

1 An ITC Study of Interaction and Complexation of
2 Asphaltene Model Compounds in Apolar Solvent II:
3 Interactions with Asphaltene Inhibitors

4 *Duo Wei***, Sébastien Simon*, Mathilde Barriet, Johan Sjöblom*

5 Ugelstad Laboratory, Department of Chemical Engineering, the Norwegian University of

6 Science and Technology (NTNU), N-7491 Trondheim, Norway

7 KEYWORDS. Precipitation, solubility, interaction, asphaltene model compounds, asphaltene
8 inhibitor.

9

1 ABSTRACT. The interaction and complexation of asphaltene model compounds containing
2 functional groups with other crude oil compounds in a mixture of xylene and heptane have been
3 studied to shed new light on the association and interaction between components in the
4 asphaltene fraction and with asphaltene inhibitors. The model compounds are N-(1-
5 undecyldodecyl)-N'-(5-carboxylicpentyl)perylene-3,4,9,10-tetracarboxylbisimide (C5PeC11)
6 and N,N'-bis(1-undecyldodecyl)perylene-3,4,9,10-tetracarboxylbisimide (BisAC11).
7 C5PeC11 has a very low solubility limit in a mixture of 70 vol% heptane / 30vol% xylene. This
8 solubility is increased by the presence of BisAC11 most likely due to the formation of a soluble
9 (BisAC11)(C5PeC11) complex. The association constant of this complex is found to be ≈ 700
10 corresponding to a ΔG of ≈ -16 kJ/mol. The interaction between model compounds and model
11 asphaltene inhibitors, nonylphenol (NP) and dodecyl benzene sulfonic acid (DBSA), have been
12 investigated as well by isothermal titration calorimetry (ITC). Compared to NP, DBSA can
13 interact more strongly with C5PeC11 through a combination of hydrogen bonding and π - π
14 stacking. DBSA can also enhance the solubility of C5PeC11 more efficiently than BisAC11 due
15 to (DBSA)(C5PeC11) complex formation. The calculated association constant of this complex is
16 $\approx 8.53 \times 10^3$ which corresponds to a ΔG of -22.4 kJ/mol.

17

1 1. INTRODUCTION

2 Petroleum crude oil is a complex mixture of thousands of compounds spanning from
3 hydrocarbons like alkanes, waxes and aromatic molecules to polar components like resins,
4 naphthenic acids and asphaltenes^{1, 2}. Asphaltenes are the fraction of petroleum insoluble in n-
5 alkanes (typically heptane, but also hexane or pentane) but soluble in toluene^{3, 4}. They are
6 responsible to cause flow assurance problems like the formation of solid asphaltene deposits⁵
7 or/and the stabilization of water-in-crude oil emulsions⁶⁻⁸ which need to be solved to ensure the
8 proper transportation and processing of crude oils.

9 Asphaltenes are composed of thousands of different molecules differing by their chemistry and
10 molecular weight. Mullins et al. in the early 2000's have shown that the typical mean molecular
11 weights of asphaltenes were ca. $750 \text{ g}\cdot\text{mol}^{-1}$ with a factor of 2 in the width of the molecular
12 weight distribution⁹⁻¹². Asphaltenes are strongly aromatic and contain polar groups such as
13 pyrrole and pyridine rings, carboxylic acid, thiophene, sulfide and sulfoxide functions^{13, 14}.

14 Asphaltenes can self-associate in model hydrocarbon solvents like toluene or mixture of toluene
15 and alkane and petroleum crude oils. Two different association levels and phenomena need to be
16 differentiated.

17 -First, the nanometer scale. In toluene or in correspondingly "good" enough solvent, asphaltenes
18 self-associate to form nanometer-sized aggregates. Different models have been proposed to

1 describe the structure of these aggregates namely the Yen model^{15, 16} and its newer version the
2 Yen-Mullins model^{17, 18}, the Peptization model¹⁹ and the fractal concept²⁰⁻²². These aggregates
3 seem to be stable with time.

4 -Second, the micrometer scale. This corresponds to the precipitation of asphaltenes⁵. The term of
5 flocculation is also used. If the solvent is too aliphatic and not aromatic enough, asphaltenes
6 precipitate by flocculating until forming micrometer-sized flocs.^{23, 24}

7 Precipitation and more particularly deposition^{25, 26} (i.e. adhesion on a solid surface after
8 precipitation) are detrimental to oil production and transportation. This can lead to costly well-
9 fluid flow restrictions and unplanned production irregularities and shut-ins. Asphaltene
10 precipitation can be imposed by depressurization during oil production²⁷ or mixing incompatible
11 fluids^{28, 29}.

12 Deposition of asphaltenes can be prevented by addition of well solvents or specifically-designed
13 asphaltene inhibitors. Chang and Fogler³⁰ have studied the stabilization of asphaltenes in alkane
14 solvents by a series of alkylbenzene-derived amphiphiles. They found that increasing the polarity
15 of the amphiphile's head group strengthens the interaction between asphaltene and amphiphiles.
16 Moreover increasing the tail length of an amphiphile can improve its effectiveness to stabilize
17 asphaltenes which is compatible with a peptisation mechanism of asphaltenes by the tested
18 amphiphiles. Recently Merino-Garcia et al.³¹ then Wei et al.³² have investigated the interaction

1 of asphaltenes by model asphaltene inhibitors: nonylphenol (NP) and dodecyl benzene sulfonic
2 acid (DBSA) by isothermal titration calorimetry (ITC). The latter found that asphaltenes and NP
3 interact most likely by formation of complexes $(Asp)(NP)_1$ and $(Asp)(NP)_2$. For the interactions
4 between DBSA and
5 asphaltenes, it was shown that the main mechanism depends on the self-aggregation of DBSA as
6 well as the concentration of asphaltenes.

7 This paper is the second in a series of 2. In the first one, the self-association properties of
8 asphaltene model compounds C5PeC11 and BisAC11 containing different functionalities and
9 their mixtures were determined by isothermal titration calorimetry (ITC)³³. It was found that the
10 combination of carboxylic groups and polyaromatic rings makes C5PeC11 more prone to self-
11 association than BisAC11. In addition mixtures of these two model compounds can well
12 quantitatively mimic the polydisperse asphaltene system properties probed by ITC. This work is
13 continued in this sequel by investigating the interplay, interaction and complexation between
14 different model compounds and between asphaltene model compounds and asphaltene inhibitors.

