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Evidence of molecular complex formation between asphaltene and *o*-chloranil in aqueous micellar medium: A spectrophotometric study

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HIGHLIGHTS

- Coal derived asphaltene studied in aqueous micellar media of CTAB and TX-100.
- Asphaltene forms 1:1 complex with *o*-chloranil.
- The formation constant determined by fluorescence and absorbance are in good agreement.
- The wavelength of maximum absorption of the complexes are in the order of SDS > CTAB > TX-100.

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ABSTRACT

The spectral (both absorption and steady-state fluorescence) studies of interaction of asphaltene with *o*-chloranil have been carried out in aqueous micellar media of cationic cetyl trimethyl ammonium bromide (CTAB), and neutral triton X-100 (TX-100). Spectroscopic results indicate formation of a complex between asphaltene and *o*-chloranil. The fluorescence band positions of the complexes are identical in both the medium. The absorption spectrum of the complex has been detected by difference spectral method. The position of maximum absorption of the complex in these micellar media have been compared and found in the order of SDS > CTAB > TX-100. The formation constant (*K*) has been determined using Benesi–Hildebrand equation utilizing absorption spectral data. Formation of ground state complex involving asphaltene and *o*-chloranil has also been observed from the study of quenching of asphaltene fluorescence by *o*-chloranil. The value of *K*, as obtained by Stern–Volmer plot, agrees well with that obtained by absorption spectrophotometric method.

1. Introduction

Asphaltenes, consisting of a group of polyaromatic compounds, are interesting systems primarily due to their ability to form nanoaggregates in solution [1,2]. Besides the conventional methods involving surface tension [3–6], viscosity [7] or calorimetry [8] techniques such as light absorption and fluorescence [9–18] have been widely used to elucidate the properties of asphaltene. Generally, asphaltenes are not crystallized and cannot be separated into individual components or narrow fractions. Thus, purification, separation and quantitative studies are extremely difficult. The non-volatile fraction of crude oil which contains most of the heavy aromatics known as, asphaltenes that is generally defined as a solubility class: the fraction soluble in toluene and insoluble in n-heptane (or n-pentane). Asphaltenes are important in the oil industry, due to their deleterious effects in many industrial operations (such as production, refining, storage and transportation). These problems arise due to the self-aggregational phenomena of asphaltenes causing difficulty mainly in transportation and storage among other inconveniences. However, considering the rising energy demand day by day and fast depletion of crude oil reserves, it is clear that the world's reliance on crude oil will have to end sooner or later. Fortunately, a wide variety of carbonaceous materials – including shale, coal, and bitumen – may be upgraded to produce synthetic fuel. These startup sources are abundant and readily available. India has some largest reserves of coal in the world (approx. 267 billion tones). For crude oils in particular, asphaltenes tend to aggregate and precipitate out of the liquid phase: leading to clogged formations and pipelines. Due to this behavior it has earned the title of 'bad cholesterol' of oil. However, these problems are not exclusive to crude oils. Materials derived from coal liquefaction are also known to form similar aggregates in organic solvents [1,19]. The fact that asphaltene plays an important role in

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coke forming tendency of the oil [19] also makes a significant point for the researchers dealing with liquefaction of coal, as asphaltene is also an important heavy intermediate for the coal to oil conversion. Considering asphaltene self-association phenomenon already established, it is important to investigate the nature of interaction of asphaltene at molecular level with different species (electron acceptors) in variety of environments. This may provide guidance towards prevention or minimization of the extent of self-aggregation of coal derived asphaltenes particularly in the field of direct coal liquefaction processes that will help to curb the problems arising due to self aggregation.

In this context, the micellization behavior of asphaltene in surfactant environment is important in connection with stabilization of asphaltenes in such medium. Micellization is the phenomenon describing the self-association of surfactants in aqueous solution, initiated by the hydrophobic–hydrophilic imbalance. When the concentration of the surface-active materials reaches the critical micelle concentration (CMC), these molecules begin to self-aggregate to lower their free energy for better suspension in the solution. In a micelle formed in aqueous media, surfactant molecules would cluster with their hydrophobic heads together in the micellar core and their hydrophilic tails in the organic phase. The similarity between asphaltene and surfactant molecules was suggested after observing sharp transitions in some measurable physical properties of asphaltene (such as viscosity [7], surface tension [3], or by calorimetry [8]), similar to micelles formed in surfactant solutions. Many authors have considered the self-association of asphaltene equivalent to the formation of surfactant reverse micelles. Thus, the small asphaltene aggregates or particles are sometimes referred to as “micelles” in the literature. It is important to point out that the asphaltene micelles are different from the traditional micelles that are usually formed by the surfactant molecules. That is why the term critical micelle concentration (CMC) is replaced by critical aggregation constant (CAC) in case of asphaltenes. However, the interactions between asphaltenes and resins or natural surfactants play an important role in asphaltene stabilization in the solution.

