

# Applications of photothermal displacement spectroscopy to the study of asphaltenes adsorption

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## Abstract

We have developed an application of photothermal surface deformation (PTD) to study asphaltenes adsorption on inorganic surfaces. Using an appropriate ratio of the probe and excitation beam spot size at the sample surface we have been able to measure the magnitude of the PTD using a single photodiode detector. The magnitude of the PTD signal is shown to be related to the amount of adsorbed asphaltene. This technique offers a direct non-perturbing and completely contactless detection of adsorbed asphaltenes. Solute-solid adsorption isotherms (SSA) of asphaltenes from two Venezuelan extra-heavy oil (Jobo and Hamaca) were measured using a glass thin plate as adsorbent. The results obtained are in good agreement with those reported using conventional indirect techniques but better precision is achieved. © 1998 Elsevier Science B.V.

*Keywords:* Photothermal displacement spectroscopy; Adsorption studies; Asphaltenes

## 1. Introduction

In the past few years, spectroscopic techniques based on photothermal surface deformation have proved to be valuable tools to perform surface studies. These techniques offer great advantages such as high sensitivity, high spectral, spatial and temporal resolution and the possibility of carrying non-destructive and contact-less measurements [1,2]. Photothermal Deformation (PTD) technique, also referred as photothermal displacement, is based on detecting the deformation of the sample surface produced by the energy absorption from an incident light beam (called pump or 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 adsorbate which transforms the energy of the incoming laser in heat. This surface changes can be detected by measuring the reflectance, scattering transmittance or deflection of a weak probe beam that is reflected from the sample. If the pump beam irradiation is modulated, the photoinduced displacement rise and falls, and the reflected probe beam suffers changes in its reflection

angle. Measuring the magnitude of this deflection one can obtain the induced PTD amplitude.

Important features of photothermal displacement spectroscopy (PDS) include the ability to distinguish between surface and bulk properties and the absence of any electrical or mechanical contact with the samples during the measurement. These features have been used advantageously to developed techniques to study different systems [3–7].

Olmstead et al. [1,8] introduced PDS as a sensitive technique which directly measures the optical and thermal parameters of solids, surfaces and thin films. They describe three different experimental schemes for measuring the magnitude and phase of the optically induced surface displacement: Beam Deflection, Interferometric and Attenuated Total Reflection. The first method measures the curvature of the displacement while the other two detect the displacement itself. The beam deflection scheme was found to be the easiest of the three to implement and should be the most useful. In this method the sample is irradiated by a focused pump beam and a weak probe beam intensity is detected as reflected from the sample.

Both beams are highly focused onto the surface of the sample and offset by a small distance from each other. The pump beam is directed normal to the sample plane while the probe is directed at an angle of  $45^\circ$  with respect to the normal. As the intensity of the pump beam is modulated, the photoinduced displacement rises and falls, and the probe beam is reflected at different angles depending on the curvature of the displacement at the point where the probe is reflected from the sample. The deflection of the probe beam is detected through a position sensitive photodiode.

Ospal et al. [9] developed a method for measuring the thickness of opaque and transparent thin films using PDS. To interpret their results, they used a 3-D model for thermal wave propagation in a layered medium. They developed an experimental setup with both the pump and probe beams highly focused ( $\approx 4 \mu\text{m}$ ), directed normal to the sample surface, and offset by a small distance. The probe beam deflection is detected by a position sensitive device. This configuration allows to measure changes in the local curvature of the optically induced displacement of the surface. These authors conclude that their experimental system provides a truly quantitative method for efficiently measuring both opaque and transparent thin films thickness in a non-destructive and contact-less manner.

Welsch et al. [10] report PTD to be a feasible technique for separating absorption losses of single-layer film and substrate absorption from each other by a completely contactless detection of the thermoelastic response of the surface, provided the focus radius of the pump beam is appropriately chosen. They used a  $250 \mu\text{m}$  spot size at the sample surface for the pump beam and the probe beam is focused using a cylindrical lens in order to cover only a small longitudinal portion of the surface deformation. The magnitude of the displacement is measured as a change in the probe beam reflection angle. In conclusion, the author's suggested method shows that PTD technique can be applied to separate absorption losses of single layer coatings on substrates.