15

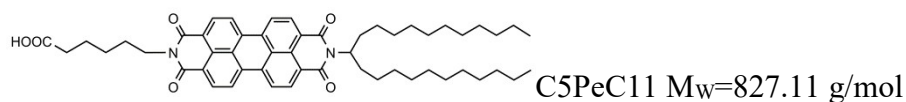
16 **2. MATERIALS AND METHODS**

17 All chemicals were used without purification and were purchased from VWR, except 4-
18 dodecylbenzenesulfonic acid (DBSA, mixture of isomers $\geq 95\%$) which was from Aldrich.

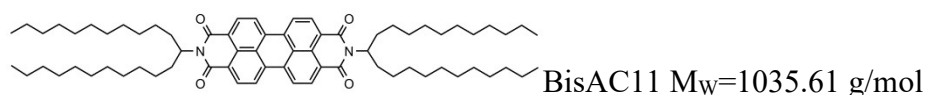
1 Xylene (AnalaR Normanpur®) was a mixture of isomers and had a purity of 99.2%. The
2 specification of the product given by VWR indicates a water content of max. 0.03 %. Xylene
3 was used instead of toluene owing to its higher boiling point. The asphaltene model compounds
4 C5PeC11 and BisAC11 were synthesized according to previously reported procedures.^{34, 35}
5 Intermediate and final products were characterized by ¹H NMR spectroscopy in CDCl₃. All the
6 peaks are accounted for and yield a match with the expected chemical structure; hence the purity
7 of these compounds is assumed to be very good. Structures and molecular weight of the model
8 compounds are presented in Figure 1.

9

10



11



12

13 **Figure 1.** Chemical structure of C5PeC11 and BisAC11

14

15 **2.1 Isothermal titration calorimetry (ITC)**

16 NANO-ITC Standard volume from TA instruments was used to perform isothermal titrations.

17 The procedure of the experiments has been well documented in our previous article.³² All tests

18 were carried out at 25 °C with a stirring rate of 250 rpm. The injection interval was 400 s to let

1 system equilibrate. A blank experiment with xylene titrated into xylene accounting for friction
2 heat was subtracted from the experimental data before any further analysis. NanoAnalyze™ (TA
3 Instruments) was applied to analyze and fit the ITC data. Solutions of asphaltene model
4 compound were prepared by dissolving the solid compounds in xylene and then sonication for 30
5 min. The solutions were kept in the dark overnight prior to each measurement to ensure
6 homogeneity. All solutions were re-sonicated for 30 min right before measurements to ensure
7 that no bubbles were present. All the experiments have been repeated at least twice.

8 ***2.2 UV-visible spectroscopy***

9 UV-240PC (Shimadzu) was used to obtain the UV-visible spectra. A 2 mm cell was used. The
10 wavelength range was from 700 nm to 240 nm with the interval of 1 nm. Scanning speed was
11 slow and slit width was 2.0 nm. To eliminate background effects, the reference cuvette was filled
12 with the same mixture of xylene/heptane.

13 ***2.3 Determination of C5PeC11 solubility by HPLC***

14 Stock solutions of 2.4 mM C5PeC11 (corresponding to 2 g/L) and concentrated BisAC11 and
15 NP in xylene were prepared as described above. Note that C5PeC11 is soluble in xylene at 2.4
16 mM. The stock solutions were re-sonicated for 10 minutes before sampling. An amount of stock
17 solutions was added into a vial and then diluted with xylene and heptane. The samples were
18 magnetically stirred for 4 days and filtered with a 0.2 µm PTFE filter prior to measurements and

1 the concentration of C5PeC11 in solution after filtration was determined by HPLC. For DBSA
2 stock solutions, DBSA was directly diluted with 70 vol% heptane instead of pure xylene due to
3 its limited solubility in pure xylene. The setup of HPLC system was presented in a previous
4 paper.³⁶ The C5PeC11 was detected with an UV/vis detector (Shimadzu RID-10A) at 260 nm
5 and 323 nm. Elution was performed on a Phenomenex Luna 5 μ silica (2) 100 Å 250 \times 4.6 mm
6 column at a flow rate of 1 mL \cdot min⁻¹ with different volume ratios of acetic acid and chloroform
7 depending on the systems studied (typically between 2.5 to 4 % v/v of acetic acid). Shimadzu
8 Class VP version 6.13 SP2 software was used to collect and analyze the experimental data. All
9 experiments have been repeated at least twice.

10 **3. RESULTS AND DISCUSSION**

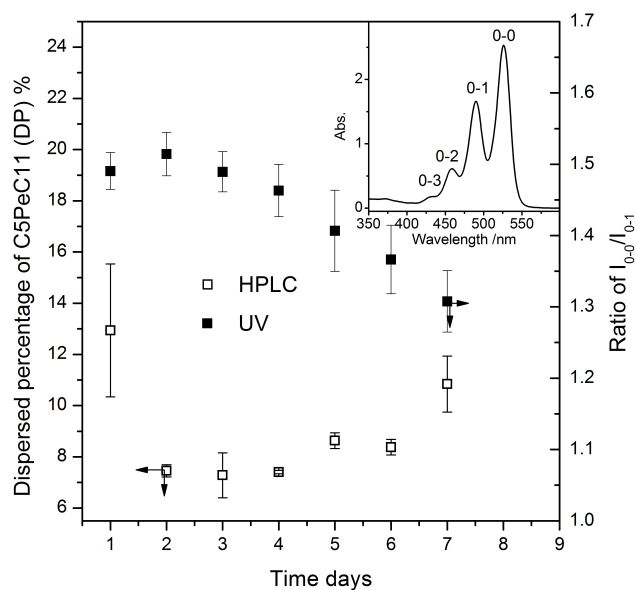
11 *3.1 C5PeC11 precipitation onset in mixtures of xylene and heptane*

12 Before determining the effect of BisAC11 on the solubility of C5PeC11, the precipitation onset
13 of a 0.1 mM solution of C5PeC11 in mixtures of xylene and heptane was determined.

