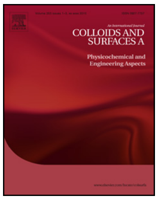
Colloids and Surfaces A: Physicochem. Eng. Aspects 494 (2016) 108–115

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa



An ITC and NMR study of interaction and complexation of asphaltene model compounds in apolar solvent I: Self-association pattern

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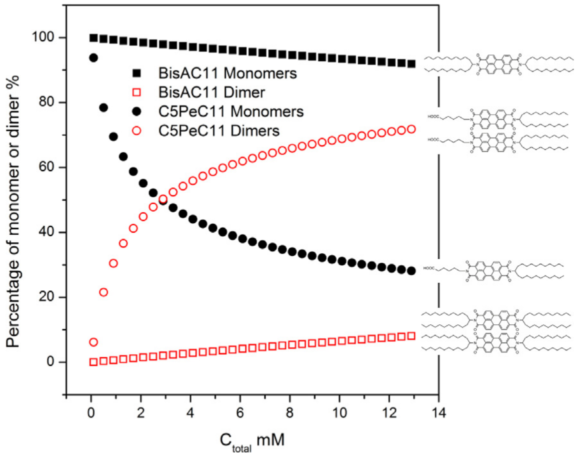
HIGHLIGHTS

- Study self-association properties of asphaltene model compounds in xylene.
- Asphaltene model compounds form dimers in solution.
- Combination of hydrogen bonding and π–π stacking leads to higher association extent.
- Mixtures of model compounds can quantitatively fit the self-association features of extracted asphaltenes probed by ITC

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 1 November 2015
Received in revised form 10 January 2016
Accepted 13 January 2016
Available online 16 January 2016

Keywords:
Self-association
Precipitation
Solubility
Interaction
Asphaltene model compounds

ABSTRACT

The self-association pattern of asphaltene model compounds with different functional groups in xylene and mixtures of xylene and heptane have been studied by isothermal titration calorimetry (ITC) to shed new light on the association and interaction between components in the asphaltene fraction. The model compounds are *N*-(1-undecyldodecyl)-*N*′-(5-carboxylicpentyl)perylene-3,4,9,10-tetracarboxylbisimide (C5PeC11) and *N*,*N*′-bis(1-undecyldodecyl)perylene-3,4,9,10-tetracarboxylbisimide (BisAC11).

The results show that a combination of hydrogen bonding due to carboxylic groups and π–π stacking due to polyaromatic rings leads to higher association extent of C5PeC11 compared to that of BisAC11 in xylene. A dimerization model can well fit the association of both model compounds in xylene obtained both by ITC and NMR. Mixtures of C5PeC11 and BisAC11 can well quantitatively fit the features of self-association of real extracted asphaltenes probed by ITC. This could mean that the total asphaltene fractions are composed of polydisperse compounds displaying very different association properties.

Finally, increasing the heptane content in the solvent results in higher extent of π–π stacking between C5PeC11 molecules, which indicate formation of larger aggregates or tighter arrangement of aromatic rings.

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http://dx.doi.org/10.1016/j.colsurfa.2016.01.018
0927-7757/

1. Introduction

Asphaltenes are a fraction of petroleum crude oil and responsible for numerous problem during oil production, separation and transportation [1–4]. They can stabilize water-in-oil emulsions[5,6] impacting oil–water separation. They can also precipitate and form organic deposits in reservoirs, wells, piping and equipment by change of pressure[7–9] or mixing with incompatible fluids [10,11]. This can lead to costly well-fluid flow restrictions and unplanned production irregularities and shut-ins.

Asphaltenes are insoluble in *n*-alkanes but soluble in aromatic solvents like toluene or xylene. They constitute thousands of molecules with different molecular weights and functionalities. The typical mean molecular weight of asphaltenes is ca. 750 g/mol with a factor of 2 in the width of the molecular weight distribution [12–18]. Two main models have been proposed to describe a typical asphaltene molecule: the archipelago model in which asphaltenes are thought to consist of small polyaromatic parts linked together by aliphatic or naphthenic moieties, and the continental model considering asphaltene molecules constituted of single polyaromatic ring with side-linked aliphatic or naphthenic chains [19,20]. In both models heteroatoms occur in a variety of cyclic and aliphatic locations. Asphaltenes are both basic and acidic, the latter due to the presence of carboxylic acid functions most likely in the alkyl-side chains [21,22].

The asphaltenes are prone to self-associate in model hydrocarbon solvents or petroleum crude oils. Two different scales and phenomena need to be differentiated.

