

INTRODUCTION

Raman spectroscopy has been identified as a viable method for *in situ* planetary analysis¹, and is a useful tool for identifying mineralogical and organic/biological features/molecules. Due to the reactive nature of some molecules and the extreme environments observed extra-terrestrially, it is likely that molecules will interact with; each other, the mineralogy or degrade. This provides an issue in detection as any molecular interaction will fundamentally change the observed Raman spectra. In the Martian environment possible interactions fall into 3 major areas:

- 1) Modification due to organic-organic interactions - e.g., crystal phase and/or habit modification
- 2) Modification due to organic-inorganic interactions - e.g., inclusions within matrices and salt or complex formation
- 3) Modification due to chemical reactions - e.g., photoreactions (from either sunlight or solar energetic radiation) and reactions due to oxidative species.

To understand any interactions a model system has been chosen for this study, this consists of polycyclic aromatic hydrocarbons (PAHs) as the organic component and calcium carbonate as the adaptable mineral component.

This poster reports the work into determining phase behaviour of naphthalene, anthracene and pyrene in various mixture and states. PAHs have been chosen as the organic component of our model system as they have been identified as inter-stellar sources of carbon and as a recognised marker molecule from the degradation of cellular structures Interactions². PAHs are a strongly electron donating species and are therefore react with oxidant species under UV conditions³. Derivatives of PAHs have been characterised using X-ray diffraction & Raman spectroscopy and binary phase diagrams for selected mixtures have also been developed with a high-throughput thermal analytical methodology.

PHASE BEHAVIOUR IN SOLUTION

A systematic investigation of the interactions of various PAHs with each other was undertaken by creating mixed solutions of PAHs in various compositions and allowing time for crystallisation. Although no co-crystal/salt type adducts were formed, a number of interesting observations were made.

Mixtures of;

- A. Naphthalene and anthracene were made up in dichloromethane ($R = \frac{1}{2}, \frac{1}{3}, 1, 2, 3$).
- B. Naphthalene and pyrene were made up in dichloromethane ($R = \frac{1}{2}, \frac{1}{3}, 1, 2, 3$)

Results

- Due to the highly soluble nature of naphthalene in this solvent only anthracene and its derivatives were seen to crystallise in **A**, however only pyrene crystallised in **B**.
- Raman spectra of **A** (Figure 2) clearly showed the presence of 3 different products. Figure 3 shows an enlarged section of the spectrum and displays an important band shift due to the 9,10 substitution of the anthracene molecule