14 It was observed that the precipitation of C5PeC11 shows significant aging effects as seen by
15 measuring the dispersed percentage (DP) of C5PeC11 and ratio of band I₀₋₀ and I₀₋₁ (ratio of
16 absorbances at ca. 526 nm and 490 nm) in 70 vol% heptane as a function of aging time (Figure
17 2). DP represents the percentage of C5PeC11 solubilised compared with the total C5PeC11
18 concentration and is obtained by measuring the C5PeC11 concentration in solution by HPLC and

1 dividing by the total C5PeC11 concentration (C_x). The ground π (HOMO) to excited π^* (LUMO)
2 transition of the C5PeC11 monomers is isolated from other allowed 4-transitions, including
3 $v=0 \rightarrow v'=0, 1, 2, \text{ and } 3$, where v and v' are quantum vibrational numbers of the ground and
4 excited states, respectively³⁷. The assignment of each band to different transitions is shown in
5 inset of Figure 2. As described in previous papers^{33,37,38}, the stronger enhancement of bands 0-1,
6 0-2 and 0-3 compared to 0-0 implies strong excitonic interactions between polyaromatic rings,
7 thus, the ratio of intensity of 0-0 transition band and of the 0-0 band can be applied to monitor
8 the interactions between the aromatic rings.

9 The C5PeC11 concentration in solution was determined after filtration (0.2 μm PTFE filter) by
10 HPLC. Other terms than DP could be used like for instance “dissolved or solubilised percentage
11 of C5PeC11”. DP values decrease with aging and then approach a plateau after which a slight
12 increase is observed. Meanwhile, the ratio of I_{0-0} / I_{0-1} remains the same at first, and then
13 decreases progressively. Combining DP and I_{0-0} / I_{0-1} ratio results implies that tighter C5PeC11
14 aggregates are formed with aging, which can go through the filter (0.2 μm). Another possibility
15 would be that the solubility kinetic is slow and the equilibrium state is reached after several days.
16 In any case, to get reproducible results, all the rest of HPLC measurements were conducted after
17 4 days stirring.



1

2 **Figure 2.** Dispersed percentage of 0.1 mM C5PeC11 and ratio of I_{0-0}/I_{0-1} (UV) in 70 vol%

3 heptane with aging time, the samples were filtered before measurement. The inset is the

4 absorption spectrum of 0.2 mM C5PeC11 with assignment of each band.

5

6 Consequently the solubility of C5PeC11 solutions (DP) in different ratio of xylene/heptane was

7 measured 4 days after solution preparation (Figure 3). As heptane content is lower than 40 vol%,

8 the concentration is constant at 0.1 mM, and then abruptly decreases, finally a plateau at around

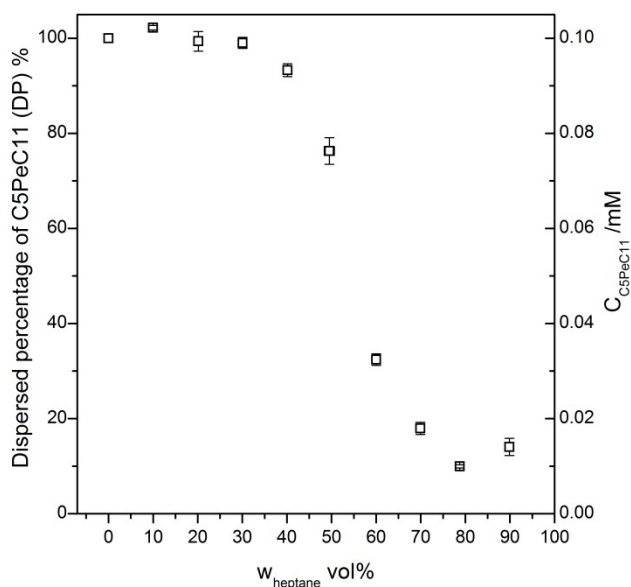
9 0.01 mM is achieved as heptane content is over 70 vol%. Thus, 40 vol% of heptane is the

10 precipitation onset point of C5PeC11. The fact that the solubility of C5PeC11 in heptane is very

11 low corresponds to the operational definition of asphaltenes (insoluble in n-alkane such as

1 heptane) and justifies the designation of C5PeC11 as a representative asphaltene model
2 compound.

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4

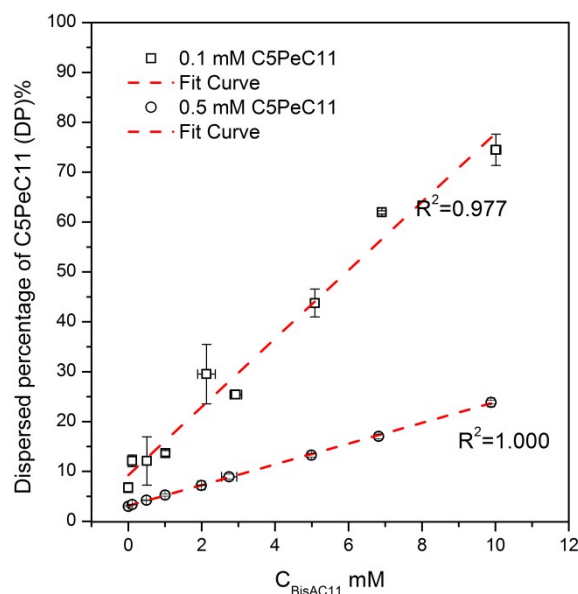
5 **Figure 3.** Dispersed percentage of C5PeC11 with different fraction of heptane.

6

7 ***3.2 Complexation between C5PeC11 and BisAC11 at precipitating conditions for C5PeC11***

8 In this part, the influence of BisAC11 on the solubility of C5PeC11 was studied to display the
9 interactions between the two model compounds. Hence solutions of C5PeC11 in xylene were
10 prepared. These were then diluted to concentrations of 0.1 or 0.5 mM in 30/70 v/v%
11 xylene/heptane in the presence of different concentrations of BisAC11. After stirring and
12 filtration, the final concentrations of C5PeC11 in solution and therefore the DPs were determined

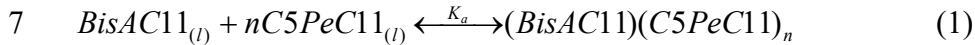
1 by HPLC. Figure 4 presents the variations of DP as a function of the BisAC11 concentration. It
2 can be seen that the solubility limit of C5PeC11 is very low (≈ 0.01 mM) in the tested medium
3 without BisAC11 which is consistent with Figure 3. In the presence of BisAC11, the proportion
4 of dissolved C5PeC11 increases and this increase is proportional to the concentration of
5 BisAC11. This view the importance of the interactions between the two model compounds on
6 the solubility. Apparently, BisAC11 can perform as a dispersant for C5PeC11.



