



Full Length Article

Steady state fluorescence spectroscopic studies on the aggregation of coal derived asphaltene at lower concentration

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ARTICLE INFO

Article history:

Received 19 April 2016

Received in revised form 27 July 2016

Accepted 27 July 2016

Keywords:

Asphaltene

Aggregation

Fluorescence

Coal

ABSTRACT

Steady state fluorescence spectroscopic technique has been used to investigate the aggregation of coal derived asphaltene (CDA) sourced from Lodna Coke Plant situated at Dhanbad, India. The emission spectra of CDA provide information regarding the various stages of onset of aggregation in carbon tetrachloride medium. Almost similar results have also been inferred from the analysis of corresponding excitation spectra. It has been observed that the onset of aggregation of CDA occurs at concentration beyond a concentration of 10 mg L^{-1} . Studies indicate the formation of a trimer at this concentration range. The association constant (K) for the trimer formation has also been evaluated from the spectroscopic data.

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1. Introduction

Presently, there is a slump in the price of crude oil, that is understandably transient and the resumption of upward trend sooner or later cannot be denied. This provokes every country to rethink and expedite the search and research leading to alternate sources of energies other than petroleum crude. In this context, direct coal liquefaction (DCL) processes are important in order to decrease reliance on oil imports and improve energy security to a country like India, which is very rich in coal but has limited petroleum reserves. Asphaltene is one of the unwanted yet unavoidable heavy intermediate during conversion of coal to liquid fuel by DCL technique [1]. It has tendency to self-associate and promote aggregated structures leading to coke like formation [2] which inhibits the coal liquefaction processes. Thus, investigation of the self aggregation phenomenon of CDA at molecular level becomes important especially in the domain of coal liquefaction. There are a number of research papers and books in the literature that provide evidence of molecular-level association of asphaltenes that includes appreciable number of studies done by spectroscopic techniques [3–14]. There are fewer studies of CDA aggregation compared to studies on asphaltene derived from petroleum origin. In addition, most studies on aggregation have used toluene. In the present work we are extending studies on aggregation of CDA in a

different solvent, namely, carbon tetrachloride. However, in our lab we have studied the steady state fluorescence spectra of coal derived asphaltene sourced from Barari coke plant situated at Dhanbad, India as a function of concentration in benzene, toluene and carbon tetrachloride with an intention to observe the self-aggregation of the solute [15]. Aggregation was found to occur as a gradual process and the concentration characterizing onset of aggregation process coincided for all the three solvents. The critical nanoaggregate concentration (CNAC) appeared to be at ca. 90–100 and 180–200 mg L^{-1} for all the solvents indicating stagewise nanoaggregate formation in asphaltenes. However, we could not study aggregation at lower concentration. Andreatta et al. have demonstrated asphaltene nanoaggregates at $\sim 100 \text{ mg L}^{-1}$ by the use of high-Q ultrasonics [16].

The objective of the present work is to study the aggregation of CDA particularly at lower concentration using fluorescence spectroscopy. Since the solution of CDA does not show any prominent absorption maximum the aggregation properties could not be studied by absorption spectroscopic method. On the other hand, over the time it has been perceived that fluorescence spectroscopy is an useful investigating tool to address the asphaltene aggregation particularly at very low concentration range. To this end we have studied steady state fluorescence and excitation spectrum of CDA in CCl_4 medium as a function of concentration ranging from 2.50 to 98.04 mg L^{-1} . The experimental results on aggregation at lower concentration have been analyzed assuming nanoaggregate formation and the number of molecules involved in the process has been found out by a suitable analysis.

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2. Experimental section

CDA sample was prepared from the crude anthracene oil obtained from Lodna coke plant, Dhanbad, Jharkhand, India by the method described previously [17–19]. The crude anthracene oil was distilled under atmospheric pressure and the boiling fraction >360 °C was collected. The fraction >360 °C so obtained was then mixed with *n*-hexane (1:40 = oil:*n*-hexane) and was kept for two days, and then the soluble portion was decanted out. The boiling range of the *n*-hexane used was 67–69.2 °C. The *n*-hexane insoluble part was again mixed with little *n*-hexane and was decanted out; this process was repeated several times to ensure the removal of *n*-hexane soluble oil. Now, the sticky black mass was dissolved in a minimum quantity of toluene. The mixture was warmed to reduce the volume, and then petroleum ether (40–60 °C) was added. It was then filtered through Whatman 41 filter paper. The residue was washed with *n*-hexane several times once again so that the hexane soluble oil, if any, was removed. The residue (asphaltene) was dried and kept in a desiccator. The sample of CDA has been characterized by elemental (C, H, N) analysis in dry ash free basis. The sample contained weight of C = 88.00%, H = 5.05%, N = 3.50% and rest is oxygen. Sulphur was found to be present in trace quantity (<0.5%) only. The elemental analysis was done in CHNSO analyzer (ELEMENTAR, Vario Macro Cube, Germany). The solvent, carbon tetrachloride, was of UV-spectroscopic grade. It is known that the presence of trace of water modify the fluorescence of CDA [20]. The solvent was further dried by keeping it in fused calcium chloride for 24 h and then distilling just before use. Stock solution of asphaltene was prepared by dissolving asphaltene in dry carbon tetrachloride. Solutions were homogenized after mixing by proper sonication. The UV-visible absorption spectroscopic measurement was made on a Shimadzu UV-1800 spectrophotometer fitted with a peltier controlled thermo-bath. Fluorescence spectra of solution with varying concentration (2.50 mg L⁻¹ to 98.04 mg L⁻¹) of CDA were recorded at 298 K on a Hitachi F-7000 spectrofluorimeter (Japan) with 150 W xenon lamp as the excitation source. Fluorescence was collected at 90° sample geometry. Corrected fluorescence spectra were recorded in all cases. Fluorescence intensity values have also been corrected for inner filter effect *vide infra*. Temperature was controlled to 25 ± 0.5 °C by circulating water from a constant temperature bath. Data were collected in the ASCII mode and graphs were plotted by using Origin 6.0 software.

