1}) could be obtained using the Eqs. (1) and (2) below:

$$v_t = [(A_0 - A_t)a/A_0 w]C_0 \quad (1)$$

$$C_t = (A_t/A_0)C_0 \quad (2)$$

where: A_0 and A_t are the absorbances at zero and t min, respectively, C_0 (mg l^{-1}) is the initial solution concentration, a the solution aliquot (l) and w the weight of adsorbent solid (g).

A desorption experiment was performed as follows: a silica plate obtained after adsorption experiment with 200 mg l^{-1} solution concentration for 72 h. (after this time the quantity of asphaltenes adsorbed was equivalent to 133 mg l^{-1}) was left in clean vial with 8 ml of pure toluene. The solution absorbance was monitored in a similar way to adsorption experiments.

For isotherms experiments the silica plates were dipped into solutions contained in glass vials capped with Teflon stoppers. The container were placed at room temperature and withdrawn for analysis when is required. Isotherms were measured using the photothermal surface deformation (PSD) method described earlier [14]. Briefly, in this method the amount of solute adsorbed on the surface is determined by measuring the photothermal surface deformation induced by the energy absorption from excitation beam directed to the sample. The sample surface is expanded as a consequence of the temperature increase due to a non-radiative decay of the optically excited sample. This surface change is detected by measuring the profile of a weak probe laser beam that is reflected from the sample. The magnitude of the PDS signal is related to the amount of adsorbed solute.

Area per asphaltene molecule A_a.

The area per asphaltene molecule (A_a) in Å^2 was estimated from Eq. (3):

$$A_a = 0.166(MA_s/v) \quad (3)$$

here A_s is the area of the silica in m^2 g^{-1}, v is in mg g^{-1} and M is the molecular weight.

It should be mention that blank experiment show no evidence of asphaltene precipitation from toluene for the relatively diluted solutions used in this work. This is expected in view of the relatively high solubility of Furrial asphaltene in toluene at room temperature (about 57 g l^{-1}).

2.3. Molecular weight measurements

Number average molecular weight (M_n) and molecular weight distribution (MWD) were measured by GPC in THF as described earlier[17]. The samples were analyzed as follows: Toluene solution of asphaltenes were contacted with silica for periods of 1, 4, 8 and 24 h. After these times, an aliquot was withdrawn, the toluene was evaporated, and the residue dissolved in THF and finally M_n and MWD of Furrial asphaltenes were determined in each case.

3. Results

In 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 mg l^{-1} runs. However, for the 200 and 400 mg l^{-1} runs the results suggested that the readings at long times should correspond to a slower rate (see Fig. 1).

Fig. 2 shows the kinetic results for the desorption experiment. It is notice that the solution absorbance increase less than 3%. After 50 h no further change in absorbance signal was observed. It can be conclude that only 3% of the material initially adsorbed by the silica surface were des-

Table 1
Apparent first order rate constant k, for the adsorption of toluene solution of furrial asphaltenes on silica[a]

Initial concentration (mg l^{-1})	$k \times 10^3$ (min^{-1})[a]	R^{2b}
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 coeficient for first order fitting.
[c] See text.

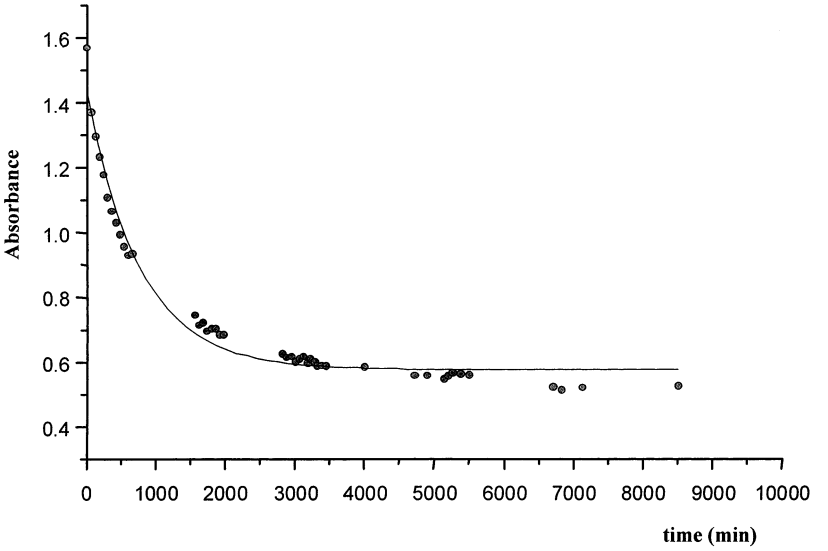

Fig. 1. Adsorption kinetics for a toluene solution of Furrial asphaltenes (200 mg l^{-1}) obtained on silica at room temperature. Points are experimental and the curve is the fitting to a first order.