7
8 **Figure 4.** Dispersed percentage (DP) of C5PeC11 (0.1 mM and 0.5 mM) in 70 vol% heptane
9 with increasing BisAC11 concentrations. The error bars represent the standard deviation from
10 repetitions.

11

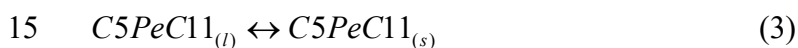
1 Several mechanisms can account for the increase in solubility of C5PeC11 in the presence of
 2 BisAC11 (peptisation, and decrease of the floc size of C5PeC11 by BisAC11, complexation
 3 between C5PeC11 and BisAC11), but only the complexation mechanism is considered in the
 4 following because it can quantitatively explain the experimental results. It is assumed in this
 5 model that BisAC11 and C5PeC11 form a complex that is soluble in the oil phase. The formation
 6 of this complex has an equilibrium association constant K_a :



$$8 \quad K_a = \frac{[(\text{BisAC11})(\text{C5PeC11})_n]}{[\text{BisAC11}_{(l)}][\text{C5PeC11}_{(l)}]^n} \quad (2)$$

9 where K_a is association constant; $[(\text{BisAC11})(\text{C5PeC11})_n]$ is the concentration of the complex
 10 consisting of one BisAC11 molecule and several C5PeC11 molecules; $[\text{BisAC11}_{(l)}]$ is the
 11 concentration of BisAC11 in solutions; $[\text{C5PeC11}_{(l)}]$ is the concentration of C5PeC11. In the Eq
 12 2, activities of dissolved species are simplified to their concentrations in mol/L.

13 If a solid phase exists all the time, the equilibrium between solid and dissolved C5PeC11 can be
 14 described as:



$$16 \quad K_s = \frac{a_{\text{C5PeC11}_{(s)}}}{[\text{C5PeC11}_{(l)}]} \quad (4)$$

1 where $a_{C5PeC11(s)}$ is activity of solid C5PeC11 particles which is equal to 1. Since the solubility of
 2 C5PeC11 in xylene at a certain temperature, pressure and solvent should be constant, it is
 3 assumed that $[C5PeC11_{(l)}]$ is constant which is equal to the concentration of C5PeC11 (C_s)
 4 without BisAC11. C_x is total concentration of C5PeC11 in the samples.

5 The total concentration of C5PeC11 in solution measured after filtration (C_{meas}) is the sum of the
 6 species incorporating C5PeC11 in solution, that means C5PeC11 and the complex
 7 $(BisAC11)(C5PeC11)_n$. Consequently:

$$8 \quad C_{meas} = [C5PeC11_{(l)}] + n[(BisAC11)(C5PeC11)_{(l)}] \quad (5)$$

9 By defining C_x : total concentration of C5PeC11 in the samples, DP_{meas} is equal to:

$$10 \quad DP_{meas} = C_{meas}/C_x, \quad (6)$$

11 With $DP_s = C_s/C_x$, the dispersed percentage of C5PeC11 in the absence of BisAC11.

12 Consequently:

$$13 \quad DP_{meas} = DP_s + \frac{n[(BisAC11)(C5PeC11)_{(l)}]}{C_x} \quad (7)$$

14 In equation (7), the left term represents the solubility of C5PeC11 without BisAC11 while the
 15 second term corresponds to the increase of solubility due to the presence of BisAC11.

16 From equations (2), (4) and (7), the following equation can be obtained:

$$17 \quad DP_{meas} = DP_s + \frac{nC_x^{n-1}}{\frac{1}{K_a DP_s^n} + C_x^n} C_t \quad (8)$$

1 where $DP_{meas} = C_{meas}/C_x$, $DP_s = C_s/C_x$. According to Eq 8, the DP variations with the (total)
2 BisAC11 concentration (C_t) should be linear which is experimentally verified (Figure 4). If more
3 than one BisAC11 per complex is considered, then the relationship between DP_{meas} and the
4 BisAC11 concentration should deviate from linearity. This case is ruled out by experimental
5 data.

6 By applying a linear regression (the coefficients of determination R^2 are indicated in Figure 4)
7 and according to Eq 8, the association constant is estimated and listed in Table 1 for different
8 values of n . Based on the association constants, ΔG values can be calculated according to $\Delta G = -$
9 $RT \ln K_a$, and are also summarized in Table 1. It is found that only when n is equal to one, the
10 association constant does not depend on the initial C5PeC11 concentration. This implies that this
11 model can well fit experimental data only if $(\text{BisAC11})_1(\text{C5PeC11})_1$ complex is formed. The
12 values of ΔG of complexation (-16 kJ/mol) are compatible with van der Waals forces.
13 Considering the results obtained by mixing C5PeC11 and BisAC11 i.e. one precipitating and one
14 soluble compound, it can be speculated that some compounds of higher solubility could increase
15 the solubility of less soluble compounds in polydisperse asphaltene solutions. This result is
16 consistent with experimental observations that resins increase the solubility of asphaltenes and
17 the onset of flocculation.^{39,40} As the limit between asphaltenes and resins is arbitrary and blurry
18 since the molecules present in petroleum crude oil are part of a polarity and molecular weight

1 continuum⁴¹, it is quite appropriate to link the behavior of mixture of asphaltene model
 2 compounds with asphaltene and resins solutions, BisAC11 could be envisioned as either one of
 3 the most polar resins or as one of the least polar asphaltenes. It must be noticed that the
 4 possibility of co-precipitation of BisAC11 has not been checked..

5

6 **Table 1.** Association constant and Gibbs free energy (ΔG) of the association between C5PeC11
 7 and BisAC11 with different initial C5PeC11 concentrations (0.1 and 0.5 mM) in 70 vol%
 8 heptane determined from data presented in figure 4.