The molar mass of petroleum derived asphaltene has been reported to vary between 500 and 1000 g mol⁻¹ using fluorescence depolarization measurements [11]. Mullins and his group have

determined molecular weight using various methods viz., Laser desorption ionization, fluorescence correlation spectroscopy and laser-based mass spectrophotometric method [21–23] that are superior to vapor pressure osmometer technique. However, several studies have revealed that coal derived asphaltene have lower molar mass in comparison to petroleum derived asphaltene [24–26]. The reported molecular weight of asphaltene varies considerably depending upon the method and conditions of measurement. Although the value of molecular weight is not required for a qualitative study of aggregation process, the determination of equilibrium constant for an aggregation process however, requires the knowledge of molecular weight. For our studies, molecular weight of 400 g mol⁻¹ has been assumed for the CDA sample. This value is close to the formula weight corresponding to the structure of coal derived asphaltene as proposed by Mullins et al. [27].

3. Result and discussion

Fig. 1(a) shows the absorbance spectra of CDA in CCl₄ as a function of concentration. The spectrum is characterized by a monotonically decreasing trend of absorbance as the wavelength changes from 300 to 450 nm. However, the absorbance spectrum shows a change of slope in certain wavelength. The absorbance at a particular wavelength (375 nm) varies linearly with concentration as represented in Fig. 1(b). The value of molar absorbance (ϵ) for the absorbing species at 375 nm has been calculated assuming the molar mass of the sample as 400 g mol⁻¹. Thus, molar absorbance comes out to be $\epsilon = 3 \times 10^4$ L mol⁻¹ cm⁻¹. This value is comparable with the values obtained for a different coal derived asphaltene sample sourced separately [15].

It is known that CDA consists of molecules formed by fusion of polycyclic aromatic and naphthenic units (PANU) with several functional groups attached. Excitation of these molecules causes π - π^* transition as is reflected from the high values of molar absorbance obtained. The fluorescence spectrum has been studied using various excitation wavelengths namely 300, 400, 450, 500 nm. Fig. 2(a) shows the fluorescence spectra of CDA at $\lambda_{\text{ex}} = 300$ nm as a function of concentration. Spectrum in all cases appears as structured. The observed fluorescence spectra indicate the shoulders at ca. 365, 410, 430, 450, 495 nm independent of wavelength of excitation chosen. However, the intensity of fluorescence at a particular wavelength changes with the concentration of CDA. The intensity at first increased with an increase in concentration and then showed a decreasing trend. To check whether the result is real or due to any artifact we corrected the spectrum for inner filter (IF) effect. To correct for the significant absorbance of the solutions

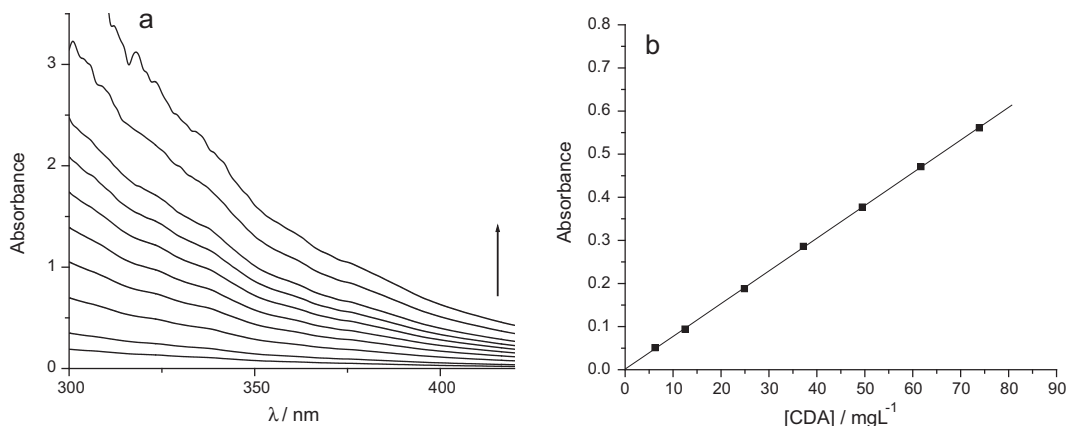


Fig. 1. (a) Absorption spectra of CDA in CCl₄ at different concentration. The concentration increases in the direction indicated by the arrow. (b) Plot of absorbance at $\lambda = 375$ nm as a function of concentration.

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