

# Association Behavior of Pyrene Compounds as Models for Asphaltenes<sup>†</sup>

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Asphaltene association in solution has been studied extensively using methods such as vapor-pressure osmometry and neutron scattering. These methods give relative data on association as a function of solvent strength, temperature, and concentration, but interpretation of the results is hampered by the polyfunctional nature of asphaltenes and the distribution of molecular weight. In this work, we present data on association of representative model structures for asphaltenes, as measured using vapor-pressure osmometry in *o*-dichlorobenzene at 75–130 °C, and using small-angle neutron scattering in toluene. A series of compounds were synthesized based on the four-ring aromatic compound pyrene. The synthetic compounds were designed to give interactions between aromatic rings, alkyl chains, and selected functional groups through aromatic interactions, hydrogen bonding, and polar interactions. Even in this strong solvent, polar interactions between oxygen functional groups gave average molecular weights of up to twice the true value, indicating dimer formation. An alkyl pyrene compound, dipyrenyl decane, gave much less significant association. Pyrene itself exhibited little or no self-association.

## Introduction

Two of the defining characteristics of the asphaltene fraction of crude oils are their chemical complexity and their tendency to associate in solution. The components that precipitate from *n*-heptane all share a common lack of solubility, but they can include a broad range of functional groups, molecular weights, and aromatic carbon content. The difficulty in separating the asphaltenes into distinct chemical classes makes it difficult to determine which chemical properties contribute to their physical behavior in crude oil.

A number of methods have been used to examine the associative properties of the asphaltenes, including rheology,<sup>1</sup> small-angle X-ray and neutron scattering,<sup>2,3</sup> fluorescence depolarization,<sup>4</sup> vapor-pressure osmometry (VPO),<sup>5</sup> and calorimetry.<sup>6</sup> The widespread availability

of equipment for vapor-pressure osmometry, as well as the direct relationship between the apparent molecular weight and colligative properties, has led to the use of this method in studying the supramolecular association behavior of pure compounds.<sup>7</sup> The challenge in the case of VPO is understanding the dependence of the measured number-average apparent molecular weight on the underlying chemical properties of the asphaltene, including the distribution of the molecular weight of the “monomers” in the mixture and the contribution of different chemical structures to the formation of aggregates, including polar functional groups, polycyclic aromatic hydrocarbons, and alkyl substituent groups.

One method to improve our understanding of liquid-phase association behavior relevant to asphaltenes is to synthesize pure compounds that contain selected chemical structures, and then to examine their behavior in solution. In this paper we report on the association behavior of pure compounds derived from pyrene in *o*-dichlorobenzene, a strong solvent commonly used for VPO of asphaltene materials. By synthesizing pure compounds with different functional groups on the relatively large pyrene ring system, we can investigate the association behavior due to specific structural features that appear in authentic asphaltenes, including hydroxyl groups which can give hydrogen bonding, ketones, and other polar groups, and a structural backbone of polycyclic aromatic hydrocarbons, alkyl side chains, and alkyl bridges.<sup>8</sup>

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### Theory

We consider only the average molar mass of mixtures of monomers and dimers, because no evidence of higher-order association was observed in our experiments. The extension of this model to allow noncooperative association, leading to a distribution of oligomers, is straightforward. The average molar mass of a mixture of monomers and dimers can be derived from a material balance and an equilibrium relationship. A material balance on the dissolved species gives

$$A_0 = A_1 + 2A_2 \quad (1)$$

where  $A_0$  is the initial concentration assuming all in monomer form,  $A_1$  is the equilibrium monomer concentration, and  $A_2$  is the equilibrium dimer concentration. At equilibrium conditions, the dimer concentration is related to the monomer concentration as follows:

$$A_2 = KA_1^2 \quad (2)$$

where  $K$  is the monomer association constant. Combining eqs 1 and 2 gives

$$2KA_1^2 + A_1 - A_0 = 0 \quad (3)$$

then solving for  $A_1$ :