9

n	1		2		3	
	K_a	ΔG kJ/mol	K_a	ΔG kJ/mol	K_a	ΔG kJ/mol
0.1 mM	746	-16.39	4.03×10^7	-43.38	2.90×10^{12}	-71.10
0.5 mM	677	-16.15	2.17×10^7	-41.86	9.33×10^{11}	-68.29

10

11 ***3.3 Interactions between asphaltene model compounds and asphaltene precipitation inhibitors***

12 In this section the interactions between asphaltene model compounds and two other compounds
 13 nonylphenol (NP) and dodecyl benzene sulfonic acid (DBSA) are studied. They are generally
 14 considered as model asphaltene precipitation inhibitors or dispersants and studied as

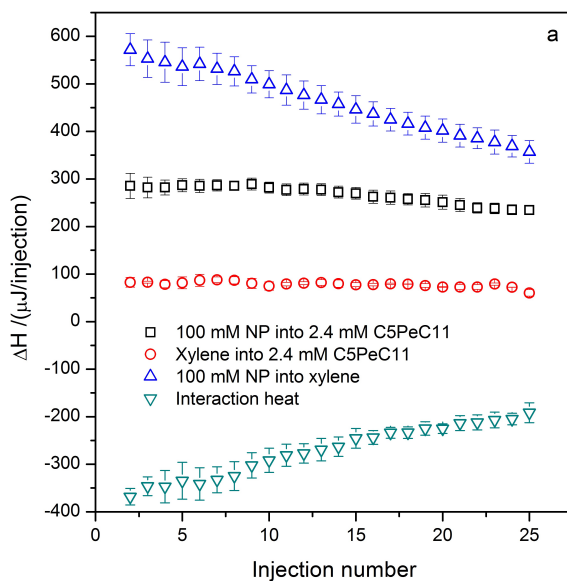
1 references.^{30, 32, 42} Contrary to BisAC11, NP and DBSA are surfactants with a hydrophobic tail
2 and a hydrophilic head.

3 3.3.1 Interactions probed by ITC

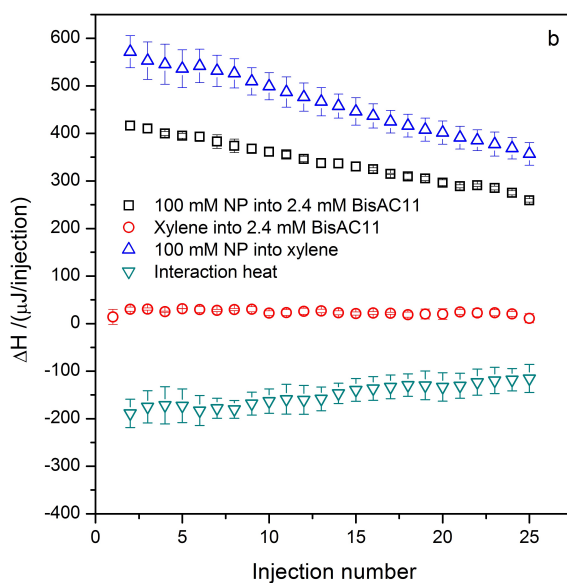
4 For the ITC studies, aliquots of 10 μL of solutions of inhibitors in xylene were injected in a 943
5 μL cell containing C5PeC11 or BisAC11 xylene solutions. The experimental data represents a
6 sum of different contributions (ΔH_{Total}),³² and therefore two extra experiments have been carried
7 out in order to calculate the heat corresponding to interactions between model compounds and
8 inhibitors. These extra measurements consist of the titration of C5PeC11 solutions (cell) with
9 pure xylene (burette) accounting for the dissociation process of C5PeC11 ($\Delta H_{C5PeC11}$), and the
10 titration of pure xylene (cell) with solutions of inhibitors in xylene (burette) here also to account
11 for the inhibitor dissociation process ($\Delta H_{Inhibitor}$) (see Figure 5 for the case of NP). The net
12 enthalpy of interactions (ΔH_{Int}) was obtained by Eq 9:

$$13 \quad \Delta H_{Int} = \Delta H_{Total} - (\Delta H_{Inhibitor} + \Delta H_{C5PeC11}) \quad (9)$$

14 It should be mentioned that dissociation of individual components in mixtures is assumed to be
15 the same as those in corresponding individual solutions.



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2

3 **Figure 5.** Heat contributions of all the major processes when injecting nonylphenol (NP) into 2.4

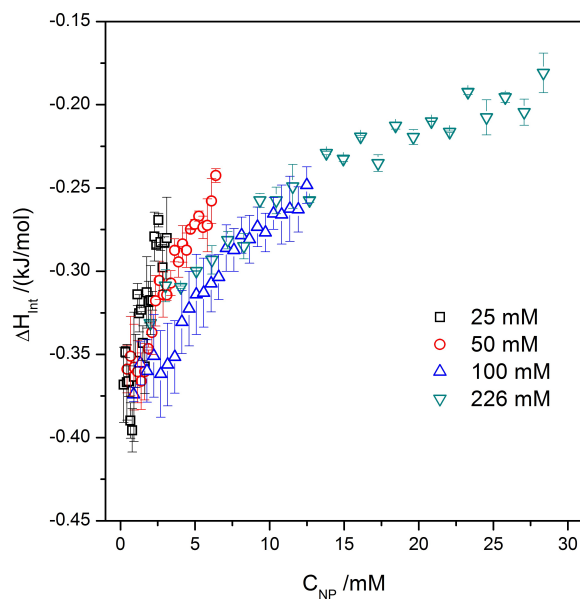
4 mM C5PeC11 (a) or BisAC11 (b). Contributions shown: dilution of C5PeC11 or BisAC11;

5 dilution of NP at different concentrations; titration of C5PeC11 or BisAC11 with NP; interaction

6 enthalpy between C5PeC11 or BisAC11 and NP. Error bars represent the standard deviation

7 from repetition.