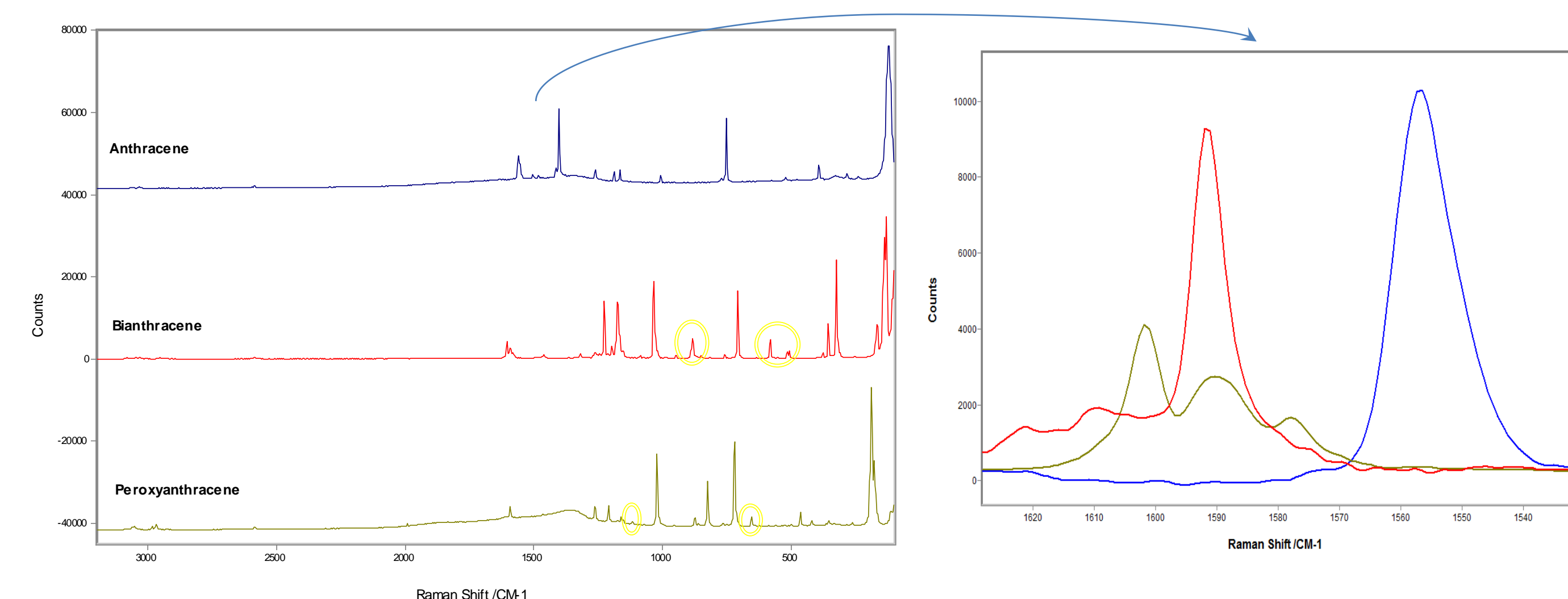


Figure 2 – Raman spectra of Anthracene, Bianthracene & Peroxyanthracene

Figure 3 – Enlarged area showing band shift due to 9,10 substitution

Suitable single crystals were chosen for X-Ray analysis and the crystal structures were determined;

- One was a simple anthracene structure (figure 4) with a transformed cell from the database structure.
- The second was a bianthracene (figure 5), formed by a photoreaction where two anthracene molecules bond at the 9,10 position.
- The third, peroxyanthracene (figure 6), formed by the addition of molecular oxygen to the 9,10 position of anthracene