$$A_1 = \frac{-1 + \sqrt{1 + 8KA_0}}{4K} \quad (4)$$

where  $A_2$  is given by eq 2. The average molar mass is given by

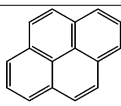
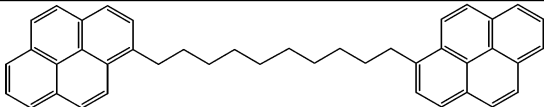
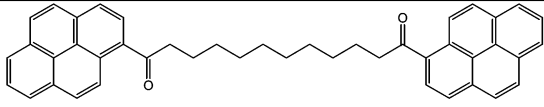
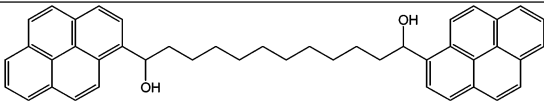
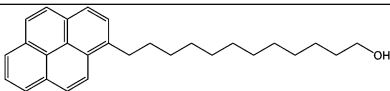
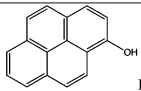
$$M = \frac{A_1M_1 + A_2M_2}{A_1 + A_2} = \frac{A_1 + 2A_2}{A_1 + A_2}M_1 \quad (5)$$

### Experimental Methods

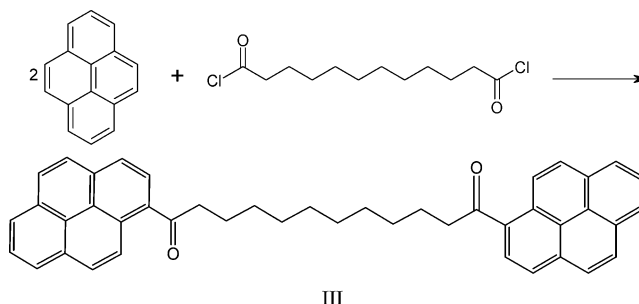
The structures of the pyrene-derived model compounds are given in Chart 1. Pyrene (**I**) was obtained from Aldrich Chemical (purity 98%). 1,10-Dipyrenyl decane (**II**) was purchased from Molecular Probes Inc. (Eugene, OR) and used as received. The synthesis of 1,12-di-(1-pyrenyl)-dodecane-1,12-dione (**III**) followed Scheme 1. Briefly, pyrene and molar equivalents of anhydrous  $AlCl_3$  were mixed in anhydrous  $CH_2Cl_2$ , chilled to  $-3^\circ C$  using a salt and ice mixture, then blanketed with dry nitrogen. The dodecane-diacyl dichloride was added drop by drop. The resulting dark-red slurry (resulting from the ketone- $AlCl_3$  complex) was then poured on a 50:50 HCl-ice solution to break the complex, and diluted with additional  $CH_2Cl_2$  to improve product partitioning to the organic phase. The product precipitated as a light-yellow solid, which was washed with acetone to remove unconverted pyrene. Further purification was achieved by recrystallizing from hot toluene. The structure was confirmed by mass spectrometry, FTIR, and NMR.

The purified 1,12-di-(1-pyrenyl)-dodecane-1,12-dione (**III**) was reduced using  $LiAlH_4$  in tetrahydrofuran. After refluxing for 4 h, the dione was reduced to the diol. Several other minor products were also formed at this step. The reaction products were separated on a silica gel column using toluene and ethyl acetate 10:1 (v/v) as eluent. Silica gel separation of a series of batches gave unreacted dione, 1,12-di-(1-pyrenyl)-dodecane-

Chart 1. Model Compounds Derived from Pyrene

Compound	Structure and Name
<b>I</b>	 Pyrene
<b>II</b>	 1,10-dipyrenyl decane
<b>III</b>	 1,12-di-(1-pyrenyl)-dodecane-1,12-dione
<b>IV</b>	 1,12-di-(1-pyrenyl)-dodecane-1,12-diol
<b>V</b>	 1-pyrenyl-dodecane-12-ol
<b>VI</b>	 Pyrenol

Scheme 1. Synthesis of 1,12-Di(1-pyrenyl)dodecane-1,12-dione (**III**)

