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A Study of Multilayer Adsorption of Asphaltenes on Glass Surfaces by Photothermal Surface Deformation. Relation of This Adsorption to Aggregate Formation in Solution

Sócrates Acevedo,* Jimmy Castillo, Alberto Fernández, Sonia Goncalves, and María A. Ranaudo

Escuela de Química, Facultad de Ciencias, Universidad Central de Venezuela, P.O. Box 47102, Caracas, Venezuela 1041-A

Adsorption of asphaltenes on glass surface has been studied by using photothermal surface deformation spectroscopy. This technique was adapted for direct measurement of the amount of asphaltene adsorbed on glass plate surfaces. Solid-solution adsorption isotherms for asphaltenes were obtained at room temperature in toluene. Stepwise or multilayer adsorption was detected in the three cases examined (Furrial, Jobo, and Hamaca) after long contact periods. After the first layer due to glass surface saturation one (Jobo and Hamaca) or two (Furrial) further layers were measured. Analysis of results suggests that this adsorption behavior could be related to the sudden increase of aggregate concentration typical of micelle formation. For instance, below 4000 mg/L Furrial asphaltenes behave like a mixture containing two surfactants with cmc of 1500 and 3000 mg/L, respectively. A slow increase in molecular weight when measured in toluene was observed for Hamaca (from 4230 to 17420) and Cerro Negro (from 5350 to 15170) over a 3 day period, suggesting a slow formation of aggregates. Accordingly, the above stepwise adsorption takes a long time to appear (more than 3 days). Isotherms measured at shorter times only showed a continuous but not stepwise increase in adsorption with concentration.

1. Introduction

Asphaltenes can be defined as high molecular weight components of crude oils. These components are a very complex mixture of compounds, which exist in petroleum as a colloidal dispersion. Flocculation of these colloids leading to clogging of pipes and other production facilities is a matter of extraordinary importance, both from the industrial and academic point of view, owing to its negative impact on the petroleum industry. Chemical analysis of these pipe deposits confirms the presence of large amounts of asphaltene and resins and lower but significant amounts of inorganic material (mostly SiO_2).[1] The presence of inorganic material in these deposits is interesting in terms of their role during the formation of the deposit itself. The free energy of asphaltenes in crude oil is probably related to the stability of their colloidal aggregates or micelles. On the other hand, instability accounts for the tendency of asphaltenes to precipitate from crude oils under a variety of circumstances and to be adsorbed on interfaces of any kind. This is a general problem related to nucleation and particle growth. For instance, it is well-known[2] that the change in free energy ΔG for the formation of spherical nuclei or colloids of radius R from

a supersaturated solution of concentration C_s is given by eq 1, where n is the number of molecules forming

$$\Delta G = -nkT \ln C_s/C_0 + 4\pi R^2 \gamma \qquad (1)$$

the colloidal particle, C_0 is the concentration of saturated solution in equilibrium with a large and flat surface of solid solute, γ is the interfacial tension, k is the Boltzman constant, and T is the absolute temperature. According to eq 1, an energy barrier given by the term $4\pi R^2 \gamma$ must be surmounted before the appearance of solid phase. The numbers of molecules forming the colloidal particle can be calculated by

$$n = \frac{4}{3}\pi \frac{R^3}{V_m} \qquad (2)$$

where V_m is the molecular volume. Substituting (2) in (1)

$$\Delta G = -\frac{4}{3}\pi \frac{R^3}{V_m} kT \ln(C_s/C_0) + 4\pi R^2 \gamma \qquad (3)$$

Therefore, ΔG goes through a maximum at R_m when plotted vs R. In fact, the Kelvin equation (4) is obtained for R_m by setting $\partial \Delta G/\partial R$ equal to zero at this point:

$$kT \ln\left(\frac{C_s}{C_0}\right) = \frac{2\gamma}{R_m} \qquad (4)$$

(1) Acevedo, S.; Ranaudo, M. A.; Escobar, G.; Gutierrez, L. B.; Ortega, P.; *Fuel* **1995,** *74,* 595–598.
(2) See for instance: Evans, D. F.; Wennerstrom, H. *The Colloidal Domain. Where Physics, Chemistry, Biology and Technology Meet;* VCH Publishers, Inc.: New York, **1994.** Chapter 4; p 136.

