

Articles

Adsorption of Asphaltenes at the Toluene–Silica Interface: A Kinetic Study

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The adsorption kinetics of asphaltenes at the toluene – silica interface has been measured for nine solution concentrations C_S (from 5 to 3000 mgL⁻¹). Results could be adjusted to an irreversible second-order adsorption kinetics, where the adsorption rate k was strongly dependent on concentration. Thus a large reduction in k was observed when C_S was increased in the studied concentration range. This rate reduction was accounted for in terms of adsorption of aggregates formed in solution. The step – wise trends observed for the adsorption isotherms of asphaltenes on mineral surfaces, could be reproduced using the above k values.

Introduction

As a result of the possible impact on reservoir wettability, change in crude composition during migration, environmental damage, and asphaltene precipitation during production, asphaltene adsorption has been the subject of studies in the past. Measurements of large quantities of phenol adsorbed on precipitated asphaltene suggested a loose structure for this solid.¹ Adsorption of toluene solutions of asphaltenes under different clay minerals afforded Langmuir-type isotherms and two-stage adsorption was observed when a toluene–heptane mixture was used as the solvent.² Changes in crude oil composition during migration have been studied.³ Adsorption of petroleum acids and phenols on argillaceous

and sandy rocks were reported.⁴ The impact of emulsions stabilized by asphaltenes adsorbed on solid particles such as goethite has been studied.⁵

Large aggregates of asphaltenes have been observed by atomic force microscopy (AFM) when toluene solutions were contacted with mica surfaces.⁶ The authors reported fractal-like objects with lengths of a few micrometers.⁶ According to a report,⁷ the adsorption of toluene solutions of resins and asphaltenes on quartz and feldspar do not change the electrophoretic mobility of these minerals, suggesting that the surface sites responsible for surface charge were not affected by the

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adsorption, although the adsorption turned the minerals hydrophobic.

Between 20 and 30 mg/g of asphaltene were adsorbed when toluene solutions were contacted with several clays⁸ and with silica.⁹ Langmuir type I isotherms were found in these cases, and wettability studies showed that water was capable of reducing but not eliminating asphaltene adsorption.⁸ As expected, adsorbed asphaltene changed the surface from hydrophilic to hydrophobic.⁸

Most of the above work describes changes in mineral surfaces related to wettability and other phenomena requiring a low coverage of surface. In this regard, just a monolayer of organic matter would be enough to change the mineral surface from hydrophilic to hydrophobic, and hence only dilute solutions of asphaltenes are needed. In this case, simple L-type isotherms are usually found.

For studies on the influence of aggregate formation on adsorption higher solution concentrations are required. However, higher concentrations of asphaltene complicate the problem due to multilayer formation, time dependence, aggregate formation, and precipitation. These phenomena, such as multilayer formation and time dependence^{10–12} as well as precipitation¹³ have been studied previously in our laboratories.

Adsorption kinetics could be a useful tool for the study of asphaltene aggregation in solution. In principle, adsorption of aggregates should lead to different adsorption rate constants, k , depending on aggregate size. Adsorption of asphaltenes on mineral surfaces leads to complex, step-wise isotherms, showing a slow and very significant change with time.¹¹ For all solutions but the very diluted ones, the high amount adsorbed on silica (ν) should be accounted for in terms of multilayer formation, aggregate adsorption, or both.

Multilayer formation is related to asphaltene–asphaltene interactions in toluene. Similarly, aggregate adsorption is related to aggregate formation in solution. Hence, adsorption could be used as a tool for the study of solution properties.

For instance, it has been reported that asphaltenes in general are a mixture of two main fractions.¹⁴ One of them, called A₁ (about 70% of the mixture), has a very low solubility in toluene (about 90 mg L⁻¹). The other, called A₂, has a much higher solubility (57 g L⁻¹) similar to the solubility of the total mixture. Thus, it is very likely that the strong tendency of aggregation of asphaltenes is due to the presence of an insoluble fraction (A₁) present in very large quantities. Thus, when the solubility value is approached, this fraction would begin to form aggregates which, when pure, would grow without limits leading to phase separation. However,

the presence of A₂ appears to limit aggregate size leading to soluble species.

The A₁ solubility suggests that aggregate formation should be expected at very low concentrations and that relatively large size aggregates could be expected for any concentration above 90 mg L⁻¹. It is the hypothesis of the present paper that some of these solution properties could be reflected in the adsorption behavior of asphaltenes.

