

# THERMODYNAMICS OF CARBONACEOUS MESOPHASE

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## Introduction

The liquid crystalline nature of carbonaceous mesophase has long been recognized [1,2] and this insight has been key to the understanding of carbonization and graphitization. Despite many advances, our knowledge of carbonaceous mesophase is incomplete and qualitative in many respects. The purpose of this paper is to gain a better understanding of carbonaceous mesophase through a *quantitative* treatment of the liquid crystal phase transformations in pitches and model PAHs.

## Phase Transitions in Single-Component PAH

Review of the literature on discotic liquid crystals reveals several interesting facts pertinent to carbonaceous mesophase. First, no known PAH structure has been reported to form a discotic liquid crystalline phase in the pure state. Further,

the only known discotic liquid crystals are limited to a small set of homologous series of organic compounds that differ from PAH or typical pitch components, most notably by the presence of multiple, long, aliphatic side chains attached to the aromatic core. The liquid crystalline nature of carbonaceous mesophase is difficult to rationalize when only single-components are examined.

## Phase Transitions in Multicomponent PAH Mixtures

Binary systems (see Fig. 1) can be understood by simultaneous consideration of solid/liquid and liquid/nematic phase equilibria. Expressions were derived for binary solid/liquid equilibrium assuming PAH do not form solid solutions. Additional relations were derived for the discotic liquid crystal / isotropic liquid transition, yielding:

$$X_A^L/X_A^N = (\gamma_A^N / \gamma_A^L) e[\Delta H_{clA}/(1/T_{clA} - 1/T)]$$
$$X_B^L/X_B^N = (\gamma_B^N / \gamma_B^L) e[\Delta H_{clB}/(1/T_{clB} - 1/T)]$$

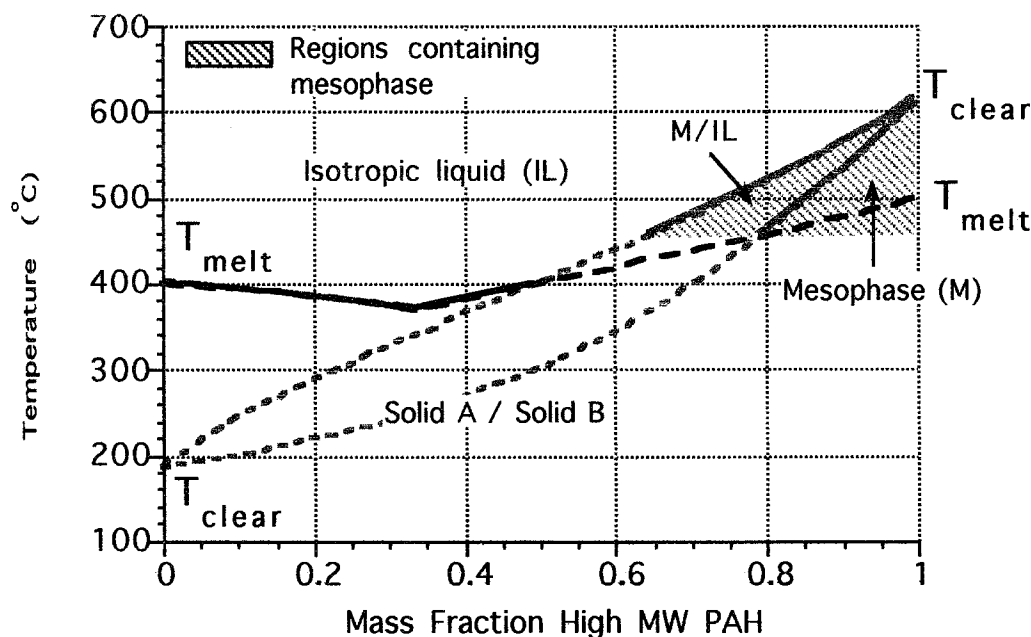


Figure 1. Example phase diagram for binary PAH mixture containing a low-MW nonmesogen and a high-MW mesogen. The regions containing carbonaceous mesophase are shaded.

where  $X$  are mole fractions,  $N$  denotes the nematic liquid crystal, and  $L$  denotes the isotropic liquid phase.  $T_{cl}$  is the equilibrium temperature of the pure components (the "clearing temperature"), while  $\Delta H_{cl}$  is the "clearing enthalpy." Solution of these equations together with species balances determines the amount and composition of the discotic nematic, isotropic liquid, and solid phases.