Table 1. Some Properties of Asphaltenes and Crude Oils

sample	% asphaltenes	API[a]	elemental analysis[b]			H/C[b]	$M_n^{b,c}$
			C	H	N		
Hamaca	12	9	81.7	7.7	1.7	1.13	2200
Furrial	21	10	85.5	6.9	1.6	0.97	1700
Jobo	10	7.6	81.6	7.6	1.7	1.12	2300

[a] API gravities of crude oils. [b] Corresponding to PA asphaltenes. [c] By GPC in THF.

Equation 3 shows that if R is smaller than R_m, ΔG would be positive and the new phase will not appear. However, if enough thermal energy is available, small nuclei (or colloids) will form when $R < R_m$. Also, any kinetic effect that hinders flocculation could stabilize the colloid at $R < R_m$. In general, given supersaturation, nuclei will grow, ΔG in eq 3 becomes negative, and crystallization or flocculation may eventually occur. Of course, the surface energy term $4\pi R^2 \gamma$ in eq 3 is the source for the flocculation barrier and usually flocculation starts at the walls or any other surface where the corresponding surface energy and capillary barrier are lower. The surface flocculation will be enhanced if the solute is being adsorbed on such surface, more so if multilayer can be formed since in such case, barriers due to surface saturation would be reduced. According to the foregoing arguments, adsorption and multilayer formation by asphaltenes on surfaces should be of paramount importance since surface flocculation could be the beginning of the clogging problems mentioned above. Although many studies have reported adsorption of asphaltenes on a variety of surfaces, these were undertaken under highly diluted conditions where Langmiur type adsorption is generally found, and no evidence for multilayer formation is reported.[3,4] Previously we tried to find a relationship between multilayer formation by asphaltene and their precipitation tendency in the crude oil. However, in general when the usual optical absorbance technique was employed we found serious difficulties in measuring the amount of adsorbed material.[1] These problems were overcome by measuring the adsorbed material directly using the photothermal surface deformation spectroscopy as reported earlier.[6]

2. Experimental Section

Asphaltenes and Resins. The asphaltenes and resins mixtures were precipitated by addition of 60 volumes of *n*-heptane to a 1:1 v/v mixture of crude oil and toluene, as described earlier.[5] The precipitate was filtered and a portion of this was studied as such and we call it sample AR (asphaltenes plus resins mixture). The other was Soxhlet extracted with *n*-heptane during 4 days to remove the coprecipitated resins. This asphaltene without resins is called PA (pure asphaltenes) in this work. The asphaltenes were obtained from Hamaca, Jobo and Furrial crude oils and some properties of these crude oils and their asphaltenes are collected in Table 1.

Adsorbent. The adsorbents used throughout this work were precleaned microscope glass slides supplied by Fisher

(3) Gonzalez, G.; Middea, A. *J. Disp. Sci. Technol.* **1987**, 8, 525–548.
(4) Collins, S. H.; Melrose, *J. C. Soc. Pet. Eng. AIME* **1987**, SPE 11800, 249–256.
(5) Acevedo, S.; Mendez, B.; Rojas, A.; Layrisse, I.; Rivas H. *Fuel* **1985**, *64*, 1741–1748.
(6) Castillo, J.; Fernandez, A.; Goncalves, S.; Mujica, V. *Opt. Commun.*, in press.
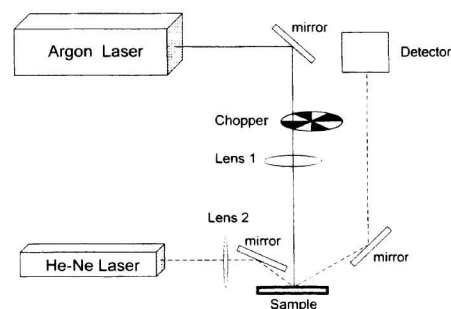

Figure 1. Optical setup for surface deformation spectroscopy measurements.

