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Nonlinear optical evidences of aggregation in asphaltene–toluene solutions

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Abstract

Evidences of asphaltene aggregation are presented through the application of the Z-scan technique to study the nonlinear optical response of solutions of asphaltenes in toluene. Strong dependence of the two photon absorption coefficients (β) with the input intensity was observed for concentrated solutions, as opposed to the observed behavior at low concentration. The results suggest that a change in (β) occurs as a consequence of aggregation. The results are of importance for the study of dark samples like those relevant for crude oils. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Asphaltenes; Toluene; Aggregation

1. Introduction

The problem of molecular aggregation is pervasive and of considerable importance in several branches of science and technology. The optical, magnetic and electric properties of polymers, colloids and emulsions are strongly influenced by aggregation.

Asphaltenes constitute a very important fraction of crude oil composed by molecules of different molecular weights and polarities yet similar in their solubility [1–3]. They are precipitated from crude oils through the addition of paraffines [4]. Asphaltenes are important in the oil industry, due to their deleterious effects in many industrial operations (production, refining, and transportation). Many of these problems are related to the capacity of the sample to form aggregates and clogging of rock pores and production facilities, catalysis fouling, and deposit formation during storage, among other inconveniences. As a consequence, an important research effort has been dedicated to the study of the relevant factors controlling the aggregation process.

Until now the structure of the asphaltenes is not well-known, but in general, it is considered to be formed by a system of poliaromatic layers with different functional groups and alkilic chains [5]. Previous studies performed in organic molecules with similar structures, indicate that asphaltene molecules have the potential to exhibit important nonlinear optical properties, mainly due to the presence of an extented π-electron system. They are also very important as chemical traps for free radicals in the crude oils [6]. To our knowledge, no previous works have been carried out to study the nonlinear optical properties of asphaltene solutions.

Despite its practical importance, experimental evidence and characterization of asphaltenes aggregation is difficult to gather through conventional studies of solubility and absorption because of the dark character of solutions which forces to work under conditions of extreme dilution. Our interest in this work is directed to the study the nonlinear optical properties of asphaltenes solutions at moderate to high concentration where other analytical techniques fail to provide conclusive information about the aggregation behavior.

In this article we present an application of the Z-scan technique [7,8] to study nonlinear absorption and refraction of asphaltene solutions. Our results indicate that there is a clear correlation between aggregation and important variations of the nonlinear optical response of the sample. In Section 2, we describe the experimental setup and the relevant theoretical expressions. Section 3 presents the results and discussion and Section 4 contains some final remarks and conclusions.

2. Experiment and methods

Asphaltene samples were obtained by the method

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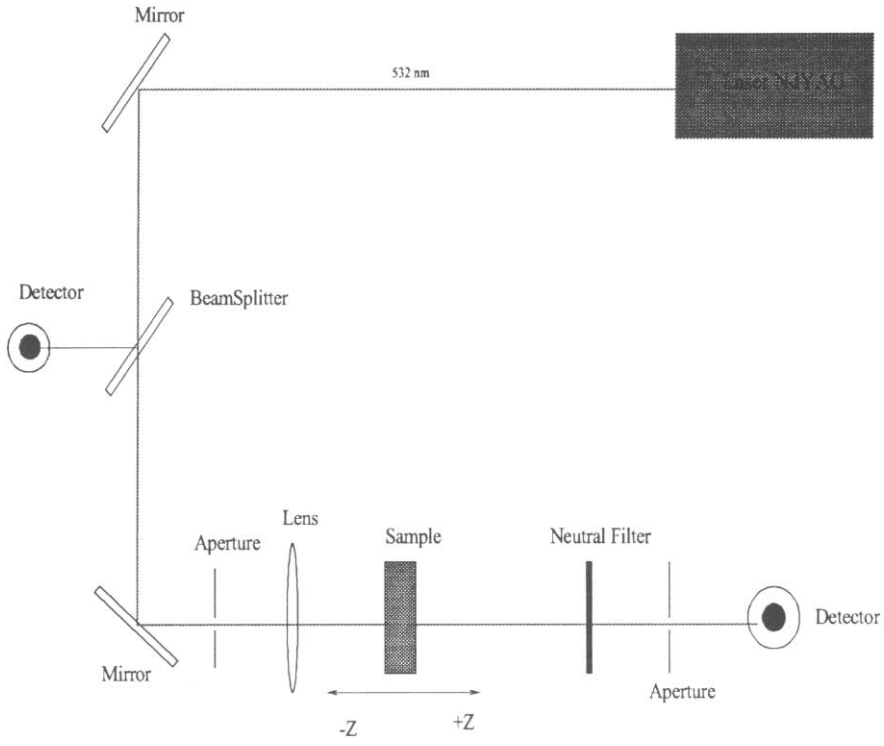