In principle, as a first approximation, a Langmuir-type adsorption kinetics model could be used to describe asphaltene adsorption, provided such a model could predict the main features of asphaltene adsorption, such as aggregation in solution and the stepwise isotherms mentioned above.

As shown elsewhere,¹² asphaltene adsorption is either an irreversible process or the desorption step is so slow that cannot be detected after normal time periods (less than 3% after one week.) This suggests that for all practical purposes, the process is irreversible and can be modeled by the adsorption step alone (no desorption).

In this paper, we have measured the adsorption kinetics of asphaltenes at the toluene–silica interface. As shown below, aggregate formation in solution is likely to be the reason for both the large reduction in k observed when C_S is increased and for the step-wise adsorption isotherms of asphaltenes. The adsorption kinetics was evaluated using a simple second-order L-type adsorption model consistent with aggregate formation and with the observed step-wise adsorption.

Experimental Section

Asphaltenes were obtained from Furril crude oil (20° API) using the following procedure: 40 volumes of *n*-heptane were added to the oil with stirring. After the addition, the stirring was continued for 6 h and the mixtures were allowed to stand overnight. The precipitated solid was filtered, washed several times with *n*-heptane to remove part of the co-precipitated resins, and placed within a Soxhlet extractor where the rest of resins were removed under continuous extraction with boiling *n*-heptane (about 24 h). About a 7% yield of asphaltenes was obtained after this treatment.

A thin-layer silica gel 60 supported on Teflon plates (from Merck) was used. An area of 44 m²/g was determined by measuring the adsorption isotherm of *p*-nitrophenol (PNP) as reported elsewhere.¹⁵

Adsorption Kinetics. Kinetics experiments were carried out by continuously measuring the light absorption in toluene asphaltene solution in contact with silica plates. The instrument used for these experiments was a dual beam spectrometer developed by using a He–Ne laser as a light source. This procedure was necessary in order to perform direct light absorption measurements in high-concentration solution.

The schematic diagram of the instrument is shown in Figure 1. A 632.8 nm laser beam from a He–Ne laser (15 mW Melles Griot) is split by 75:25 beam-splitter. One beam is focused onto the sample cell and light transmission is measured by a photodiode. The second beam is used as reference, passing through a cell containing only the solvent, measuring its intensity by using identical photodiode. Both registered signals were acquired by a personal computer using ADC/DAC board (Lab-PC card from National Instruments). Well-capped glass vials were used as spectrophotometric cells.

Solutions (5 mL) of the required concentration were placed within small vials. The silica plate (1 cm², equivalent to 10

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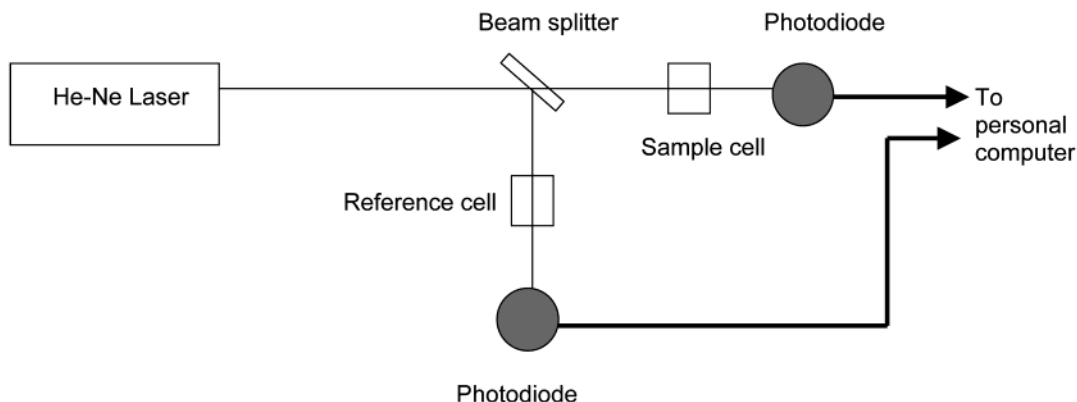


Figure 1. Optical assembly used for absorbance measurements.

mg of silica) was carefully immersed in the solution and measurements were recorded during the required time at room temperature.