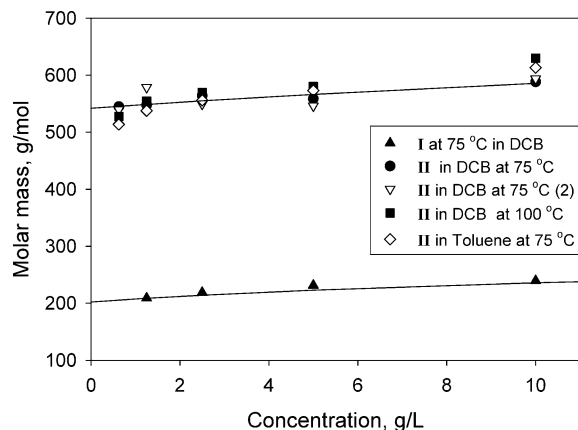


1,12-diol (**IV**) product and two fragmentation products: 1-pyrenyl-dodecane-12-ol (**V**) and pyrenol (**VI**). The structures were verified by mass spectrometry and FTIR. The diol (**IV**) was not stable in dichlorobenzene at temperatures used for VPO as a result of rapid dehydration to form the diene; therefore, it was studied by small-angle neutron scattering.

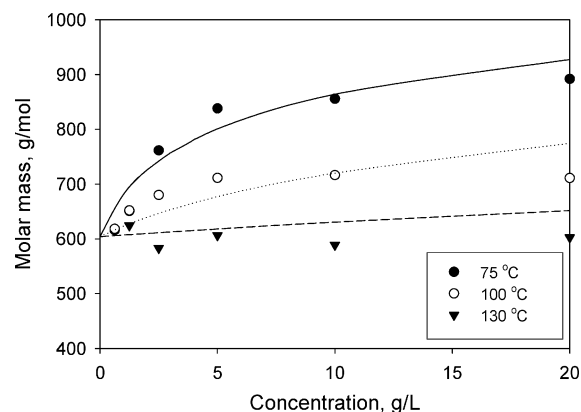
The measurement of molar mass followed the method of Agrawala and Yarranton,<sup>5</sup> using a model 833 vapor-pressure osmometer from Jupiter Instruments. Sucrose octaacetate (679 g/mol) was used as a calibration standard. Measurements were conducted at concentrations ranging from 0.6 to 20 g/L in *o*-dichlorobenzene at temperatures of 75, 100, and 130 °C. The ketone and alcohol compounds were relatively insoluble in toluene; therefore, only very limited experiments used toluene as a solvent.

A solution of diol (**IV**) was prepared in a mixture of D-toluene (CDN Isotopes, 99.6 atom % D) and deuterated methanol (Acros, 99.8 atom % D) was added in order to facilitate dissolution. The final concentration of the diol solution was 0.82% (w/w) solute, 14.52% (w/w) D-methanol, and 84.67% (w/w) D-toluene. Small-angle neutron scattering measurements were performed on the diol solution using the small-angle neutron diffractometer (SAND) at the Intense Pulsed Neutron

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**Figure 1.** Molar mass of pyrene (I) and dipyrenyl dodecane (II) in *o*-dichlorobenzene. One data set is given for compound II in toluene.



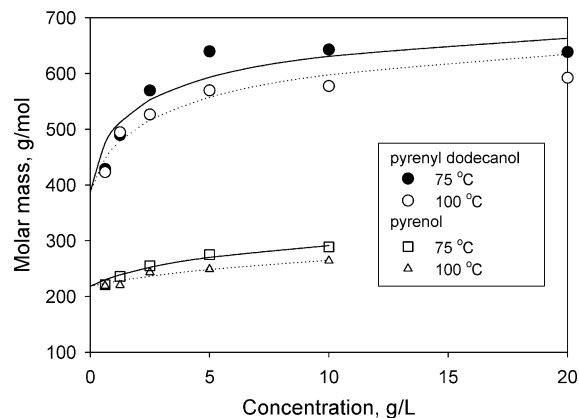
**Figure 2.** Molar mass of dipyrenyl dodecane dione (III) in *o*-dichlorobenzene. Curves are from eq 5, with association constants from Table 1.