1
2 The net enthalpy of interaction per mol of inhibitors (ΔH_{Int} kJ/mol) for the system C5PeC11/NP
3 is presented in Figure 6. The interaction between NP and C5PeC11 is exothermic. Absolute
4 enthalpy values decrease with increasing NP concentrations, and no significant difference can be
5 observed when the concentration of NP in injection syringe is varying. No significant differences
6 in molar enthalpy indicate that interplay between NP and C5PeC11 is not related to the self-
7 association of NP within the concentration range studied. Even if we must be cautious by doing
8 the comparison, it must be noticed that the interaction enthalpy values are close to that of
9 asphaltenes (from -1.5 to -0.3 kJ/mol) previously reported assuming a molecular weight of 750
10 g/mol³² even if different concentrations of asphaltenes (10 g/L) and C5PeC11 (2 g/L) solutions
11 were used in the two studies. The driving force for the interactions might be related to formation
12 of physical bonds such as van der Waals forces and hydrogen bonds between the two
13 compounds.



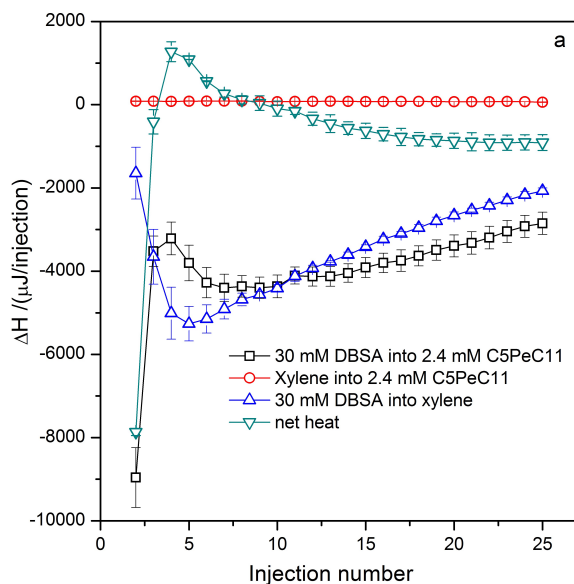
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 2 **Figure 6.** Net interaction heat per mol of nonylphenol (NP) (ΔH_{Int} kJ/mol) as a function of NP
 3 concentration; the concentration of C5PeC11 in the cell was 2.4 mM.

4
 5 The second inhibitor studied is DBSA. This model precipitation inhibitor displays complex self-
 6 association properties strongly concentration and aging dependent.³² The self-association of
 7 DBSA has significant consequences on the interaction with asphaltenes. The contributions to the
 8 net heat due to different processes are specified in Figure 7. The variations in the interaction
 9 enthalpy between C5PeC11 and DBSA per mol of DBSA are shown in Figure 8. The enthalpy
 10 value decreases with DBSA concentrations to a minimum value first (ca 0.4 mM), and then
 11 increases to reach a maximum value (ca. 1.4 mM). Finally a slight decrease is displayed at higher
 12 concentrations of DBSA. The concentrations at each extreme are close to transition

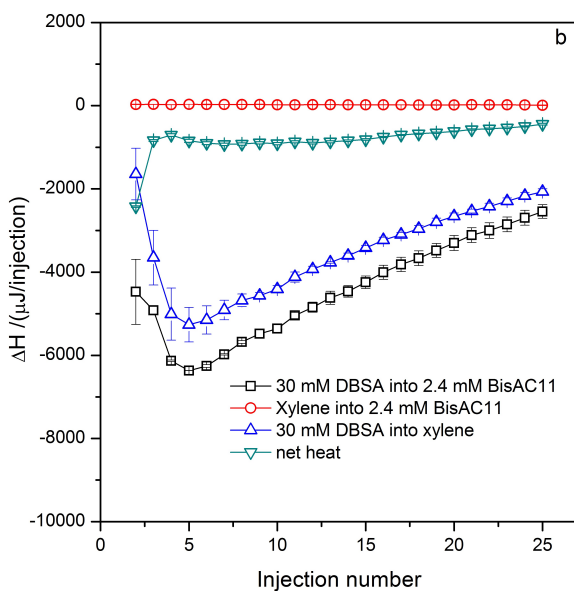
1 concentrations of DBSA self-aggregation (Figure 9). This transition might be related to the
2 different aggregation states of DBSA with increasing concentrations: small aggregates like
3 dimers are formed at lower concentration, while bigger DBSA aggregates tend to be formed at
4 higher concentrations³². This reflects that the interactions between C5PeC11 and DBSA are also
5 related to the state of DBSA (dashed lines in Figure 8). At around 0.9 mM of DBSA, the sign of
6 net enthalpy turns to positive, which is related to breaking of bonds. Thus, the behavior observed
7 in the case of NP (Figure 6) is not repeated for DBSA, and this implies that several complex
8 processes contribute to build up the net enthalpy and not only creation of interaction between
9 DBSA and C5PeC11. DBSA might be able to promote the dissociation of C5PeC11 aggregates,
10 and this ability would increase at higher DBSA concentrations. The enhanced dissociation of
11 C5PeC11 aggregates which is endothermic contributes to the enthalpy values and drives the net
12 enthalpy to be positive. Similar phenomena were also observed in the asphaltene system.³² The
13 maximum enthalpy values are almost 80 times higher than that for NP, which indicates a higher
14 level of complexation processes.

15 For the sake of comparison, the interaction between BisAC11 and inhibitors were also
16 investigated (**Figures 5 and 7**). The interaction between BisAC11 and NP seems to be 2 times
17 lower than in the C5PeC11 case.

18



1



2

3 **Figure 7.** Heat contributions of all the major processes when injecting dodecyl benzene sulfonic

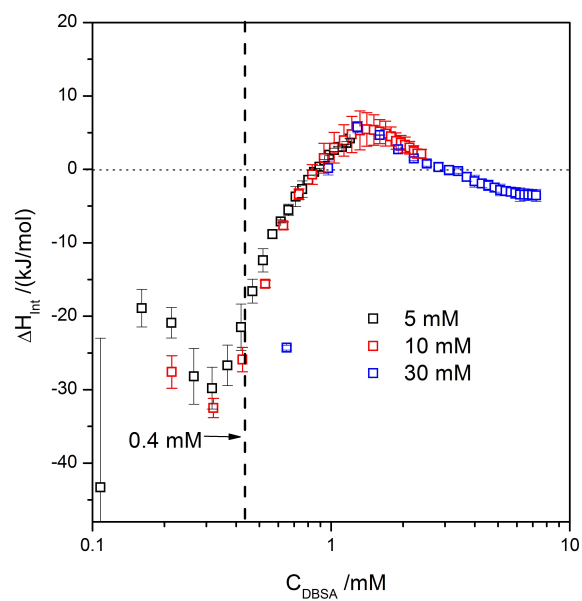
4 acid (DBSA) into 2.4 mM C5PeC11 (a) or BisAC11 (b). Contributions shown: dilution of

5 C5PeC11 or BisAC11; dilution of DBSA at different concentrations; titration of C5PeC11 or

6 BisAC11 with DBSA; interaction enthalpy between C5PeC11 or BisAC11 and NP. Error bars

7 represent the standard deviation from repetition.