Fig. 1. Experimental setup for Z-scan measurements.

proposed by Acevedo et al. [9]. Asphaltenes were studied as toluene solutions in concentrations ranging from 10–600 mg/l. A UV-Spectronic Genesis 2 spectrophotometer, with a modified 1 mm cell path to increase resolution, was used to obtain the linear absorption spectrum.

The Z-scan experiments were carried out with the second harmonic of a Nd:YAG (532 nm) laser Surelite II Continuum, through the generation of pulses of 7 ns at 10 Hz. In order to obtain the nonlinear refraction and absorption coefficients, a Z-scan experiment with open and close aperture was carried out. The intensity of the radiation in the focus was determined by calibration with the standard CS_2.

In Fig. 1, we present the experimental set-up to measure the nonlinear absorption and refraction index. The sample under investigation is placed near the waist of a focused Gaussian beam, which is then directed onto a finite aperture. At higher intensities, the sample acts as a lens due to the spatially nonuniform refraction index. When the sample is moved from before to after the focal point an increasing (decreasing) following a decreasing (increasing) of the transmitted intensity is observed. The sign and magnitude of the nonlinear refraction index is determined and by removing the aperture in front of the detector one can also determine the nonlinear absorption coefficient with the same setup.

In the Z-scan experiments, the light intensity transmited across the nonlinear material is measured through a finite aperture in the far field as the sample is moved along the direction of propagation (z-axis) of a focused Gaussian laser beam. This method is based on a self-focusing effect and permits to obtain the magnitude and the sign of the nonlinear refraction coefficient. Removing the aperture in front the detector permits the study of the absorption effects.

If $E(r,z,t)$ is the electric field of the incident beam, and assuming that the nonlinear sample thickness, L, is much smaller than the Rayleigh range at the exit surface of the sample, one can use the Gaussian decomposition [7] to propagate the electric field to the plane of the aperture, where it is given by [7]

$$E_e(r,z,t) = E(r,z,t)\exp(-\alpha L/2)\exp[-\mathrm{i}\Delta\,\phi(r,z,t)], \qquad (1)$$

where

$$\Delta\phi(r,z,t) = \frac{kL_{\mathrm{eff}}\Delta n_0(t)}{(1+(z/z_0))^2}\exp\left[\frac{2r^2}{w_0^2(1+(z/z_0)^2)}\right], \qquad (2)$$

α is the linear absorption coefficient, $L_{\mathrm{eff}} = [1 - \exp(-\alpha L)]/\alpha$ and $\Delta n_0 = n_2 I_0(t)$, with $I_0(t)$ being the beam intensity at the focus in the beam axes.

The difference between the peak and the valley in the output intensity figure is proportional to the phase distortion of the beam, which is, in turn related to the nonlinear refractive index n_2. The transmitance at the detector can be calculated using the Z-scan theory described in [7,8]. In this model, changes in the phase shift, $\Delta\phi$, of the transmitted beam are transformed into changes in intensity and these changes are related to n_2. Fitting the experimental data to the theoretical expression we can obtain the $\Delta\phi$ value. In the far field and for a thin sample, ($\Delta\phi = kn_2 I_0 L_{\mathrm{eff}}$), where $k = 2\pi/\lambda$ is the wavenumber in free space.