Figure 1 presents example results for a hypothetical binary mixture consisting of a low molecular weight, nonmesogenic PAH, component A, and a higher molecular weight mesogenic PAH, component B. Note for pure A that the melting temperature lies above the clearing temperature, making the discotic liquid crystal a virtual phase masked by the crystalline solid. Overall, the binary model reproduces some major features of carbonizing systems, but can be greatly improved by considering multicomponent systems ( $n > 2$ ).

A multicomponent ( $n > 2$ ) banded model was developed that is more effective at suppressing solid phases and revealing larger regions containing discotic liquid crystalline phases. The multicomponent banded model is general enough to describe phase equilibrium in a wide variety of PAH mixtures.

### Application to Pitch Pyrolysis

The multicomponent model was applied to the analysis of pitch carbonization experiments performed by Greinke and Singer [3]. In these experiments, a petroleum pitch was heat treated at 400 °C for various hold times, after which the carbonaceous mesophase and isotropic phase were separated by high speed centrifugation, and their molecular weight distributions determined by gel permeation chromatography [3]. Greinke and Singer present their results as molecular weight distributions and as derived partition coefficients (isotropic / mesophase) for the various molecular weight fractions. The latter presentation is shown in Fig. 2.

Also shown in Figure 2 are the predictions of the multicomponent model (lines). In addition to the general equilibrium equations, the model is based on an assumed linear relationship between clearing temperature,  $T_{cl}$ , and molecular weight, and a constant, mass-specific value of  $\Delta H_{cl}$ . The final value of  $\Delta H_{cl}$  was determined by comparison of model predictions to the complete set of partition coefficients in Fig. 2, yielding 9 J/gm for  $\Delta H_{cl}$ . This value is much less than typical heats of fusion for known PAH, which are estimated at 110 J/gm. Calorimetric studies of phase transitions

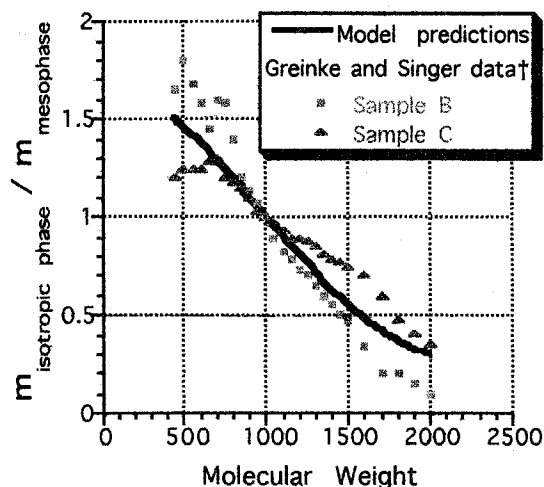


Figure 2. Comparison of multicomponent model with partition coefficients measured during pitch carbonization.

for liquid crystal systems typically yield clearing enthalpies that are small fractions of the heat of fusion. The inferred  $\Delta H_{cl}$  is therefore deemed reasonable.

### Conclusions

1. Known, fully-condensed PAH in their pure state do not form discotic liquid crystals. The temperature ceilings for the liquid crystalline phases lie below the solid melting points and/or the decomposition temperatures, masking the liquid crystal phase. Mixture effects are key to understanding carbonaceous mesophase.
2. A quantitative model of a generic carbonaceous mesophase has been developed based on solution thermodynamics of multicomponent PAH mixtures. The thermodynamic model successfully describes the species phase partitioning in the pitch pyrolysis data of Greinke and Singer, if  $\Delta H_{cl}$  is  $\sim 9$  J/gm, or 8% of typical heat of fusion values for fully condensed PAH.

### References

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2. Taylor, G.H. *Fuel* 40 465 (1961).
3. Greinke R.A. and Singer, L.S. *Carbon* 26 5 665-670 (1988).