Source Division of Argonne National Laboratory (Argonne, IL). The available  $Q$  range for the SAND instrument extended from 0.0035 to 2  $\text{\AA}^{-1}$ . The absolute scattering intensity,  $I(Q)$ , for the sample was obtained from the total detector counts corrected for background radiation, neutron transmission through the samples, scattering from the quartz cells, and detector sensitivity.<sup>3</sup>

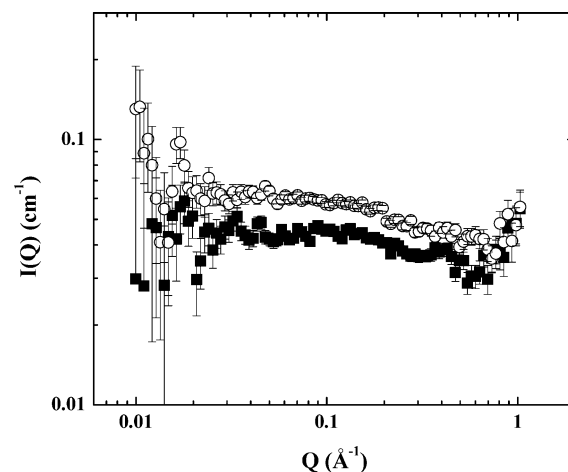
## Results

The apparent molar mass of pyrene and the dipyrenyl decane (compounds I and II) are shown in Figure 1. The lines are from eq 5, based on a best-fit value of the association constant  $K$ . The apparent molar masses of both compounds increased slightly with increasing concentration, but this increase was independent of temperature and choice of solvent in the case of dipyrenyl decane. This lack of sensitivity to temperature suggests that the change was due to measurement errors at these concentrations rather than to actual association in solution. Consequently, changes on the order of 20% or less in molar mass over this range of concentration at 75 °C in *o*-dichlorobenzene and values of the association constant  $K$  of 6  $\text{L g}^{-1} \text{mol}^{-1}$  or less were not considered significant.

The molar mass of the dipyrenyl dodecane dione (III) is given in Figure 2. In this case, the apparent molar mass increased significantly with concentration, and the increase was strongly dependent on the temperature. At 130 °C the molar mass was almost constant, while



**Figure 3.** Molar mass of pyrenyl dodecanol (V) and pyrenol (VI) in *o*-dichlorobenzene. Curves are from eq 5, with association constants from Table 1.



**Figure 4.** Small-angle neutron scattering intensity curves for (○) dodecane diol (IV) and (■) D-toluene.

**Table 1. Association Constants for Pyrene Compounds**

compound	association constant, $K$ (L/mol)			enthalpy of association (kJ/mol)
	75 °C	100 °C	130 °C	
dipyrenyl dodecane dione (III)	100	18	3.0	-77
pyrenyl dodecanol (V)	290	160		-27
pyrenol (VI)	22	9.2		-38

at 75 °C the change in apparent molar mass indicated that a significant amount of dimer formed in solution. Similar trends were observed for the two hydroxyl compounds IV and V, as illustrated in Figure 3.

The best-fit values of the monomer association constants are given in Table 1. The estimates for the enthalpies of association are from the van't Hoff equation, assuming that the enthalpies are approximately constant over the range of temperature. As discussed above, association constants less than 6 L/mol could not be distinguished from experimental error.

Scattering intensity versus scattering angle ( $I(Q)$  vs  $Q$ ) curves for the diol (IV) solution and a D-toluene blank solution are shown in Figure 4. The magnitude of the scattering intensity curve for the diol solution in Figure 4 was comparable to the data for the D-toluene solution, suggesting that this model compound did not associate to give strong scattering in the D-toluene/D-methanol solvent mixture. The radius of gyration of the diol aggregates was 3.5  $\text{\AA}$ , as determined by Guinier analy-

sis.<sup>9</sup> The scattering curve for the diol (**IV**) compound shown in Figure 4 has not been corrected for solvent background. The value of  $I(Q = 0)$  or  $I_0$  is estimated as the difference in the plateau values for the diol (**IV**) solution and the toluene blank. The toluene blank is not exactly the correct solvent background, because the diol (**IV**) solution contains D-methanol. The value of  $I_0$  for the background corrected spectra is  $\sim 0.02 \text{ cm}^{-1}$ . The weight-average molecular weight of the aggregates is calculated by the equation

$$M_w = \frac{I_0 N_A d_m}{\phi(\Delta\rho)^2} \quad (6)$$

where  $N_A$  is Avogadro's number,  $d_m$  is the scatterer mass density ( $\sim 0.95 \text{ g/cm}^3$ ),  $\phi$  ( $\sim 0.0081$ ) is the scatterer volume fraction, and  $\Delta\rho$  ( $4.3 \times 10^{-6} \text{ \AA}^{-2}$ ) is the scattering contrast between solute and solvent. The aggregate molecular weight obtained from the above parameters is  $\sim 800 \pm 300 \text{ Da}$ . The monomer molecular weight is  $603 \text{ Da}$ . These neutron scattering results indicated that the diol did not significantly self-associate in the solvent mixture and that aggregation was limited to the formation of some dimers.