The refractive index contains contributions from both nonlinear absorption (NLA) and refraction (NLR) [7]

$$n_2 = \gamma + i\beta, \tag{3}$$

where γ is the nonlinear refraction index and β is the nonlinear two-photon absorption (TPA) coefficient. The Z-scan technique allows a separate determination of β and γ from a closed-aperture Z-scan curve [10].

The (TPA) coefficient is defined through the equation [11]

$$\frac{dI}{dz} = \alpha I - \beta I^2, \tag{4}$$

which can be integrated to give the total transmittance

$$T^{-1} = \frac{I_o}{I} = -\beta\frac{I_o}{\alpha} + \left(1 + \beta\frac{I_o}{\alpha}\right)e^{\alpha L}, \tag{5}$$

with L the length of the sample.

One can invert (5) to find β as a function of the initial intensity

$$\beta = \frac{\alpha}{e^{-\alpha L} - 1}\left(\frac{1}{I} - \frac{e^{-\alpha L}}{I_o}\right). \tag{6}$$

For $I_o \gg \alpha/\beta$, the coefficient β becomes independent of the initial intensity and takes on the asymptotic value

$$\beta = \frac{\alpha}{e^{-\alpha L} - 1}\left(\frac{1}{I}\right). \tag{7}$$

3. Results and discussion

3.1. Linear absorption

The linear absorption spectrum of the asphaltenes solution is shown in Fig. 2 for three different concentrations. The inset displays the calibration curve at 532 nm. The single absorbance maximum (which disappears at the highest concentration) at 305 nm for the two lower concentrations indicates that the linear absorption process is rather insensitive to aggregation processes in the observed concentration range. This observation is confirmed by the almost perfectly linear calibration curve.

The fact that the excitation wavelength is close to twice the value at the absorbance maximum, hints to the possibility of observing two-photon absorption, a conjecture that is confirmed by the experiments.