In the present work, we introduce a method for the direct determination of asphaltenes adsorbed on inorganic adsorbent (glass plate) based on a PTD technique using a two beam configuration, similar in some respects to the methods employed by the above quoted authors [1–3,6,8,9]. However, our experimental setup differs in some important aspects. First, the pump and probe beam are directed to the same point at the sample surface, second we use a larger probe beam spot size compared to the pump beam. As a consequence of this optical configuration, when a sample surface deformation is induced the net effect on the probe beam is an appreciable variation in its intensity profile and a negligible deflection is observed. The variation of the probe beam intensity can be easily measured using a single photodiode. The PTD signal can be related to the amount of adsorbed material onto the glass plate. To show the

potential use of the technique, it was used to monitor the solid–surface adsorption (SSA) isotherms of asphaltenes from Venezuelan extra-heavy oil adsorbed on a glass plate surface.

The asphaltenes are coarsely defined as the non-volatile fraction of a crude oil that is insoluble in n-heptane [11]. The precipitation of asphaltenes in oil well production tubing is an important problem, due to its negative impact on the petroleum industry. The solubility of asphaltenes in crude oils is probably related to the stability of their colloidal aggregates or micelles. Some authors have proposed that the tendency of asphaltenes to form aggregates should be related to their capacity for multilayer formation on a solid surface. This problem is very important because the changes in wettability due to asphaltene adsorption would determinate the displacement of fluid in the oil well tubing. Acevedo et al. [11] report on the SSA of asphaltenes and resins and their correlation with production well tubing. To construct the SSA they use a transmission technique (molecular light absorption at 400 nm) of an asphaltene toluene solution in order to evaluate the amount of adsorbed material on the inorganic adsorbent. This technique has strong limitations insofar it can only be used at relatively low concentration due to the very low transmittance of the solution. In a typical asphaltene adsorption experiment measurements in the concentration range of 100 to 10000 mg/L are required. In order to perform the measurements in the high concentration range a large dilution factor is required, resulting in a large uncertainty and consequently no useful information can be obtained. We show in the present work that our technique offers a more direct and precise method for monitoring adsorption in complex systems such as the asphaltene.

## 2. Experiment

### 2.1. Experimental setup

A diagram of the experimental assembly is shown in Fig. 1. The 514 nm beam from a Coherent Innova 300  $\text{Ar}^+$  ion laser (excitation beam) is intensity modulated with a mechanical chopper at 15 Hz and then focused to a  $50 \mu\text{m}$  diameter spot on the sample to induce the surface deformation. The 632.8 nm beam of a 5 mW Melles Griot He-Ne laser (probe beam) collinear to the pump beam is focused to a  $220 \mu\text{m}$  diameter spot on the sample. Both beams are focused using independent lenses in order to be able to control the ratio of their spot size at the sample position and their waist localization related to the sample. Both beams are directed incident at  $45^\circ$  with respect to the sample surface. The reflected beams were passed through an absorption filter to isolate the probe beam. Two different experimental setups were used to measure the reflected probe beam. In the first configuration the entire beam profile is monitored using a CCD camera (Silicon Graph-