Scientific Co., without pretreatment, and cut in pieces of approximately 10 × 25 mm. In this preliminary study, we use glass as a convenient surface to perform the adsorbtion experiments. At the moment we are developing tecniques to work with surfaces of any kind.

Solution Preparation. For adsorption isotherms, a stock asphaltenes solution (around 10 000 mg/L) was prepared by dissolving an appropriate amount of dried asphaltenes in toluene. The mixture was left in a thermostated ultrasonic bath for 30 min to ensure a complete dissolution. Finally the solution was diluted to a desired volume using the appropriate amount of toluene.

Isotherms. For these experiments, the glass plates were dipped into solutions contained in cylindrical glass vials and capped with Teflon stoppers. The containers were placed within a desiccator at room temperature in a toluene atmosphere and withdrawn for plate analysis when required. Photothermal surface deformation signals were measured for each plate at different points of the surface and appropriate averages of the signals were made. Care was taken to measure away from plate borders where erroneous measurements could result. Adsorption isotherms were obtained by plotting the asphaltenes surface concentration in mg cm^{-2} as a function of solution concentration (C_s) in mg/L. Adsorption isotherms were studied in the concentration range of 100–6000 mg/L.[6–8]

Molecular Weight Measurement. These were measured in toluene by the VPO technique using benzyl as calibration standard as described earlier.[5] With this technique it is intended to measure molecular weigth changes with time of the asphaltenes fractions in toluene solution as a result of aggregates formation.

Photothermal Surface Deformation Measurement. The adsorption of asphaltenes and resins was determined by measuring directly onto the glass surface plates the amount of adsorbed material using the photothermal surface deformation (PSD) technique. PSD offers some advantages[6–8] compared to the traditional spectroscopy absorption techniques: Direct measurement of the adsorbed material can be made; its wide linear dynamic range allows to perform experiments with high concentrated asphaltenes solutions (0–10 000 mg/L).[6–8]

Experimental Setup. A diagram of the experimental assembly shown in Figure 1 has been previously described.[6] The 514 nm beam from CW argon laser (Coherent Innova 300) was intensity modulated with an mechanical chopper at 15 Hz and then focused to a 50 μm diameter spot onto the sample surface. The photothermal surface deformation was monitored with a He−Ne laser (Melles Griot) whose beam was focused to a diameter of 200 μm. The reflected probe beam was directed to a silicon photodiode situated after a 150 μm pinhole.

(7) Olmstead, M.; Amer N.; Kohn, S.; Fournier, D.; Boccara, A. *Appl. Phys.* **1983**, *A32*, 141–154.
(8) Welsh, E. *Absorption Measurement, in Thin Films for Optical Coating*; Hummel, R. E., Guenthe, K. H., Ed.; CRC Press Inc.: Boca Raton, Fl, 1995; Chapter 9, pp 243–274.
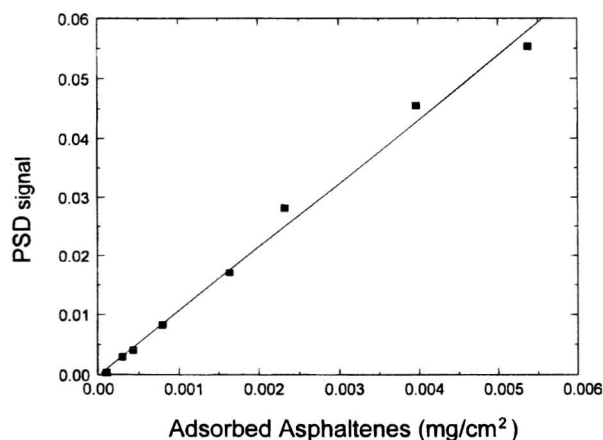
Figure 2. Calibration curve for surface deformation spectroscopy measurements for Hamaca asphaltenes. Parameters for this lines were intercept -4.3×10^{-6}, slope 1.08, and $r^2 = 0.996$.