1

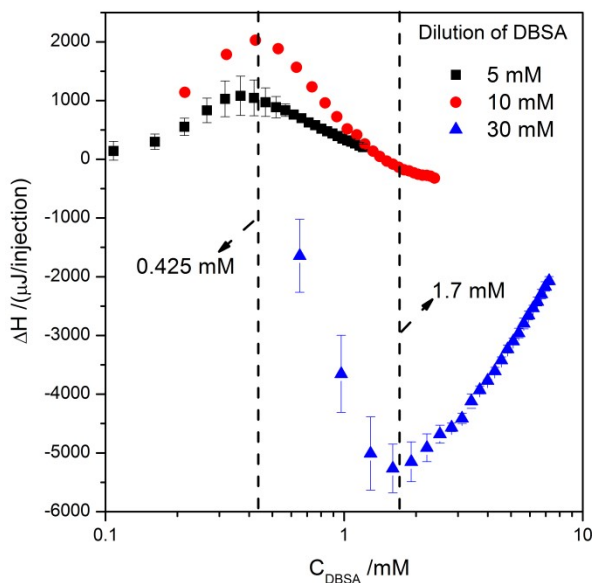


2

3 **Figure 8.** Interaction heat per mol of dodecyl benzene sulfonic acid (DBSA) (ΔH_{int} kJ/mol) as a
4 function of DBSA concentration; the concentration of C5PeC11 in the cell was 2.4 mM. Dashed
5 lines represent different self-aggregation regions of DBSA.

6

7



1
2 **Figure 9.** Enthalpy for dilutions of DBSA solutions at different concentrations as a function of
3 DBSA concentration in cell.

4
5 The contributions become even more complicated for DBSA. As mentioned above, the
6 interaction between DBSA and C5PeC11 is strong enough to eliminate the C5PeC11 self-
7 association which would also contribute to the net enthalpy obtained in Eq 9. However, BisAC11
8 only shows a slight tendency of self-association as demonstrated in the 1st article. The
9 contribution of an enhanced dissociation of BisAC11 aggregates is negligible, thus, the net
10 enthalpy values calculated by Eq 9 are always negative reflecting only the contribution from the
11 interplay between BisAC11 and DBSA. The interaction enthalpy is almost 5 times higher than
12 those for the NP case.

1

2 *3.3.2 Complexation experiments*

3 In this section the influence of NP and DBSA on the solubility of C5PeC11 in a mixture 30/70
 4 v/v% xylene/heptane is determined with a strategy similar to the one used for BisAC11 (part
 5 3.2).

6 The DP values of C5PeC11 as a function of inhibitor concentrations are presented in Figure 10.

7 The addition of NP (Figure 10a) to precipitated C5PeC11 system shows a negligible effect on the

8 DP values. Even if NP and C5PeC11 interact in solution, these interactions are not strong enough

9 to influence the solubility of C5PeC11. For DBSA, the DP values increase linearly with

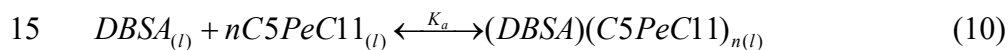
10 increasing DBSA concentration (Figure 10b), and reach 100 % for a DBSA concentration of ca.

11 1.0 mM. This result indicates that the C5PeC11 precipitate is re-dispersed at a molar ratio of

12 DBSA and C5PeC11 ≈ 10 . As the variations of DP are proportional to the concentration of

13 DBSA, similar to the case of BisAC11, it is proposed that this compound also forms a soluble

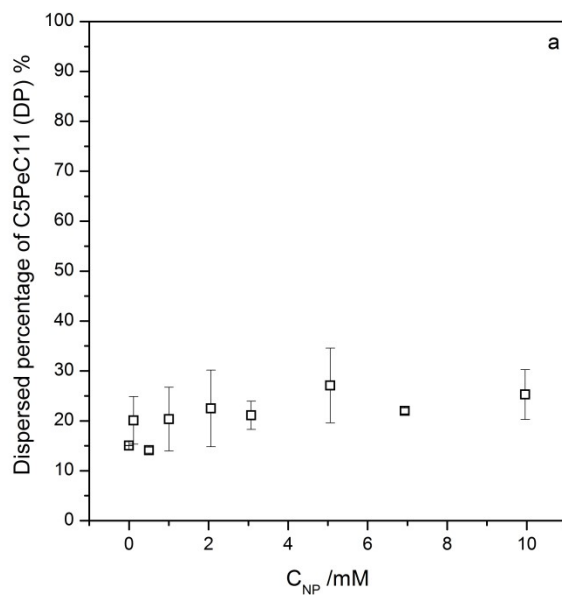
14 complex with C5PeC11:



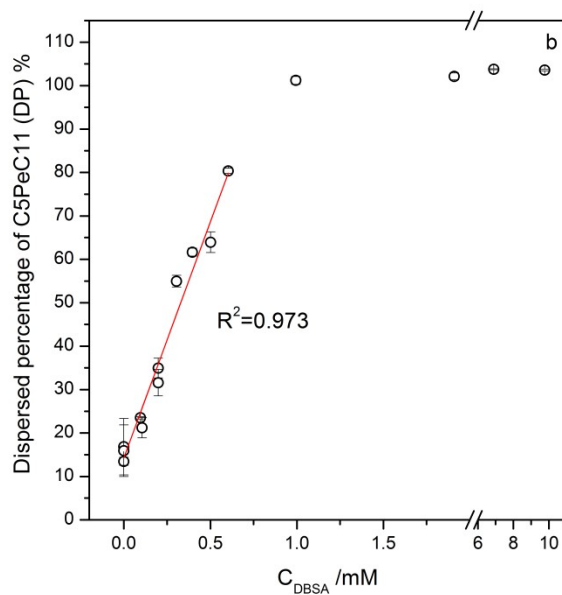
$$16 \quad K_a = \frac{[(DBSA)(C5PeC11)_{n(l)}]}{[DBSA_{(l)}][C5PeC11_{(l)}]^n} \quad (11)$$