3.2. Nonlinear refraction

As discussed in Ref. [7], the normalized transmittance of

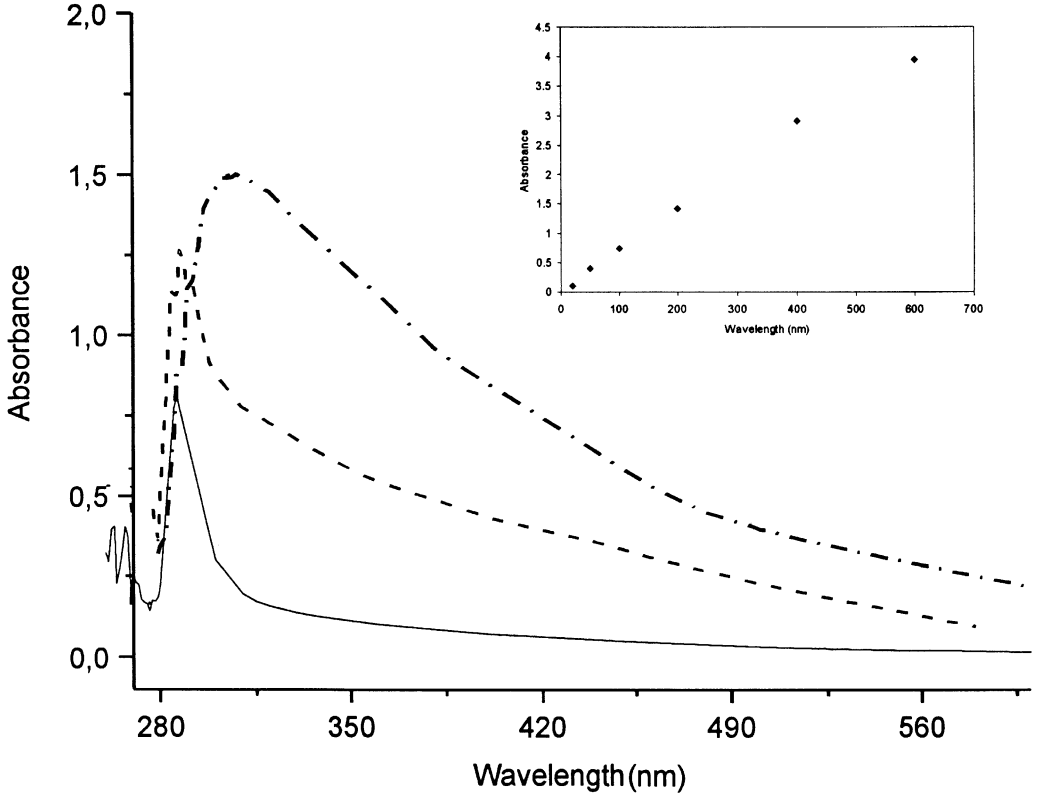

Fig. 2. Normalized linear absorption spectrum for a 20, 100 and 600 ppm asphaltene solution. Inset: absorbance vs concentration calibration curve for $\lambda =$ 532 nm.

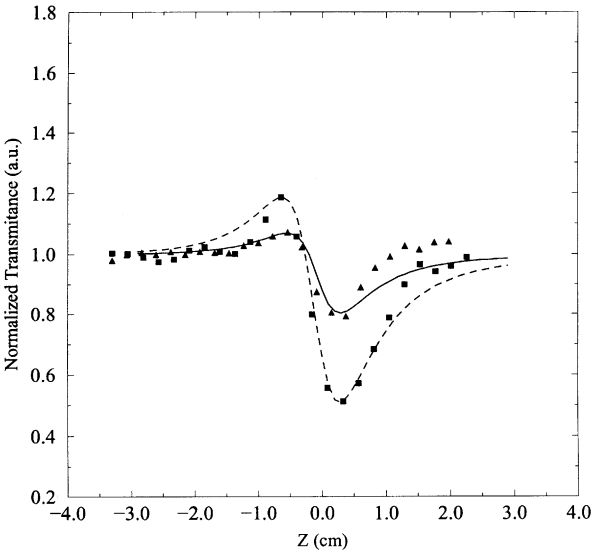

Fig. 3. Z-scan with closed aperture for solutions of 10 ppm (triangles) and 100 ppm (squares). The curves are theoretical fittings using the model described in Ref. [7].

an aperture placed in the far field is measured as a function of the position Z with respect to the focus. This 'closed aperture' Z-scan provides a measure of NLR and NLA. If the aperture is removed, in a 'open aperture' setup the NLR component vanishes and the experiment is only sensitive to NLA.

Fig. 3 shows the curves of Z-scan with close aperture for different solution concentrations at the same laser intensity. The obtained curve 'peak-to-valley' is characteristic of a negative non linearity. Experiments made with toluene show that the blank signal is negligible. Using the model described in Ref. [7], which can be applied to this case, the experimental values were fitted and $n_2 = 44.12 \times 10^{-12}$ esu (10.38×10^{-13} cm^2/W) is obtained.

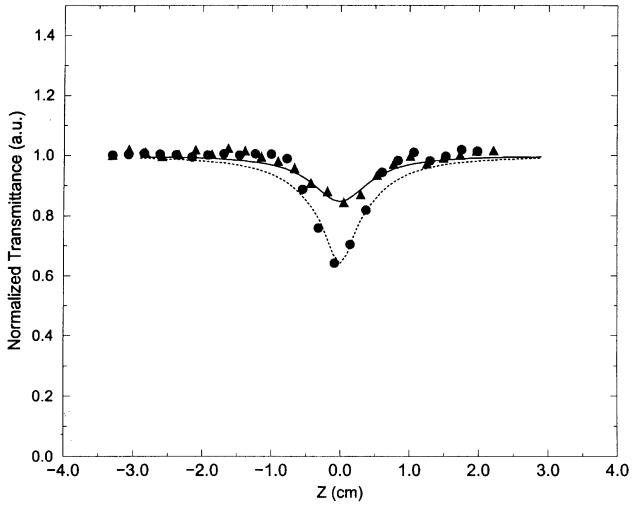

Fig. 4. Z-scan with open aperture for solutions of 10 ppm (triangles) and 100 ppm (squares). The curves are theoretical fittings using (2).

