Aggregation and Adsorption of Asphaltenes: A kinetic Study.

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Introduction

Adsorption kinetics could be a useful and simple tool for the study of asphaltene aggregation in solution and some preliminary results has been reported[1]. In principle adsorption of aggregates should lead to different adsorption rate constant k depending on aggregate size. Since a dependence of aggregate size with concentration could be expected this should lead to a dependence of k and ν_∞ with concentration. Here ν_∞ is the surface concentration ν required for surface saturation (see below). It has been reported elsewhere[1] that for diluted toluene solutions, adsorption of asphaltenes on silica is an essentially irreversible process. As shown below this fact could be used to simplify the adsorption kinetics. In this paper, we have measured the adsorption kinetics of several asphaltenes solutions at the silica – toluene interface. The results were fitted to a second order irreversible kinetics and the k and ν_∞ evaluated. As shown below, the strong dependence of these parameters on initial C_0 concentration could be allow for in terms of aggregate size in solution.

Experimental

Asphaltenes were obtained from Furrial oil (20° API) by addition of 40 volumes of n – heptane. The flocculated solid was thoroughly washed with this solvent in Soxhlet as described earlier[2]. A thin layer silica gel 60 supported on Teflon plates, (from Merck) was used. Kinetic measurements were performed by dipping the plates within vials containing the toluene solutions of asphaltenes (5 to 3000 mg/L). Absorbance changes with time was monitored using a He – Ne laser beam (632.8 nm) by passing the beam through solution and solvent using a beam splitter.

Kinetics plots wereobtained by plotting the solution absorbance $A(t)$ as function of the time. $A(t)$ was converted to solution concentration $C_S(t)$ (mg/L) using equation 1:

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

Here C_0 and A_0 are the initial concentration and initial absorbance respectively. Amount adsorbed at any time ν (mg L^{-1}) was obtained from equation 2 and could be converted to mg/g using equation 3.

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

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

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

Kinetic runs were fitted to a second order Langmiur type irreversible process. The corresponding equation was derived as follows. Let ν be the amount of sample adsorbed after time t. Let C_0 be the initial solution concentration. Let k and ν_∞ be the second order rate constant and the saturating surface concentration respectively. Then the increase of ν with time can be written as follows:

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

Solution of this equation is:

$$\nu = C_0\nu_\infty \frac{\exp[(C_0 - \nu_\infty)kt] - 1}{\exp[(C_0 - \nu_\infty)kt]C_0 - \nu_\infty} \qquad 5$$

It could be easily shown that for any values of C_0, ν_∞ and k, ν will increase from 0 to the limiting value of ν_∞ when either the time or C_0 are increased.

Results and Discussion

Figure 1 shows the results of the kinetic run for C_0 = 200 mgL^{-1}. Similar results were obtained for other initial concentrations and the complete results are shown in Table 1. In this Figure, the points are experimental and the curve is the fitting to equation 5 with the corresponding k and ν_∞ values. As shown in Table 1, these parameters depends strongly on C_0. Thus over the concentration range, k decreases 760 fold whereas ν_∞ increases about 100 fold.

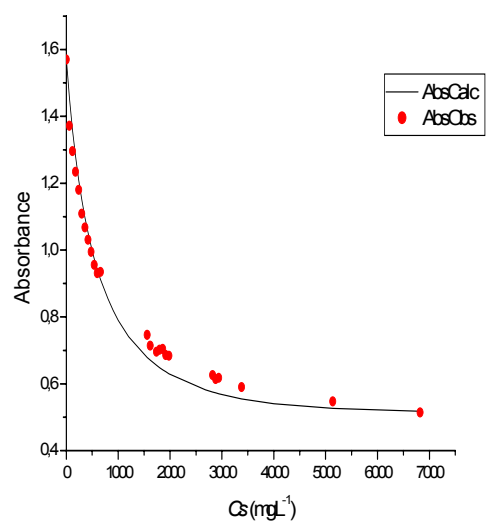

Figure 1. Comparison of observed and calculated absorbances for C_0= 200 mgL^{-1}. Curve is the fitting of equation 5 to the experimental results.

Table 1. Change of Second Order Rate Constant k and ν_∞ With the Initial Concentration C_0

C_0 (mg L^{-1})	ν_∞ (mg g^{-1})	k (L s^{-1} mg^{-1})	k/k$_5$
5	1.58	3.8E-4	1
20	4.32	1.0E-4	3.8
50	13.61	5E-5	7.6
100	10.88	4E-5	9.5
200	43.04	1E-5	38
400	118.7	2.7E-6	140
800	103.7	1.00E-6	380
1500	160	8.00E-7	475
3000	160	5.00E-7	760

These results are consistent with aggregate formation in solution and with a change in aggregate size as the initial concentration is increased. A decrease in k should be expected with an increase in aggregate size. This could easily be seen using a simple mass balance argument. Let A_T be the total molar concentration of asphaltene (equivalent to C_0), let A_S be the molar solution concentration of free asphaltene (equivalent to C_S) and let A_n be the molar concentration of aggregates where n is aggregation number. Then according to mass balance:

$$A_T = A_S + n\ A_n \qquad 6$$

Adsorption on the silica surface occurs through bonding between functional groups in molecules and sites on the silica surface. Let f_i be the number of these functional groups in each molecule. Their total number in solution would be:

$$A_T\ f_i = A_S\ f_i + n\,(f_i\ A_n) \qquad 7$$

As suggested by equation 7, many functional groups would be involved in aggregate formation and would not be available for adsorption. In other words, all but those in the aggregate surface would not be available for adsorption.

Figure 2 is a plot of –ln k against C_0 which suggest that aggregate size grows "sigmoidaly" with C_0, approaching a sort of limiting size.

One could imagine that, when contacted with the silica surface, every solution in Table 1 "sees" the same surface. Thus the high values of ν_∞ found at most C_0 in Table 1 should be due mainly to aggregate adsorption and not to multilayer formation. In principle mean aggregate size could be estimated from these ν_∞ values.

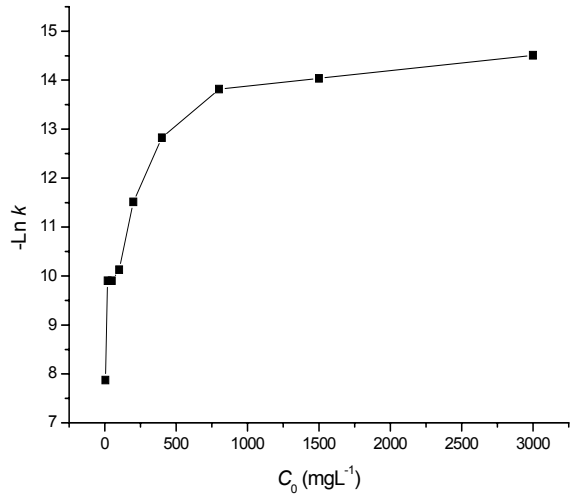

Figure 2. Change of –Ln k with the initial concentration C_o

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