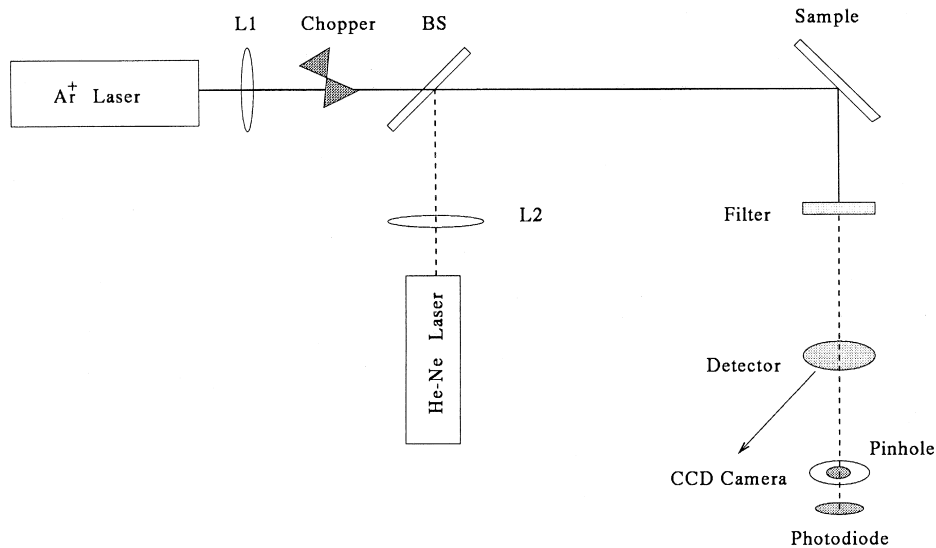


Fig. 1. Experimental configuration of laser photothermal displacement technique.

ics). The image of the reflected probe beam acquired by the camera as rgb format was transformed to a numerical matrix. A two-dimensional profile for the most intense row was chosen as the radial beam profile. These profiles are represented as intensity versus position in  $\mu\text{m}$ . In the second configuration, a probe beam center intensity selected with a  $100\ \mu\text{m}$  precision pinhole is measured by a single silicon photodiode situated after the pinhole, the photocurrent is amplified by a trans-impedance amplifier (Melles Griot 13-AMP-003). The amplified photocurrent was transduced to a PC (AT 386) with an ADC/DAC board (Lab-PC card, National Instruments).

## 2.2. Samples and adsorption experiments

The samples used were two different asphaltenes obtained from Venezuelan extra heavy oils (Hamaca and Jobo) using conventional techniques [11]. As adsorbent we used plates of clean thin glass without previous treatment. The asphaltenes were adsorbed on the glass plate by an immersion technique in a toluene asphaltene solution for 86 hours at room temperature ( $25^\circ\text{C}$ ). Solutions in the range of  $0.02$  to  $10\ \text{g L}^{-1}$  were studied.

## 3. Results and discussions

Fig. 2 depicts the scheme for measuring the magnitude of the induced deformation using the proposed configuration. The probe and pump beams are directed at the same point of the sample surface. Using a larger probe beam spot size compared to the pump beam, allows the use of the entire surface deformation since the probe beam is reflected by a surface bigger than the deformed area.

Theoretical calculations reported by Ospal [9] and Olmstead et al. [1] show that the photothermal displacement is a small perturbation of the sample surface and the deformed area is about three times the spot size of the excitation beam. We choose a probe beam spot size at the surface sample larger than four times the excitation beam spot size.

The first step in our work is to support the conjecture that changes in the probe beam intensity profile are related to the deformation of the adsorbed asphaltenes.

A study of the influence of the probe beam waist position with respect to the sample was performed. This study was carried out by detecting the probe beam profile for different adsorbed samples using two optical configurations: one where the probe beam waist is located before the sample and the second one where the waist is located after the sample. In both cases the ratio of the spot size at the sample surface of both laser beams was held constant

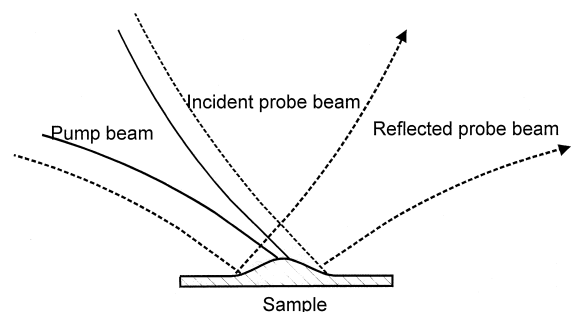


Fig. 2. Schematic description of the various physical processes affecting the laser probe beam for measuring the magnitude of the induced surface deformation.