Asphaltene molecules are known to contain fused aromatic and heteroaromatic rings and as such, they are likely to behave as π-electron donors. The electro donor behavior of asphaltene and coal has been explored by several researchers over the years. For example, the variable temperature EPR studies of Illinois No. 6 coal with known donor and acceptor molecules has been reported by Thompson et al. [20] where, the infrared spectroscopy suggested that electron transfer from coal occurs after treatment with electron acceptors such as TCNQ and TCNE. The trapping of compounds by asphaltenes in guest–host complexes has been investigated by Acevedo et al. [21]. Further, complex formation of petroleum asphaltene with *p*-nitrophenol as the acceptor has also been reported from the same laboratory [22]. Recently, reaction of asphalt and maleic anhydride (MAH) was also studied by FTIR and chemical titration [23]. Again, as asphaltene remains as a monomer and also aggregates in solution, it is important to know about the state of aggregation of asphaltene that is involved in the formation of the electron donor–acceptor (EDA) complex with the acceptor. Recent studies in our laboratory revealed that asphaltene forms molecular complexes with chloranils and bromanils in carbon tetrachloride solution [24–26]. Spectroscopic studies indicating formation of a complex between asphaltene and *o*-chloranil in SDS micellar medium [27] have also been carried out by our group.

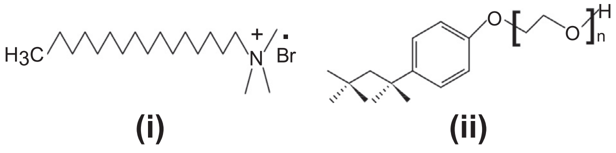
Asphaltene samples are practically insoluble in water and as such complexation studies in aqueous medium is not possible. It is known that aqueous micellar system provides an interesting medium for solubilizing organic compounds. After a successful study in a micellar medium with the anionic surfactant SDS, it is instructive and important to explore the complexation behavior of asphaltene in aqueous micellar media with cationic and neutral surfactants with an eye to explore the stabilization of asphaltene in solutions by minimizing self-aggregation. Hence, the purpose of this work is to study complex formation between asphaltene and an electron acceptor in aqueous micellar media of TX-100 and CTAB. We have chosen *o*-chloranil as electron acceptor for its reasonably good solubility in aqueous micellar media [27]. Hence, the concentration of *o*-chloranil in TX-100 and CTAB could be easily varied as desired. The structures of the surfactants are represented in Scheme 1. To this end, the absorption and fluorescence spectra of mixtures of asphaltene and *o*-chloranil have been monitored in solutions containing TX-100 and CTAB. Spectral observations have been analyzed to evaluate the formation constant of the complexes.

2. Materials and methods

Asphaltene sample was prepared from the crude anthracene oil obtained from Barari coke plant, Dhanbad, Jharkhand, India by a method described previously [24–27] and kept in a desiccator. The sample of asphaltene has been characterized by elemental (C, H, N) analysis in dry ash free basis and characteristic fluorescence spectrum in toluene and carbon tetrachloride. The sample contained weight of C = 87.70%, H = 5.08%, N = 3.56% and the empirical formula comes as $C_{29}H_{20}N$. *o*-Chloranil (Fluka) was purified by sublimation before use. TX-100 (Sigma), CTAB (Sigma) was purified by recrystallization from ethanol. Triply distilled water was used for all the experiments. The UV–visible absorption spectroscopic measurement was made on a Hitachi (U-4110) and Simadzu UV-1800 spectrophotometer. Fluorescence spectra were recorded in Hitachi (F-7000) fluorimeter with a 150 W xenon lamp as the excitation source. Fluorescence was collected at 90° sample geometry. Corrected fluorescence spectra were recorded in all the cases. The elemental analysis was done in CHNSO analyzer (ELEMENTAR, Vario Macro Cube, Germany).

Stock solution of asphaltene was prepared by dissolving asphaltene in 20 mmol/L aqueous TX-100 and CTAB solutions followed by 4 h of sonication. Solution of *o*-chloranil was prepared in 20 mmol/L TX-100 and CTAB media similarly. For complexation studies, absorption and fluorescence spectra of mixtures containing asphaltene (5 mg/L) and *o*-chloranil of varying concentration were recorded. Solutions were homogenized after mixing by proper sonication. 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 using fluorescence depolarization measurements [28]. However, the reported molecular weight of asphaltene varies considerably depending upon the method and conditions of measurement. For coal derived asphaltene the molar mass is lower. According to a molecular structure (Scheme 2), as suggested by Mullins et al. [2] the molar mass comes as 309. For our experiment, molecular weight of 400 has been assumed for the asphaltene sample. The value is consistent with the results of C H N analysis. It can be noted that the calculated value of *K*, the equilibrium constant for the complexation process is independent of the choice of molar mass of the sample.



Scheme 1. Schematic representation of (i) CTAB and (ii) TX-100.