Kinetics plots were obtained by plotting the solution absorbance $A(t)$ as a function of the time. $A(t)$ was converted to solution concentration $C_S(t)$ (mg L^{-1}) using eq 1:

$$C_S(t) = A(t) \frac{C_0}{A_0} \quad (1)$$

Here C_0 and A_0 are the initial concentration and initial absorbance, respectively. The amount adsorbed at any time ν (mg L^{-1}) was obtained from eq 2:

$$\nu = C_0 - C_S(t) \quad (2)$$

and could be converted to mg g^{-1} using eq 3:

$$\nu = [C_0 - C_S(t)] \frac{V}{m} \quad (3)$$

Here, V is the solution volume (L) and m is the mass of silica.

Adsorption Isotherms. The adsorption isotherms were determined by measuring the reduction in concentration of asphaltenes in toluene solutions after the contact with silica plates. The concentration was determined by measuring the visible light absorption registered at 400 nm. The instrument used for these experiments was a UV–visible spectrometer from Hewlett-Packard (model 8450A). Two different calibration curves were necessary to cover the wide solution concentration ranges. These calibration curves were obtained by using cells with different optical path. Cells with 2 mm and 10 mm optical paths for relatively high and low concentration ranges were used, respectively. The experimental procedure was as follows: 25 mL of toluene solution of asphaltenes were transferred to cylindrical glass vials. Silica plates (2.5 cm^2) were placed in each of the vials and well capped using Teflon stoppers. The containers were placed within desiccators at room temperature in a toluene atmosphere. The silica plates were withdrawn for solution analysis when required.

Second-Order Kinetics. Let C_0 be the initial solution concentration and k the observed second-order adsorption rate constant. Let ν be the concentration of solute adsorbed after a time t and ν_∞ the amount adsorbed after a very long time. The adsorption rate could be written in term of eq 4:

$$\frac{d\nu}{dt} = k(\nu_\infty - \nu)(C_0 - \nu) \quad (4)$$

Equation 4 simple states that the adsorption rate at any time is proportional to the number of available sites in the surface and to solution concentration. Using standard procedures, eq

4 could be integrated between $\nu = \nu$, $t = t$, and $\nu = 0$, $t = 0$, to afford eq 5:

$$\ln \frac{\nu_\infty(C_0 - \nu)}{C_0(\nu_\infty - \nu)} = (\nu_\infty - C_0)kt \quad (5)$$

This could be rearranged to obtain eq 6 or ν in terms of time $\nu(t)$:

$$\nu = C_0 \nu_\infty \frac{\exp[(C_0 - \nu_\infty)kt] - 1}{\exp[(C_0 - \nu_\infty)kt] C_0 - \nu_\infty} \quad (6)$$

It is easily shown that this equation leads to a typical saturation curve similar to the usual Langmuir isotherm (L-type curve). For instance, for $t = 0$, $\nu = 0$; and for very long times or large solution concentration ($\exp(C_0 - \nu_\infty)kt \gg 1$ and $\exp(C_0 - \nu_\infty)kt \gg \nu_\infty$). Hence, $\nu = \nu_\infty$.

For convenience, the concentration unit used in this work is mg L^{-1} . This means that k units are $\text{L s}^{-1} \text{mg}^{-1}$. The following procedure should be used for conversion to $\text{L s}^{-1} \text{mol}^{-1}$):

$$k \frac{\text{L/s}}{\frac{\text{mg}}{\text{mg}} \frac{\text{g mol}}{\text{M} \cdot \text{g}}} = \frac{\text{L} \cdot \text{M}}{\text{s} \cdot 0.001} = 1000 M \cdot k \quad (7)$$

Here M is the molecular weight.

Results

Figures 2 to 4 show the plots of ν against time for 3 different C_0 values (20, 200, 3000 mg L^{-1}) Curves in these plots are fittings to eq 6. These were performed as follows: for each C_0 , values were given to k and ν_∞ to obtain ν from eq 6 at each time. Solution concentration C_S was found using eq 2, converted to absorbance $A(t)$ using eq 1 and plotted against time, along with the experimental absorbance as shown in Figures 2 to 4. In Table 1, the values of ν_∞ and k leading to the best fitting to eq 6 are shown. Values of r^2 were in the 0.97 to 0.99 ranges.