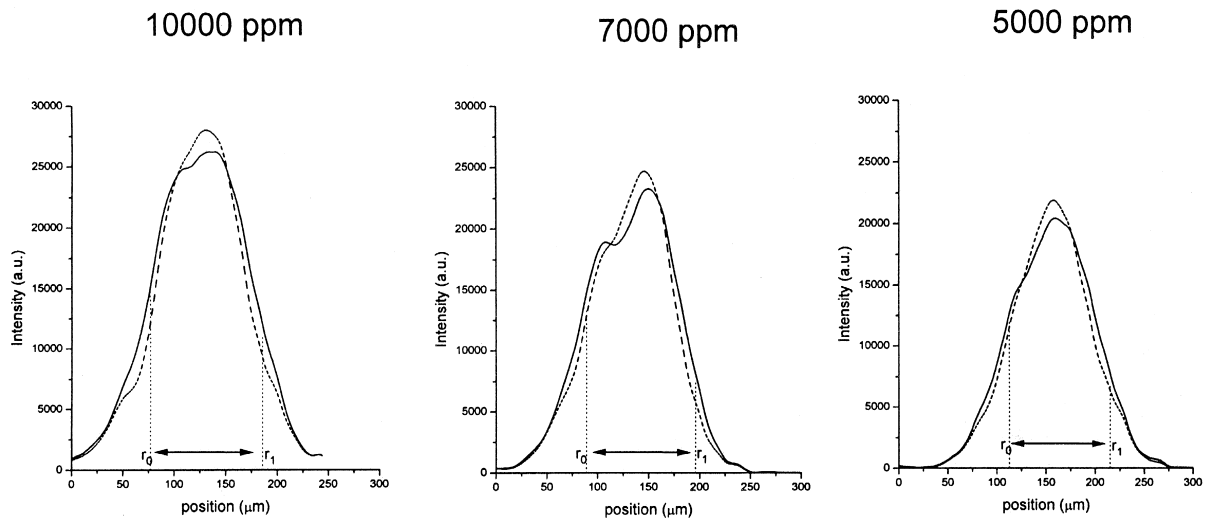


Fig. 3. Two-dimensional probe beam profile reflected by the sample surface with and without induced thermal deformation for different asphaltene solution concentrations. Pump beam power is 205 mW, probe beam waist is located 20 cm after the sample. Continuous and dashed line profiles correspond to the reflected beam by non-deformed and deformed surface, respectively.

in order to monitor the same surface area, 50  $\mu\text{m}$  and 220  $\mu\text{m}$  for the pump and probe beam respectively.

Fig. 3 shows the probe beam profile reflected from the sample surface with and without induced thermal deformation using an optical configuration where the probe beam waist is located 20 cm after the sample. These experiments were performed using an excitation beam power of 205 mW for different concentrations of the asphaltene-toluene solution. These profiles were acquired by the CCD camera

using an exposure time of 1 ms. In the case of the profile with thermal deformation it was acquired after the steady state was reached, approximately 10 ms after the excitation beam irradiation.

It is clear that the probe beam profile is affected by the surface thermal deformation. We observe that while the displacement of the beam maximum intensity is negligible, the reflected beam from the deformed surface is narrower compared to those observed for the beam reflected by the