### Discussion

The self-association of the hydrocarbon model compounds ranged from no detectable association for pyrene and alkyl-bridged dipyrene to dimerization for compounds with oxygen functional groups. Pyrene and other PAHs can form excited-state dimers, or excimers, when excited by UV radiation. Most authors consider that these complexes form only after excitation, although one study indicated aggregation of ground-state pyrene in a weaker solvent than the present study (cyclohexane at ambient temperature).<sup>10</sup> Aromatics from benzene through pyrene and coronene (seven fused rings) crystallize in a herringbone pattern, with the aromatic sheets inclined rather than stacked.<sup>11</sup> This optimum configuration in crystalline form suggests that extensive association of these aromatics in strong solvents by aromatic stacking interactions will be unlikely.

The single alkyl bridge in compound **II** was not sufficient to stabilize associations in solution. Intramolecular association of the pyrene groups in this compound cannot be ruled out, given flexibility of the decyl bridge joining the two pyrene groups; however, if such association were significant, then we would also observe some level of intermolecular association in toluene. Observations on alkyl hexabenzocoronenes suggest that either larger aromatic groups or more alkyl side groups would be required to enhance association in solution,<sup>12</sup> while the formation of bridged structures reduces the tendency to associate in liquid-crystalline structures.<sup>13</sup> In contrast, the polar compounds **III**, **IV**, and **V** all

showed evidence for dimer formation in solution, but not more extensive association. The strongest association, based on the monomer association constant,  $K$ , was exhibited by compound **V**, presumably due to hydrogen-bonding interactions. The pyrenol (**VI**) gave the weakest association of the three polar compounds. These results suggest that polar functional groups will contribute to association behavior, even in strong solvents, at elevated temperature.

A comparison with asphaltene self-association is instructive. Asphaltenes form associated structures with apparent molecular weights that increase rapidly with concentration in VPO experiments. For example, an Athabasca asphaltene increased its apparent molar mass from 800 to over 5000 at a concentration of  $10 \text{ g/L}$  in *o*-dichlorobenzene at  $75 \text{ }^\circ\text{C}$ .<sup>4</sup> The model compound results did not match this level of association in solution, indicating that these compounds lacked a key feature to mimic the behavior of asphaltenes. We can rule out association between unsubstituted 3–4 ring aromatic clusters, based on the data for pyrene. Intramolecular association in compounds **II**, **III**, and **IV** cannot be ruled out, given the flexibility of the decyl and dodecyl bridges, but the lack of association of pyrene suggests a limited driving force for such behavior. Recent studies of large (13-ring) alkyl-aromatics have shown that multiple alkyl side chains strongly enhance the stacking interactions.<sup>11</sup> The trends in the model compound data suggest that larger, more alkyl-substituted aromatic structures are required to account for the observed self-association of asphaltenes. The model compound results also suggest that heteroatomic groups also play a significant role.

It will be necessary to test larger, more complex structures to further narrow the range of possible asphaltene structures and, in particular, to distinguish between the models of asphaltenes as percondensed aromatic rings with side chains, versus smaller ring groups with bridges and side chains. However, it seems likely that asphaltene monomers must be reasonably large to incorporate sufficient features to strongly self-associate. Monomer molar masses less than 500 to 1000 g/mol are unlikely.

### Conclusions

Pyrene and dipyrenyl decane did not give significant association in dilute solution in *o*-dichlorobenzene. Polar functional groups (ketones and hydroxyls) gave stronger association of pyrene derivatives in solution, resulting in dimer formation in *o*-dichlorobenzene solution at  $75$  and  $100 \text{ }^\circ\text{C}$ .

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