According to previous work¹³ using the present silica surface, an H-type isotherm was obtained after 8 days for Furrial asphaltene adsorption at the toluene–silica interface. This is an L-type isotherm which intersects the ν axis above 0, at $C_S = 0$. It was found that for any $C_0 < 50 \text{ mg L}^{-1}$, all solute was adsorbed after this time leading to $\nu = 13 \text{ mg g}^{-1}$ at $C_S = 0$.

This quantity (13 mg g^{-1}) could be taken as the minimum required for a monolayer. Thus, division of

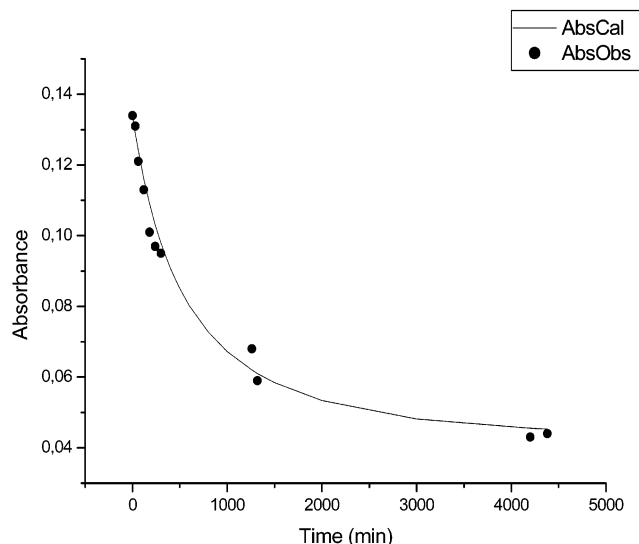


Figure 2. Comparison of calculated and experimental absorbances for the adsorption kinetics of Furrial asphaltenes at the toluene-silica interface. For $C_0 = 20 \text{ mg L}^{-1}$ at room temperature.

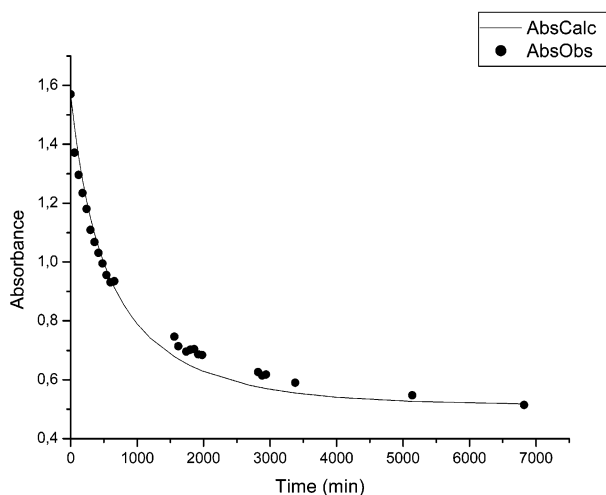


Figure 3. Comparison of calculated and experimental absorbances for the adsorption kinetics of Furrial asphaltenes at the toluene-silica interface. For $C_0 = 200 \text{ mg L}^{-1}$ at room temperature

the ν_∞ by this quantity gives a parameter related to the number of asphaltene layers adsorbed (see Table 1).

Figure 5 shows the adsorption isotherms calculated at different times using eq 6 and the results in Table 1. These calculations were performed using the values of C_0 , ν_∞ , and k in Table 1 at the particular times indicated in Figure 5. This could be compared with the experimental adsorption isotherms shown in Figure 6.

The comparison shows that the stepwise nature of the adsorption could be reasonably predicted by the present model.

Discussion

Equation 6 corresponds to a simple Langmuir-type or L-type adsorption kinetics and as such it should be valid for simple solutes adsorbing on a homogeneous surface and for monolayer adsorption without any significant interactions between the adsorbates. Also,