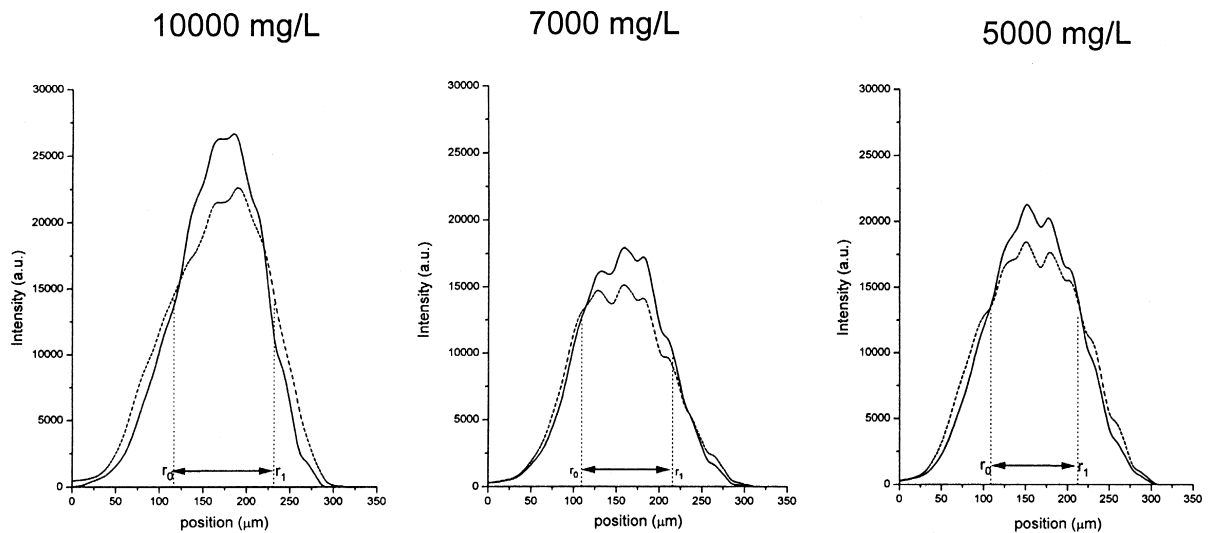


Fig. 4. Two-dimensional probe beam profile reflected from the sample surface with and without induced thermal deformation for different asphaltene solution concentrations. Pump beam power is 205 mW, probe beam waist is located 20 cm before the sample. Continuous and dashed lines profile correspond to the reflected beam by non-deformed and deformed surface, respectively.

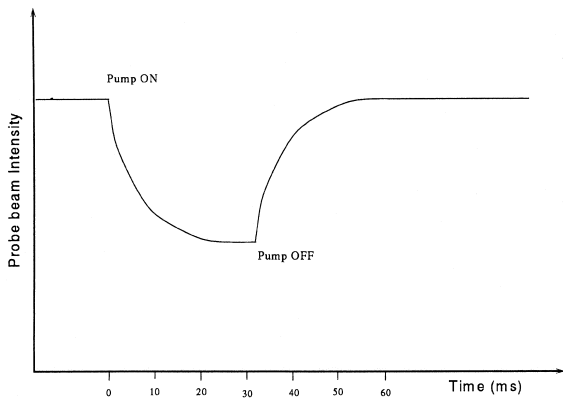


Fig. 5. Probe beam intensity variation as a function of time for a typical experimental condition. Pump beam power is 205 mW, 15 Hz frequency modulation, and probe beam’s waist located 20 cm before the sample.

non-deformed surface. By observing the central zone of the profile we can conclude that the net effect of the surface deformation is an increase in the intensity of the probe beam, i.e. a focusing effect.

Similar results are obtained when the probe beam waist is located 20 cm before the sample, but now a spreading of the probe beam profile is observed as a consequence of the surface deformation (Fig. 4) i.e. a defocusing effect. This difference in the effect on the probe beam profile (focusing or defocusing effect) can be attributed to a combination of effects as reflection onto the deformed surface and diver-

gence or convergence of the beam trajectory depending on the probe beam waist position relative to the sample.

In order to simplify the experimental setup, we have taken advantage of the fact that a negligible deflection of the probe beam is observed as a consequence of the surface deformation. A 100 μm precision pinhole is used to select the beam center and then detected using a single silicon photodiode. Fig. 5 shows the probe beam intensity detected as a function of time for a typical experimental condition, i.e. 205 mW pump beam power and 15 Hz frequency modulation, and the waist of the probe beam located 20 cm before the sample. In this case, an initial reduction of the signal until a time of about 15 ms, where a stationary value is achieved which remains until 30 ms when the excitation beam is turned off and the decay regime sets on.

The deformation signal can be defined as the relative change of the probe beam intensity at the center:

$$S = \frac{\Delta I}{I_0} = \frac{\int_{r_0}^{r_1} P_0 dr - \int_{r_0}^{r_1} P_d dr}{\int_{r_0}^{r_1} P_0 dr},$$

where  $P_0$  and  $P_d$  are the power density of the probe beam reflected before and after surface deformation, and  $r_0$  and  $r_1$  are the integration limits in our case 0 and 100 respectively corresponding to the diameter of the pinhole.