1 K_a can be obtained from the linear curve (DP) as a function of DBSA concentration (Figure 10b).
2 As the influence of DBSA has not been tested at different C5PeC11 total concentration, it is not
3 possible to unambiguously determine the values of n for the complex (DBSA)(C5PeC11) $_n$ as for
4 the complex (BisAC11)(C5PeC11) above in part 3.2. If $n=1$ then the association constant
5 between C5PeC11 and DBSA is equal to 8.53×10^3 which corresponds to a ΔG of -22.4 kJ/mol.
6 This value is compatible with van der Waals forces and is higher but in the same order of
7 magnitude than that for the case of (BisAC11)(C5PeC11) complexes. In order to have extra
8 information on the complexation mechanism between DBSA and C5PeC11, the visible spectra
9 of C5PeC11 solutions with and without DBSA were determined (Figure 11). The measurements
10 were carried out after 4 days stirring, i.e. the same procedure of the preparation as HPLC
11 experiments. The spectra show that the ratio between I_{0-0} and I_{0-1} decreases abruptly with DBSA
12 concentrations which indicates a π - π interaction between DBSA and C5PeC11. These
13 interactions are complementary to H-bonds which are considered to be the main interactions
14 between these two compounds.

15



1



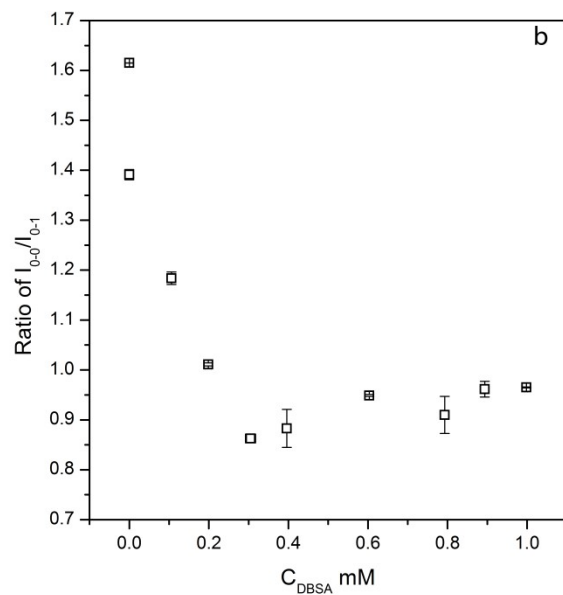
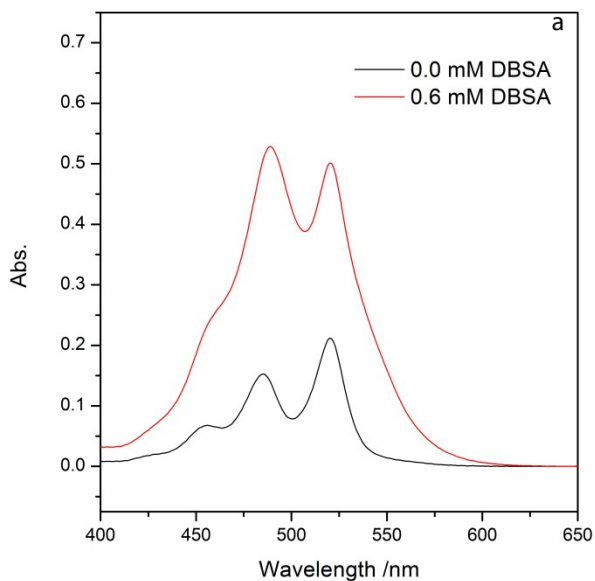
2

3 **Figure 10.** Dispersed percentage (DP) of C5PeC11 (0.1 mM) in 70 vol% heptane with increasing

4 NP (a) and DBSA (b) concentrations; the line illustrates the linear fitting at lower concentrations

5 of DBSA. The error bars represent the standard deviation from repetitions.

6



1

2

3 **Figure 11.** a) UV spectra of C5PeC11 (0.1 mM) with and without DBSA; b) Ratio of I_{0-0}/I_{0-1}

4 (UV) as a function of DBSA concentrations in 70 vol% heptane. The data was measured after 4

5 days stirring.

6

7

1

2 **4. CONCLUSION**

3 In this article the interaction and complexation between asphaltene model compounds and
4 asphaltene inhibitors are investigated by solubility and ITC.

5 BisAC11 can increase the maximum solubility of C5PeC11 in mixtures of xylene and heptane.

6 This effect is attributed to the formation of a soluble complex between C5PeC11 and BisAC11
7 for which the association constant is experimentally determined. This association energy
8 corresponds to a ΔG of ≈ -16 kJ/mol.

9 The interactions between C5PeC11 and DBSA (asphaltene inhibitor) are stronger than between
10 C5PeC11 and NP and will enhance the solubility of C5PeC11 in mixtures of xylene and heptane
11 by complexation. π - π association between DBSA and C5PeC11 complementary to H-bonds are
12 responsible for the formation of (DBSA)(C5PeC11) complex with a ΔG of -22.4 kJ/mol. FTIR
13 could be a good technique to characterize H-bonds and complement the presented solubility and
14 ITC data.

15 In conclusion, part one and two bring new light on the interaction and association pattern
16 between molecules in asphaltene samples and on the mechanism of action of asphaltene
17 precipitation inhibitors. Enthalpy values seem to be well suited to quantify the different
18 interaction forms, and hence inhibitor efficiency.

1

2 **5. CORRESPONDING AUTHOR**

3 *E-mails: sebastien.simon@chemeng.ntnu.no (Sébastien Simon) ; weiduo@yzu.edu.cn (Duo
4 Wei)

5 **Current address: Testing center, Yangzhou University, Yangzhou, China

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