The detector photocurrent was amplified by a transimpedance amplifier (Melles Griot 13-AMP-003). The amplified photocurrent was transduced to a PC (AT 486) with an ADC/DAC board (Lab-PC card, National Instruments). The first step in our work was the evaluation of PSD response as a function of the amount of adsorbed material. In this sense, calibration curves were made using standard glass plates with a known amount of adsorbed asphaltenes. These calibration plates were prepared by adding a known volume of different concentration asphaltenes toluene solutions to a clean glass plate and left at room temperature for completely solvent evaporation. The asphaltene spot was carefully measured and was used to calculate the asphaltene mass deposited per area. The PSD signals were measured in each plate and the average signal was plotted as a function of asphaltene mass deposited per area. Figure 2 show a typical calibration curve obtained for Hamaca asphaltenes. It is observed that the PSD signal increases linearly with the amount of adsorbed asphaltene; no signal saturation is observed in the studied concentration range. Similar behavior was obtained for all the asphaltenes studied in this work. Calibration lines were obtained for each sample type in a wide concentration range. These calibration lines were used to determine the amount of adsorbed sample in all further experiments. It should be mentioned that as usual, a film of toluene solution adheres to the plate when it is withdrawn from solution. We found that this introduces large errors in measurements at low concentrations (below 200 mg/L). Since in this work we are interested in solution concentrations higher than 500 mg/L for which the above has no consequence, we neglected this effect.

3. Results and Discussion

Molecular Weight. Table 2 shows the number average molecular weight (M_n) for AR and PA asphaltenes samples obtained from Hamaca and Cerro Negro crude oils determined at different times whithin 0–216 h, measured from solution preparation time. It is observed that M_n values for AR (asphaltenes plus resins) samples did not change significantly and could be averaged, yielding values of (2770 ± 370) and (2970 ± 370) for Hamaca and Cerro Negro samples, respectively. However, for PA samples (pure asphaltenes), an increase in M_n is observed after 48 h, increasing more than 3 times the M_n value obtained at 0 h. Higher values of M_n than those shown in Table 2 cannot be measured by the VPO technique.

Table 2. Number Molecular Weight (M_n) Determined by VPO for Asphaltene Samples with Resins (AR) and without Resins (PA) as a Function of Time

sample	time (hours)						
	0	24	48	72	96	144	216
Hamaca							
AR	2760	2820	2850	3350	2380	3000	2230
PA	4230	4330	17420	*a*	*a*	*a*	*a*
Cerro Negro							
AR	2570	3220	2880	2570	*b*	3500	3100
PA	5350	5470	10720	15170	*a*	*a*	*a*

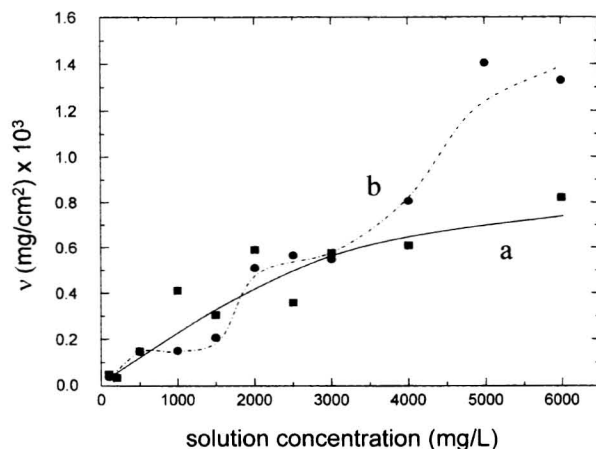*a* Too high to be measured by VPO. *b* Not determined.