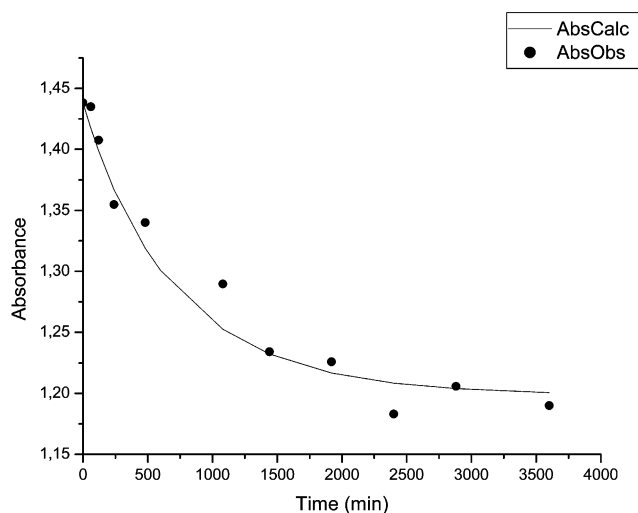


Figure 4. Comparison of calculated and experimental absorbances for the adsorption kinetics of Furrial asphaltenes at the toluene-silica interface. For $C_0 = 3000 \text{ mg L}^{-1}$ at room temperature.

Table 1. Values of ν_∞ and k Obtained after the Fitting of Kinetic Data to Eq 6

| C_0 (mg L^{-1}) | ν_∞ (mg L^{-1}) | ν_∞ (mg g^{-1}) | ν_∞ 13.61 ^a | k L/(s mg) | k_5/k^b | r^{2c} |
|---------------------------------|--|--|------------------------------------|-----------------|-----------|----------|
| 5 | 4.92 | 1.58 | 0.11 | 3.8E-4 | 1 | 0.982 |
| 20 | 13.5 | 4.32 | 0.31 | 1.0E-4 | 3.8 | 0.988 |
| 50 | 42.55 | 13.61 | 1 | 5E-5 | 7.6 | 0.965 |
| 100 | 34 | 10.88 | 0.8 | 4E-5 | 9.5 | 0.989 |
| 200 | 134.52 | 43.04 | 3.31 | 1E-5 | 38 | 0.99 |
| 400 | 369.8 | 118.7 | 8.72 | 2.7E-6 | 140 | 0.99 |
| 800 | 324 | 103.7 | 7.6 | 1.00E-6 | 380 | 0.987 |
| 1500 | 500 | 160 | 11.75 | 8.00E-7 | 475 | 0.976 |
| 3000 | 500 | 160 | 11.75 | 5.00E-7 | 760 | 0.976 |

^a Third column was used for this calculation. ^b k_5 corresponds to the 5 mg L^{-1} rate. ^c Linear correlation between calculated and observed absorbances.

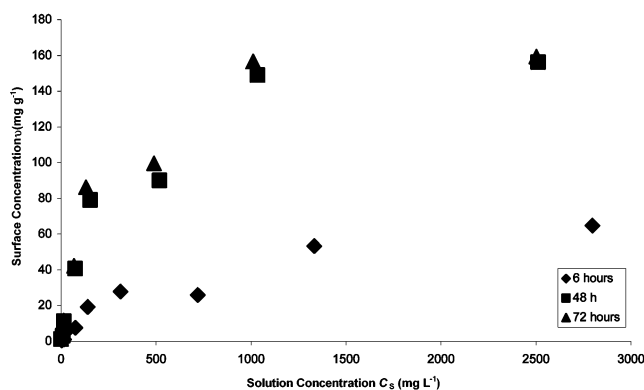


Figure 5. Calculated adsorption isotherms of Furrial asphaltenes for the toluene-silica interface computed at different times.

since concentrations instead of activities are used, ideal behavior, both in solution and at the surface, is presumed.

In real cases approaching these ideal conditions, both k and ν_∞ should be constants independent of solution concentration.

Probably none of these conditions are met by an asphaltene solution adsorbing on silica. However, eq 6 could be useful when the effect of the several factors causing non-ideality leads to systematic deviation of the

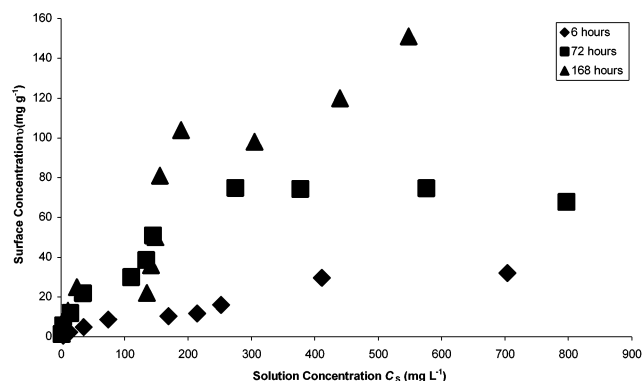


Figure 6. Observed adsorption isotherms of Furrial asphaltenes for the toluene–silica interface measured at different times at room temperature.

ideal behavior. Solute aggregation in solution is the most relevant factor in the present case. Hence, for the same surface, we should expect an increase in ν_{∞} and a decrease in k when C_0 is increased (see Table 1 and below).