The zone between  $r_0$  and  $r_1$  on the probe beam profiles (Figs. 3 and 4), indicates the area detected when a

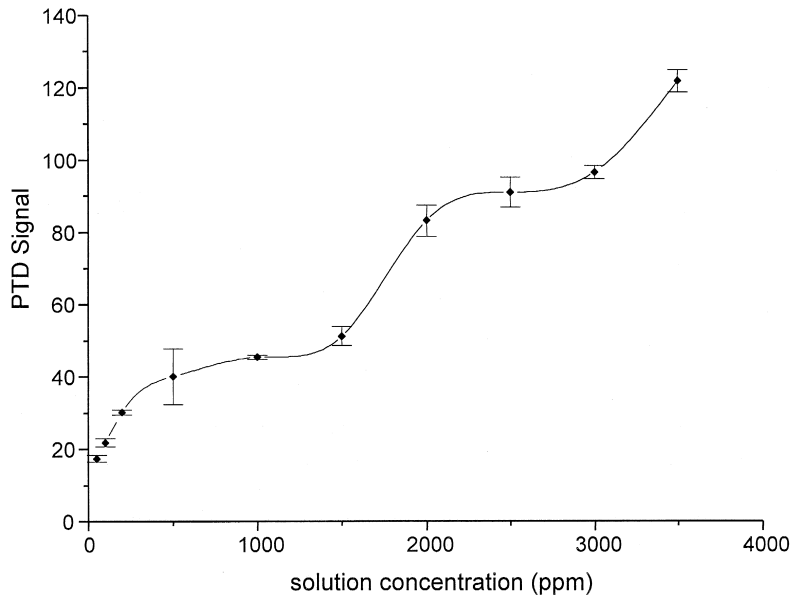


Fig. 6. Solute solid adsorption isotherm (SSA) for Jobo asphaltenes obtained with the proposed technique. Each experimental point is the average of at least five measurements made in different zones on the sample surface. Experimental errors are indicated by error bars at each point.

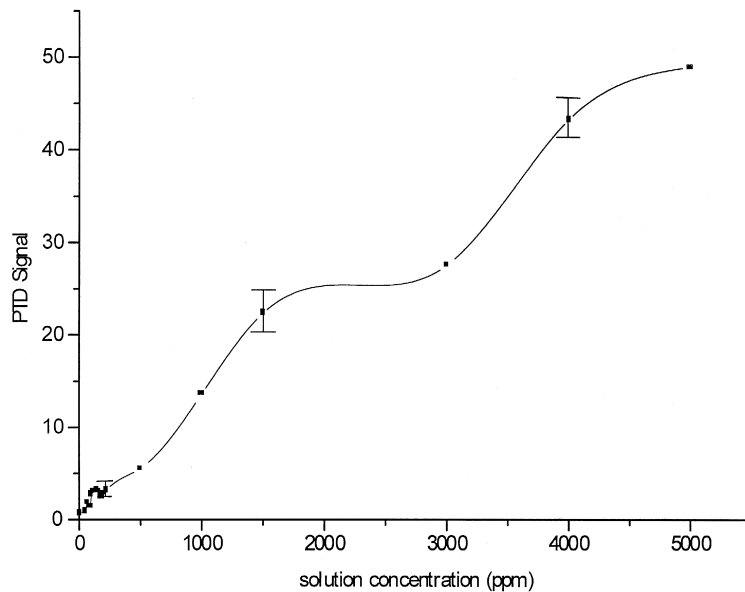


Fig. 7. Solute solid adsorption isotherm (SSA) for Hamaca asphaltenes obtained with the proposed technique. Each experimental point is the average of at least five measurements made in different zones on the sample surface. Experimental errors are indicated by error bars at each point.

100  $\mu\text{m}$  pinhole is used to select the beam center. Evaluating the relative difference between the area of the reflected beam with or without surface deformation for different samples the magnitude of  $S$  is linearly related to the amount of adsorbed material in the concentration range studied.

A comparison of the net changes in the probe beam for the two optical configurations allows us to conclude that bigger changes are obtained when the probe beam waist is located after the sample. We choose this configuration for subsequent studies because a higher sensibility can be obtained.