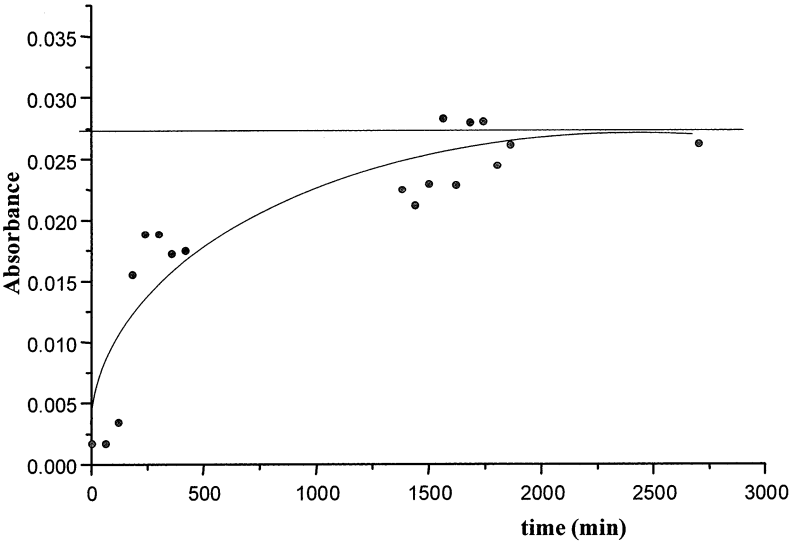

Fig. 2. Desorption kinetics of Furrial asphaltene from a silica plate at room temperature in toluene.

orbed. The amount desorbed was equivalent to 4 mg l^{-1}.

3.1. Adsorption isotherms

The results of these experiments are shown in the Fig. 3 and Table 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.