Figure 3. Adsorption isotherms for Furrial asphaltenes (sample PA) measured at different times using PDS. Surface, glass plate; solvent toluene 25 °C. (a) 48 h; (b) 120 h.

Adsorption Isotherms. The solid-solution adsorption isotherms determined using the PSD technique are shown in Figures 3–6. In general, ν values changed with time in a different way for different samples, and therefore we decided to choose for analysis those times where the resulting isotherms gave a clear change for the derivative $d\nu/dC_s$, the slope, (see below). The precision for any $\nu(C_s,t)$, obtained after probing several spots on the surface was usually good (better than 5%). Reproducibility was somewhat poorer particularly where dn/dC_s was changing rapidly and since trends were clearly reproduced in all cases we decided to present the results of a single run rather than an average of them. As shown in Figures 3–6, asphaltene adsorption isotherms change with time over long periods, suggesting that both adsorption on the surface and solution equilibrium are very slow processes. After a long time, a stepwise curve is obtained for these PA samples (see curves 3b, 4c, and 5c). The first step should correspond to glass plate surface saturation. The ν values in this region are too high due to the small amount of solution remaining in the plate after its withdrawal (see Experimental Section). After this saturation step, one or two additional steps were formed due to multilayer formation. It should be mentioned that, since a new "asphaltene surface" is continuously generated after the first step a continuous increase in adsorption, such as the ones found for Jobo after 6 and 31 h, should be expected (see curves 4a and 4b). The stepwise adsorption could be analyzed by using the adsorption results to suggest the events happening in solution. As any sample which is polydisperse in molecular weight, asphaltenes are a
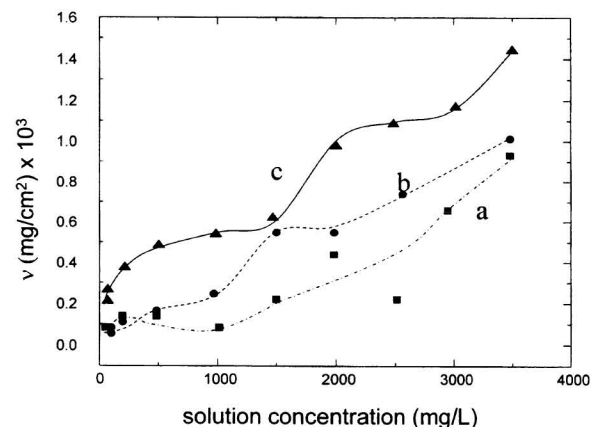
Figure 4. Adsorption isotherms for Jobo asphaltenes (sample PA) measured at different times using PDS. Surface, glass plate; solvent, toluene 25 °C. (a) 6 h; (b) 31 h; (c) 86 h.
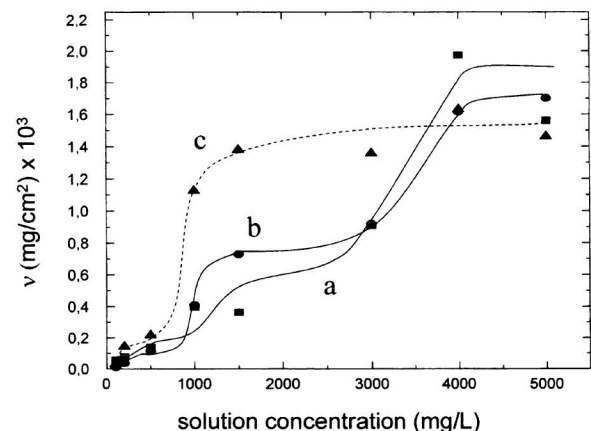