- First, the nanometer scale. In toluene or in correspondingly “good” enough solvent, asphaltenes self-associate to form nanometer-sized aggregates. The terms of nanoaggregates and clusters are sometimes used to describe more accurately the formed aggregates [20]. These aggregates seem to be stable.
- Second, the micrometer scale indicating asphaltene precipitation. If the precipitation is induced by adding a non-solvent like an alkane, then asphaltenes precipitate by flocculating until forming micrometer-sized flocs. The kinetics of formation of these flocs follows classical colloid flocculation kinetics like the diffusion and reaction-limited aggregation [23,24].

The wide distribution of molecular weight as well as the hydrocarbon complexity and heteroatom heterogeneity results in an enormous challenge in terms of description of asphaltene system from molecular levels. To solve this problem [4], one experimental approach is to fractionate asphaltenes into several sub-fractions by changing the ratio of good solvent/precipitate solvent [25–28], ultracentrifugation [29,30], or ultrafiltration [31,32]. However, even after the fractionation, the asphaltene fractions still contain a large number of compounds with a wide distributions of molecular weight and structures. In order to overcome this structural problem, several groups [4,33–36] have focused on the design of asphaltene model compounds which have high purity and well-defined molecular structure.

Sjöblom and his group have designed a family of asphaltene model molecules composed of a perylene polyaromatic core linked to a fixed hydrophobic part and a variable group, polar or apolar [35,37,38]. This structure is consistent with the continental model mentioned above even if the model molecules contain more oxygen than asphaltenes. They found that the interfacial and emulsion stabilization properties of these molecules depend strongly on the structure suggesting that a small fraction of asphaltenes could be responsible for crude oil emulsion problems [39].

For asphaltene association Mullins proposed the Yen–Mullins model claiming that the major driving force is π–π stacking. This interaction leads to asphaltene nanoaggregates with an aggregation number [20] less than 10. Gray et al. [40] proposed a supermolecular assembly model of asphaltenes, combining cooperative binding by acid-base interactions, hydrogen bonding, metal coordination complexes, and interactions between cycloalkyl and alkyl groups to form hydrophobic pockets, in addition to aromatic π–π stacking leads to strongly associated structure of asphaltenes, although all the forces taken individually are very weak. Sedghi et al. [41] studied the self-association of asphaltenes by molecular dynamics (MD). They found that interactions between aromatic cores are the major driving force for association as the energy of association increases substantially with the number of aromatic rings. Heteroatoms also influence asphaltene self-association as well as their location either in the aromatic cores or attached to the aliphatic chains. Aliphatic chains attached to the aromatic core limit aggregation by steric repulsion, also addressed by MD calculations by Jian et al. [42] In conclusion, the level of the asphaltene aggregation will depend on the size of aromatic rings, and the amount and state of heteroatoms such as N, O, and to a lesser extent S and aliphatic chains [33,34,43]. However, there are only a few experimental evidences to confirm these predictions.

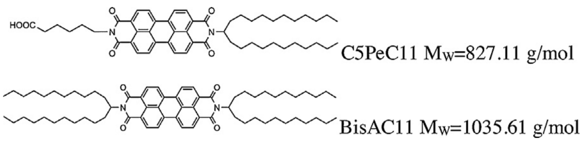

Fig. 1. Chemical structure of C5PeC11 and BisAC11.

In this paper, the first of a series of two, the self-association properties of model compounds containing different functionalities were determined. These model compounds represent the asphaltenes of the continental type, and aims to mimic only parts of the total asphaltene fraction: either acidic (C5PeC11) or non-acidic (BisAC11) (Fig. 1) [44]. The aim is to differentiate effects from the different types of molecular interactions. The interplay and complexation between model compounds and between model compounds and asphaltene precipitation inhibitors will be studied in the second part of the series.

2. Materials and methods

All chemicals were used without purification and were purchased from VWR. Xylene was a mixture of isomers and had a purity of 99.2%. The asphaltene model compounds C5PeC11 and BisAC11 were synthesized according to previously reported procedures [37,45]. Structures and molecular weight of the model compounds are presented in Fig. 1. The maximum solubility of C5PeC11 in xylene was determined to be 3.0 g/L (3.8 mM) at room temperature. Below this concentration, the C5PeC11 solutions were found stable with no variations in their UV spectra within two weeks.

2.1. Isothermal titration calorimetry (ITC)

NANO-ITC Standard volume from TA instruments was used to perform isothermal titrations. The procedure of the experiments has been well documented in our previous article [46]. All tests were carried out at 25 °C with the stirring rate of 250 rpm. The injection interval was 400 s to let system equilibrate. A blank experiment with xylene titrated into xylene accounting for friction heat was subtracted from the experimental data before any further analysis. NanoAnalyze^{TM} (TA Instruments) was applied to analyze and fit the ITC data. Solutions of asphaltene model compounds were prepared by dissolving the solid compounds in xylene and then sonication for 30 min. The solutions were kept in the dark overnight prior to each measurement to ensure homogeneity. All solutions were re-