3.2. Molecular weight

No significant 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

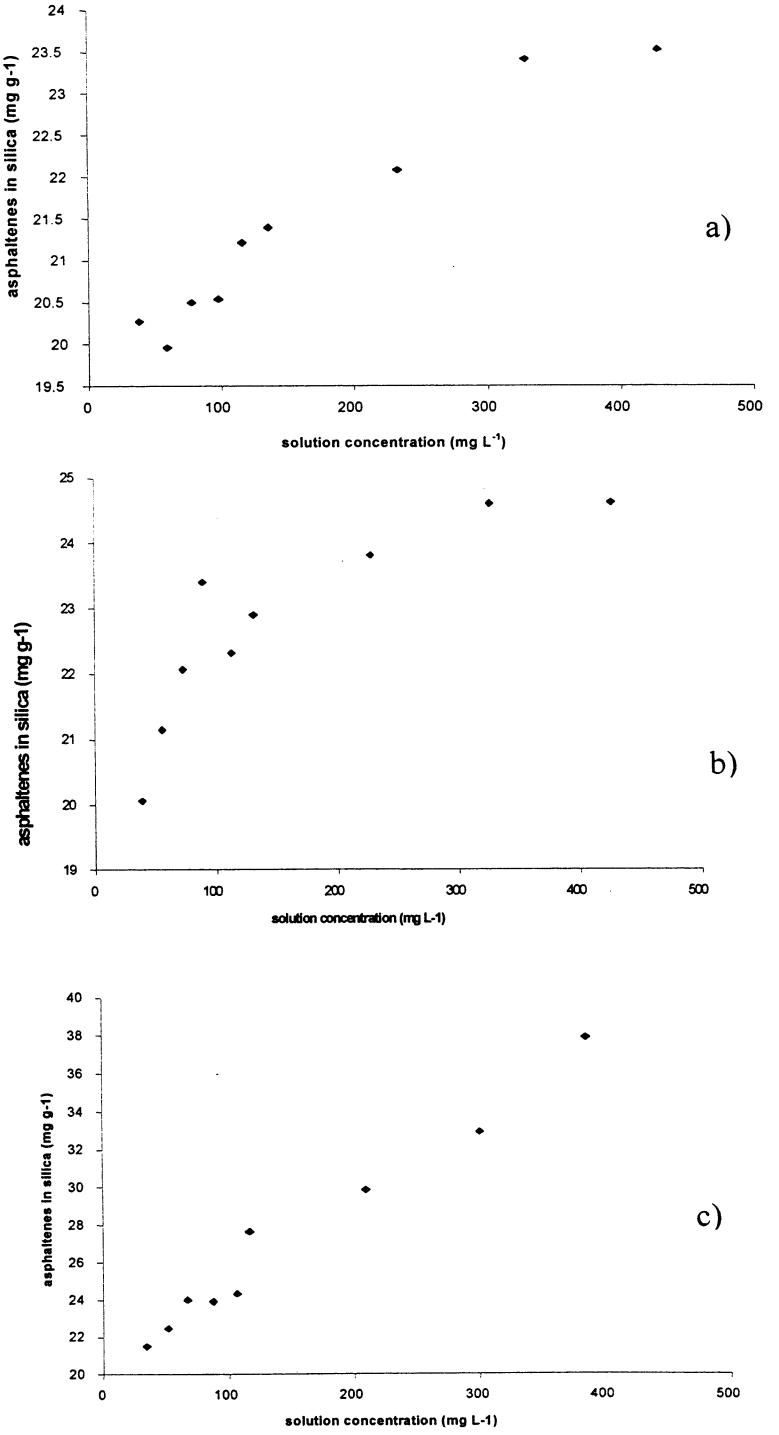

Fig. 3. Adsortion isotherm of toluene solutions of Furrial asphaltenes on silica measured by PSD at room temperature. (a) After 18 h; (b) after 48 h; (c) after 96 h.

remained constant around 1000 and the MWD measured was in the range from 12000 to 200 in all cases.

4. Discussion

It is known that the interpretation of kinetics of adsorption could be complicated by several steps such as diffusion to the outer surface of the solid, diffusion along the interface and diffusion into solid pores [15]. In the case of asphaltenes, where a wide MWD is present, some difference in the MWD should be expected after adsorption, would the diffusion step into pores be rate determining or kinetically important. No such difference was found when the MWD was measured at different contact times (see above). Stirring during adsorption did not changed the rate significantly suggesting that diffusion to the outer surface is a fast step and that diffusion along the outer surface could be rate determining (see below).

A simple calculation using Eq. (3), will show that for any reasonable assumed average value of asphaltene area per molecule (A_a), the surface will be saturated for any v value near 10 mg g^{-1} or less. For instance for methylen blue with a flat molecular area of about 120 $Å^2$, [15] and $M = 301$ the surface was saturated with 14.5 mg g^{-1}. This strongly suggest that for the case of asphaltene, saturation will require a much smaller quantity of sample, probably around 5 mg g^{-1}.

Surface coverage around 20 mg g^{-1} were found after 18 h for solutions of 100 mg l^{-1} (see Fig. 3) and larger values were found at later times. Thus these results strongly suggest the presence of multilayers.

In a previous communication we reported that aggregation of asphaltenes in toluene probably begin around 50 mg l^{-1} [18]. Thus, it is likely that formation and adsorption of aggregates on the surface would occur above this concentration. For instance, this would justify the apparent surface saturation at v values much higher than expected (see Fig. 3).

An attractive hypothesis for the first order found would be that during the first stages of adsorption and when the asphaltenes are adsorbed on the silica surface they create new active sites where other molecules could be adsorbed. In this way, surface saturation would not limit the adsorption. After all, adsorption of asphaltenes on asphaltenes is equivalent to aggregate formation. Since on comparative terms a surface region is much more concentrated than the bulk, this is a very reasonable assumption. Thus during these first stages the condition for adsorption (slow step) appears to be diffusion to the outer surface of the solid. Once there, in a fast step compared to this diffusion step, asphaltene would be adsorbed, either on 'clean' silica or on the asphaltene layer. This would be consistent with the non significant desorption found (see Fig. 2). After multilayer formation in these first stages, adsorp-

Table 2
Adsorption of toluene solutions of furrial asphaltenes on silica at diffetent times