Figure 5. Adsorption isotherms for Hamaca asphaltenes (sample PA) measured at different times using PDS. Surface, glass plate; solution, toluene 25 °C. (a) 6 h; (b) 31 h; (c) 86 h.
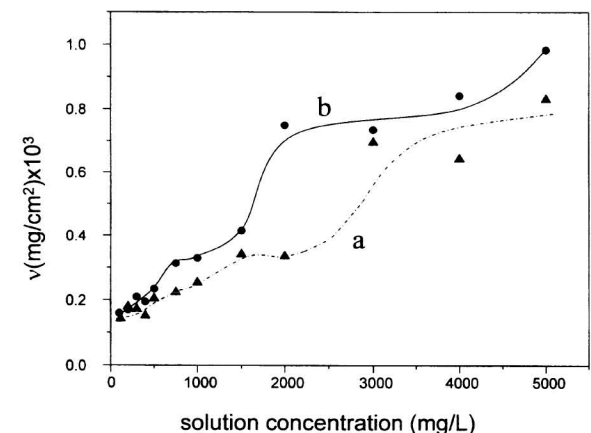

Figure 6. Adsorption isotherms for Hamaca asphaltenes measured at 120 h using PDS. Surface, glass plate; solution, toluene 25 °C. (a) Asphaltenes with resins (AR); (b) asphaltenes without resins (PA).

mixture of different molecular A_i species. These species will have different tendencies to aggregate in solution and to adsorb on surfaces. For simplicity and clarity suppose we have only two molecular types. In this case,

the total asphaltene concentration denoted by $[A]_T$ will be

$$[A]_T = A_{1T} + A_{2T} \tag{5}$$

were $[A]_{1T}$ and $[A]_{2T}$ are total concentration of molecular species A_1 and A_2 respectively. Let us suppose that from c_1 to c_2 solution concentration, only A_1, adsorbs significatively on the surface, where c_1 is the concentration corresponding to glass saturation and c_2 corresponds to significant aggregate formation for A_1. Thus, for A_1 we have

$$N_1 A_1 \rightleftharpoons A_{N_1} \tag{6}$$

$$K_1 = [A_{N_1}]/[A_1]^{N_1} \tag{7}$$

where N_1 is the number of molecules of A_1 forming aggregate A_{N_1} and K_1 is the corresponding equilibrium constant. Now, the total concentration $[A_1]_T$ is

$$[A_1]_T = N_1[A_{N_1}] + [A_1] \tag{8}$$

written in terms of the number of molecules of A_1 forming the aggregate and $[A_1]$ is the solution concentration of A_1 at c_1. Substitution of eq 7 in 8 leads to eq 9, where $[A_1]_{T,c_1}$ is the total concentration of A_1 at c_1. It

$$[A_1]_{T,c_1} = N_1 K_1 [A_1]^{N_1} + [A_1] \tag{9}$$

could easily be shown that if N_1 is high enough (N should be around 10 or more), the derivative $d[A]/d[A]_T$ suddenly becomes zero at $[A]_T = c_1$ and beyond. That is, we reach a point equivalent to a critical micelle concentration (cmc) for A_1 and therefore $[A_1]$ does not change beyond c_1.[9] Consequently, the increase in adsorption stops at c_1 and $d\nu/dc = 0$ from c_1 to c_2. At some $c_3 > c_2$ adsorption of A_2 becomes significant and repetition of the above aggregation or cmc process will lead to a second plateau. That is, each molecular type has its own cmc. Thus, at high enough total asphaltene concentration A_{Tc}, eq 10 is obtained:

$$A_{Tc_i} = \sum_{i=1}^{2} N_i K_i [A_i] N_i + \sum_{i=1}^{2} A_i \tag{10}$$

$$\sum_{i=1}^{2} A_i = \text{constant} \tag{11}$$

where N_i and K_i have the same meaning as before. Thus, the situation would be analogous to one corresponding to a mixture of independent surfactants with different K_i or cmc and eq 10 would be consistent with the two steps found in the adsorption curve for Furrial asphaltene after the glass saturation step. A similar analysis could be done for Jobo and Hamaca and the solution concentrations at which aggregation appears to begin are shown in Table 3 for these samples. Note that for Jobo $d\nu/dc$, although small, is not zero after the concentrations in this table (see also curve c in Figure 4). This could be due to an N value not high enough to make $d[A_i]/dA_T = 0$ after these c values. Although it is

(9) See ref 2, Chapter 4.