In order to show the capability of the proposed technique, a study of the solute-solid adsorption isotherms (SSA) of asphaltenes on a glass thin plate as adsorbent were made. The adsorption of asphaltenes was determined by measuring the PTD signal in glass plates after immersion in different concentration of toluene–asphaltene solutions. The PTD signals were plotted as a function of solution asphaltene concentrations. Fig. 6 shows the SSA of Jobo asphaltenes. Each experimental point is the average of at least five measurements made in different zones on the sample surface. In general, the adsorption behavior has two regimes: one observed for concentration below  $1500 \text{ mg L}^{-1}$ , where initial linear increase of adsorption is observed, reaching a saturation for concentration larger than  $500 \text{ mg L}^{-1}$  i.e. a Lagmuir or L-type adsorption curve. For concentration larger than  $1500 \text{ mL}^{-1}$  the adsorption again rises, increasing with the solution concentration. This behavior has been termed L-3 and usually attributed to multilayer formation on the surface or aggregates

formation in the solution and subsequent adsorption of these aggregates onto the surface [11,12]. A zone where the adsorption is independent of solution concentration separates these two regimes. The behavior in this zone is consistent with the formation of micelles [13]. Similar behavior is found for Hamaca asphaltenes (Fig. 7).

In general these results are in good agreement with those reported by other authors [11] using molecular adsorption techniques but with lower data dispersion, especially in the high concentration range. The lack of precision can be a serious problem when a tendency of asphaltenes to form aggregate is trying to relate to their capacity for multilayer formation on a solid surface. The higher precision in the experimental measurement using the proposed configuration of PTD would permit to perform specific experiments to study the aggregate characteristics of different asphaltene samples such as: critical micellar concentration, flocculation points, etc. These are all very important properties in the precipitation studies of asphaltenes in oil well production tubing. Works in this direction are currently under progress.

#### 4. Conclusions

In summary, we have described a method based on photothermal surface displacement using a different optical configuration than those reported in the literature. In particular our method employs a spot size ratio for pump and probe beam, which allows the measurement of the amplitude of the induced PTD using a single silicon photodiode.

A novel application of this technique has been made to the study of asphaltene adsorption SSA isotherms from two Venezuelan extra heavy oils. Our results are in good agreement with the reported ones using conventional techniques for the same asphaltene samples, but very low data dispersion is obtained with the proposed technique.

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### References

- [1] M.A. Olmstead, N.M. Amer, S. Kohn, *Appl. Phys. A* 32 (1983) 141.
- [2] E. Welsch, D. Ristau, *Appl. Optics* 34 (1995) 7239.
- [3] Z.L. Wu, M. Reichling, X.-Q. Hu, K. Balasubramanian, K.H. Guenther, *Appl. Optics* 32 (1993) 5660.
- [4] Y. Cho, T. Kumamaru, *Rev. Sci. Instrum.* 67 (1996) 19.
- [5] B. Li, Y. Deng, J. Cheng, *Appl. Spectrosc.* 49 (1995) 279.
- [6] M.A. Olmstead, N.M. Amer, *Phys. Rev. Lett.* 52 (1984) 1148.
- [7] W. Lee Smith, A. Rosencwaing, D. Willenborg, *Appl. Phys. Lett.* 47 (1985) 584.
- [8] M.A. Olmstead, N.M. Amer, *Phys. Rev. Lett.* 52 (1984) 1148.
- [9] J. Ospal, A. Rosencwaing, D.L. Willenborg, *Appl. Optics* 22 (1983) 3169.
- [10] E. Welsch, H.G. Walther, K. Friedrich, P.J. Eckard *Appl. Phys.* 67 (1990) 6575.
- [11] S. Acevedo, M.A. Ranaudo, G. Escobar, L. Gutierrez, P. Ortega, *Fuel* 74 (1995) 3169.
- [12] C.H. Giles, A.P. DSilva, *J. Colloid Interface Sci.* 47 (1974) 766.
- [13] S. Acevedo, M. Ranaudo, G. Escobar, L. Gutierrez, X. Gutierrez, *Asphaltenes: Fundamentals and Applications*, Eds. E.Y. Shue, O.C. Mullins (Plenum Press, New York, 1995).