Initial concentration (mg l^{-1})	Adsorbed concentration (v) (mg l^{-1})[a] time (h)				
	18	48	Δv	96	Δv
100	61.2	30.6	−0.6	64.9	3.7
120	60.2	63.8	3.6	67.8	7.6
140	61.9	66.7	4.8	72.4	10.5
160	62	70.6	8.6	72.2	10.2
180	64.1	67.4	3.3	73.5	9.4
200	64.6	69.2	4.6	83.5	18.9
300	66.7	71.9	5.2	90.2	23.5
400	70.77	74.3	3.6	99.4	28.7
500	71.7	74.4	2.7	114.4	42.7

[a] For conversion to mg g^{-1}, the following equation could be used: v (mg g^{-1}) = 0.321 v(mg l^{-1}) + 0.645.

tion will continue at slower rate (see Fig. 1 and Table 1). In this case, finding a site in the multilayer could be as slow or slower than the diffusion step. In other words, and for the sake of clarify, the above comments could be described by the following simple kinetic scheme.

Let $[A]_b$, $[A]_I$ and $[A]_s$ be the sample concentration corresponding to sample in the bulk, interface and surface respectively. Let k_1, k_{-1} and k_2 be rate constants corresponding to diffusion from the bulk to the outer surface, for the reverse of this process and for adsorption. Then, for the adsorption in two steps we have.

$$A_b \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A_I \quad (4)$$

$$A_I \xrightarrow{k_2} A_s \quad (5)$$

Using the steady state approach for A_I, the following equation is obtained for the rate of adsorption:

$$\text{Rate} = k_2 k_1 [A_b]/(k_{-1} + k_2) \quad (6)$$

When $k_2 >> k_{-1}$, one obtains,

$$\text{Rate} = k_1 [A_b] \quad (7)$$

Thus the diffusion step would be the slow step. This would correspond to the conditions before reaching the plateau (see Fig. 3(a)). In this case adsorption on silica or the multilayer would be of no consequence to the rate.

When $k_2 << k_{-1}$ the equation for the rate becomes:

$$\text{Rate} = k_2 K [A_b], \text{ where } K = k_1/k_{-1} \quad (8)$$

In this case finding a site in the multilayer is the slow step. If k_2 and k_{-1} are similar then Eq. (6) above applies. The situation after the plateau could be described by Eq. (6) or Eq. (8) with a rate constant smaller than k_1.

According to the arguments and results above the adsorption results obtained in this work would mainly be the consequence of multilayer formation and adsorption of small aggregates (dimers, trimers). Presumably, at higher concentrations (>1000 mg l^{-1}), larger aggregates would form and their adsorption on the multilayer would be detected. This is consistent with the stepwise adsorption isotherms on glass plates, found for toluene solutions of Furrial and other asphaltenes where the adsorption was studied in a wider concentration range (100–5000 mg l^{-1}) [14].

In this way the adsorption results could be used to follow the aggregation events occurring in solution as the concentration is increased. Thus 'saturation' of the surface at higher v values than expected (see Fig. 3) suggest the adsorption of small aggregates (dimers, trimers) formed in this diluted concentration range. At higher concentrations, larger aggregates are formed and their adsorption on the multilayer would lead to sudden changes (steps) in the derivative dv/dc_s. This is in agreement with the stepwise formation of large aggregates of asphaltenes mentioned above.

From the above results and data in the literature it is concluded that adsorption of asphaltenes on mineral surfaces could lead to the formation of thick multilayers. As discussed earlier this multilayer would be the ideal place for the beginning of any flocculation problem [14]. This is a very important consideration when designing a surfactant treatment for asphaltene deposits. In this case, rather than presumed dispersion of asphaltene flocs or aggregate by the surfactant, the displacement of asphaltene from the surface should be the first consideration.

5. Conclusions

Evidence from adsorption kinetics and from adsorption isotherms presented in this work, suggest that a proper account of asphaltene adsorption on mineral surfaces requires consideration of aspects such as multilayer formation, formation and adsorption of aggregates and change of adsorption with time. The evidence presented here is consistent with the adsorption of small aggregates before saturation of the silica surface. When combined with data from elsewhere in the literature [14] the adsorption isotherms could be used to indicate the formation of small as well as large aggregates in solution.

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