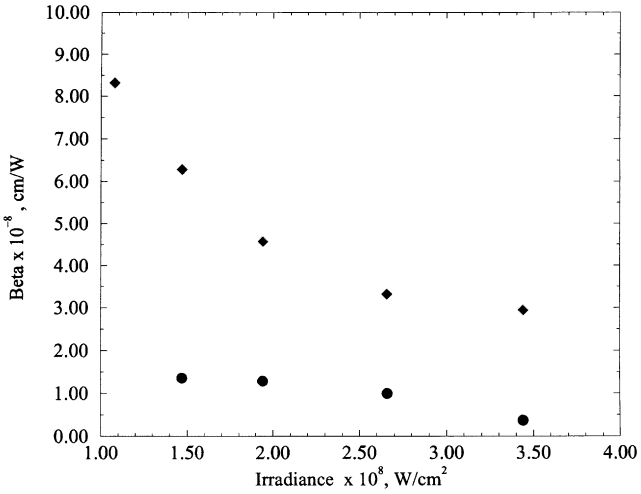

Fig. 5. Nonlinear absorption index β as a function of the intensity of the laser beam for solutions of 10 ppm (filled circles) and 600 ppm (filled diamonds).

This value is at least one order of magnitude higher than those reported for (CS_2) which is a standard and well-characterized material with positive nonlinearity at this wavelength. It is important to notice in the same Fig. 3, that when the solution concentration is increased there is a dramatic change in the signal: the depth of the valley increases while the height of the peak decreases. This behavior is characteristic of a high NLA of the sample.

3.3. Nonlinear absorption

In Fig. 4, the Z-scan curves for open aperture solutions for two different concentrations, 10 mg/l and 100 mg/l, and constant intensity $I(0)$ are shown. The solid lines are the results of fitting the data to Eq. (5), which can be applied to the case of two photon absorption. The enhanced dip in the curve for higher concentration corresponds to a ratio of transmittances of $0.7/0.85 = 0.82$ at $Z = 0$. The predicted value of this ratio, using Eq. (5), is of the order of 0.1 if the value of β is kept constant for the two concentrations. We interpret our result as a signature of a change in β due to the formation of aggregates at the higher concentration.

Fig. 5 shows the experimentally determined values of β as a function of the local input intensity inside a 2 mm path for 10 mg/l and 600 mg/l asphaltenes solution concentration. In addition to showing a higher β, the curve for higher concentration exhibits a dependence on I_o that can be understood in terms of Eq. (6). For the lower concentration curve, β is independent of I_o, in agreement with Eq. (7). The interpretation of these results is that the threshold value of intensity leading to (7) is higher for the aggregate, indicating that the ratio α/β has a larger value than that for the monomer. It is clear from the figure that β_a of the aggregate is larger than β_m of the monomer

regardless of the initial intensity, hence in order to have a consistent picture α_a must be larger than α_m, a result that is clearly compatible with the absorption curves of Fig. 2, that shows that a reduction in the number of absorbers due to aggregation does not translate into a corresponding reduction of the linear absorbance.

4. Conclusions

Changes in the nonlinear optical properties of solutions of asphaltenes in toluene as a function of concentration can be understood in terms of an aggregation model. A high value of the nonlinear refractive index was obtained (44.12×10^{-12}) and evidences of aggregation, which leads to a strong saturation behavior and changes in the NLA coefficient are found. As a continuation of our work we are considering models where the optical properties are studied as a function of the kinetics of aggregation. It would also be of interest to perform first principle calculations of the molecular susceptibility for aggregates. Work in this direction using a simple quantum model as under way.

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