As mentioned in the Introduction section, adsorption of asphaltenes from silica is practically irreversible and thus no desorption step was considered in this work.

As shown in Table 1, very different values of ν_{∞} and k were calculated in the concentration range examined. The increase in ν_{∞} and the decrease in k can both be accounted for in terms of aggregate formation in solution.

Thus, when an asphaltene solution is prepared, aggregates will form in a concentration and size depending on the total or initial concentration C_0 . For very low C_0 , aggregate concentration C_a would be very small or negligible. Both C_a and aggregate size would grow with C_0 . Thus, when C_0 is increased, aggregates and single molecules would be adsorbed in ratios depending on C_0 .

The results in Table 1 suggest that aggregate formation reduces k in a very significant extent. This is a reasonable suggestion on several accounts: adsorption on the mineral surface is due to interactions with active molecular sectors of the solute, many of which would not be available after aggregate formation. Besides, diffusion along the surface to find an adsorption site is expected to be reduced by aggregate size.

According to these arguments, all solutions appear to “see” the same silica surface. When aggregates are present they would adsorb as such on the surface. For all solutions, but the more diluted ones, complex mixtures of single molecules and aggregates of different sizes are expected. Some of these aggregates would require a relatively high C_0 to be formed or adsorbed. The result would be a stepwise isotherm such as the one shown in Figure 6.

As mentioned above, the quantity $\nu = 13.61 \text{ mg g}^{-1}$ could be reasonably taken as the amount required for a monolayer. If so, the values $\nu_{\infty}/13.61$, for any $\nu_{\infty} > 13.61$ in Table 1 could be related to the average size of the aggregates adsorbed.

According to the present results, asphaltene aggregation appears to be present at very low solution concentrations. Results in Table 1 suggest aggregation below

$C_0 = 200 \text{ mg L}^{-1}$. These results are consistent with the solubility data discussed above (see the Introduction section), and with others reported where a thermal lens technique was used to show that aggregation of asphaltenes in toluene (room temperature) could be expected between 50 and 100 mg L^{-1} .¹⁶ Similar low aggregation values were suggested by an NMR ^1H relaxation technique.¹⁷

Also, results in Table 1 suggest that large aggregates could be expected for solutions between 400 and 3000 mg L^{-1} (0.04 to 0.3%) These concentrations are well above A_1 solubility (90 mg L^{-1}), and thus presence of large aggregates in them is not surprising.

As suggested by the solubility data, formation of soluble aggregates is likely to be due to low solubility of A_1 combined with association with A_2 . The structural features, responsible for the vast difference in solubility of these fractions, are a matter for future research. However, at this time these appear to be related to the presence in A_2 of groups, such as long alkyl chains, which promotes a loose packed mixed aggregate A_1 – A_2 . Consequently, an aggregate of relatively lower solubility parameter would form, accounting for the higher solubility compared to A_1 alone.

As could be inferred from the above argument, the mechanism for the formation of soluble aggregates of asphaltenes in toluene and other organic aromatic solvents is thus quite different from the one proposed for micelle formation in oily media. In this case, the low oil affinity of the polar head is the driving force for surfactant aggregation.

Although both mechanisms appear to be quite different, they should respond in a manner similar to that of the probes used to detect them. In our view, this is the source of the confusion, which regards asphaltenes as surfactant-like materials forming “asphaltenes micelles” at some “critical micelle concentrations”.

Conclusions

The kinetics results obtained (large reductions in k and significant increases in ν_{∞} when C_0 is increased) suggest that adsorption events are dependent on the solution properties of asphaltenes and could be used to obtain important information regarding aggregation in solution. Thus, formation of large aggregates is suggested by very low k and large ν_{∞} . These large aggregates are expected in view of the very low solubility of the major fraction of asphaltenes (fraction A_1).

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