Table 3. Solution Concentration for Aggregate Formation for Pure Asphaltene Samples Studied

asphaltenes	concentration (mg L^{-1})	
	C_1	C_2
Hamaca	2000	4000
Jobo	2000	
Furrial	2500	

not very difficult to write a program to find fitting values for N and K in eq 10, this will go beyond the scope of the present paper. However, a rough calculation shows that in order to have distinguishable steps, as in curve b Figure 3, K values should differ from one another in at least one power of 10. The above stepwise adsorption behavior has been reported earlier for an organic surface prepared with Cerro Negro asphaltenes.[1] After this sample is heated at 350 °C for 11 h, a material insoluble in toluene was obtained. This was employed as the adsorbing solid and the isotherms for the same asphaltenes in toluene were obtained. A two-step isotherm resulted in this case where the first step leveled off at $c_1 = 1000$ mg/g and the second step started at around $c_2 = 3000$ mg/g and leveled off at $c_3 = 4000$ mg/g. Since the ν value corresponding to c_1 was 80 mg/g, a thick multilayer should be already present when c_1 is reached. Therefore, the second step cannot be due to multilayer formation. As discussed above, these two steps should be the consequence of aggregate formation in solution near the above c_1 and c_3 concentrations. As shown in Figures 3−5, adsorption of asphaltenes increases slowly with time. It is important to note that for reaching the stepwise behavior the system spends a time period of 3 days or more. A similar time is needed for aggregates to be detected by VPO for Hamaca and Cerro Negro experiments (see Table 2). When isotherms are taken before this time period, a fairly continuous increase in adsorption is observed beyond the zone corresponding to glass surface saturation. According to the arguments above, this behavior is expected when there are not aggregates in solution or their concentration is too low. It should be mentioned that in view of the complex nature of asphaltenes, quite different adsorption rates for different components of the mixture could be expected. This, no doubt, complicates matters even more. For instance, the above stepwise adsorption evidence could be blurred by later adsorption of very slow adsorbing compounds. As shown in curve b Figure 6 this seems to be the case for Hamaca asphaltenes for which an almost continuous adsorption was observed at 120 h. The changes in this isotherm as the concen-

tration is increased, are similar to those for AR sample (Figure 6) for which sudden changes in adsorption were not observed, probably due to the presence of resins. In spite of these complications due to the time dependence, we suggest that the above stepwise adsorption is a general property of asphaltenes due to aggregate formation in solution. If so, simple cheap methods such as the one reported[1] and commented above for Cerro Negro asphaltenes could be used for cmc determinations. Whatever the arguments used to account for the shape and time dependence of the above adsorption isotherms, these results give clear evidence for the formation of a thick asphaltene multilayer even in diluted toluene solutions. It is expected that under less favorable conditions, such as any approaching flocculation, flocks would form preferentially on this surface. Thus, if plugging of pores in rock well or clogging of production facilities by asphaltenes is to be avoided by the use of surfactants, we suggest that its ability to hinder asphaltene adsorption should be examined. As in the case for resins in sample AR (see Figure 6) a good dispersing surfactant such as resins[10] does not necessarily avoid asphaltene adsorption.

4. Conclusions

The stepwise adsorption observed in the isotherms of the examined asphaltenes has been related to aggregate formation in toluene solution. Sudden decrease of dν/dc near to zero value is described in terms of sudden increase in concentration of aggregates typical of micelle formation. Evidence for more than one solution concentration behaving like a cmc was found for some asphaltenes. Aggregate formation and asphaltene adsorption are very slow process which after several days gives evidence of changes. The thick multilayer formed in all cases examined should be a very favorable place where flocculation can start leading eventually to clogging and plugging problems.

(10) Leontarits, K. J.; Mansoori, G. *Soc. Pet. Eng.*, *SPE Paper No. 16258* **1987**, 149−158.