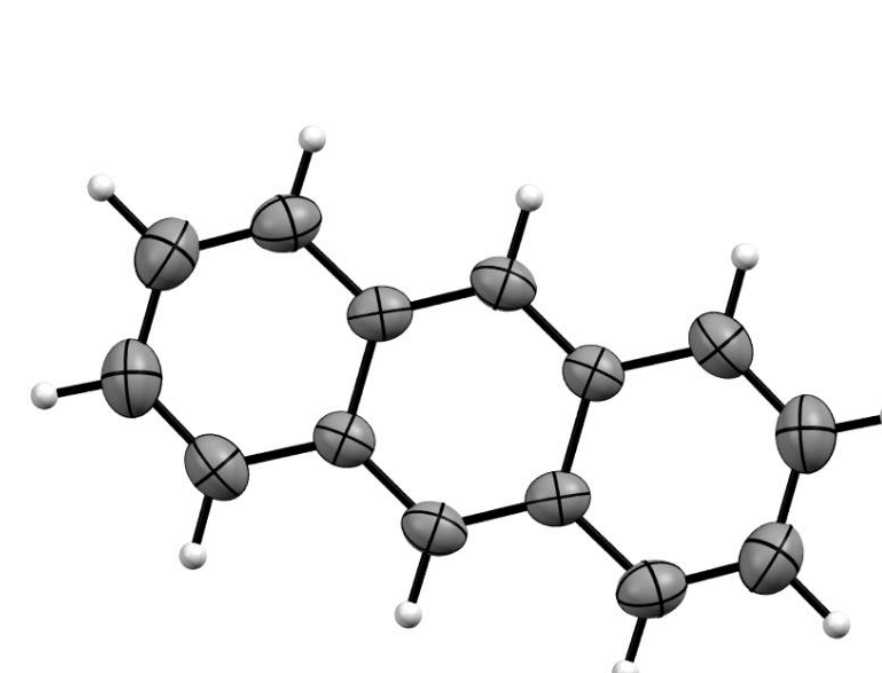


Figure 4 - Anthracene

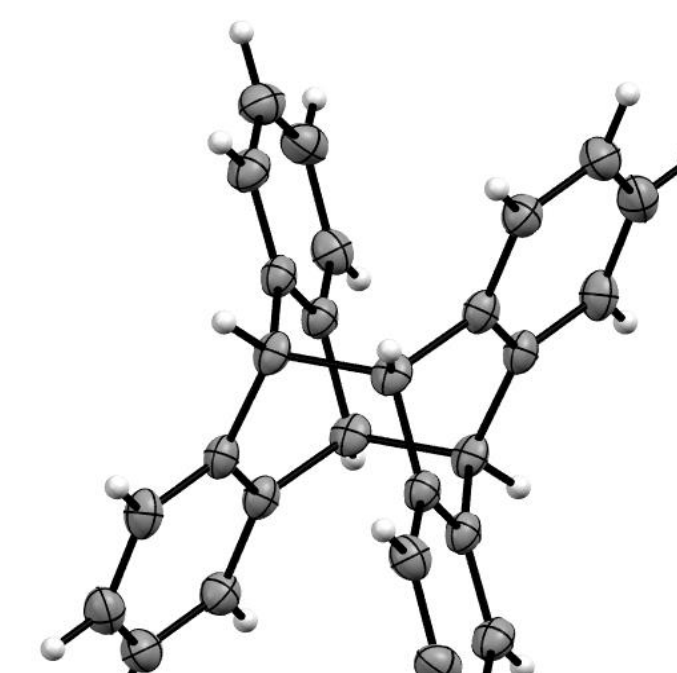


Figure 5 - Bianthracene

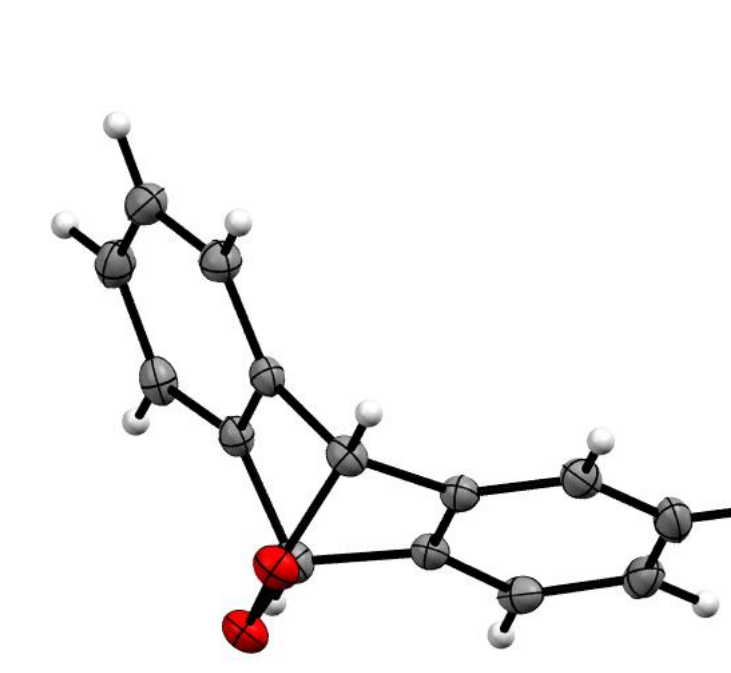


Figure 6 - Peroxyanthracene

PHASE BEHAVIOUR IN THE SOLID STATE

DSC experiments were carried out on various molar ratio mixtures of;

- I. Naphthalene and pyrene
- II. Naphthalene and anthracene
- III. Anthracene and pyrene

The mixtures were prepared in hermetically sealed DSC pans and heated through the melting points of each, allowed to cool then reheated to melt any new phase that had formed. The data was extracted from the DSC traces and plotted to make phase diagrams (I - Figure 8, II – Figure 9 & III – Figure 10). The phase diagrams show:

- All systems display simple eutectic behaviour.
- All systems also show a slight deviation from the ideal, this suggests that weak interactions are taking place, they are, however too weak to form a new molecular adduct.

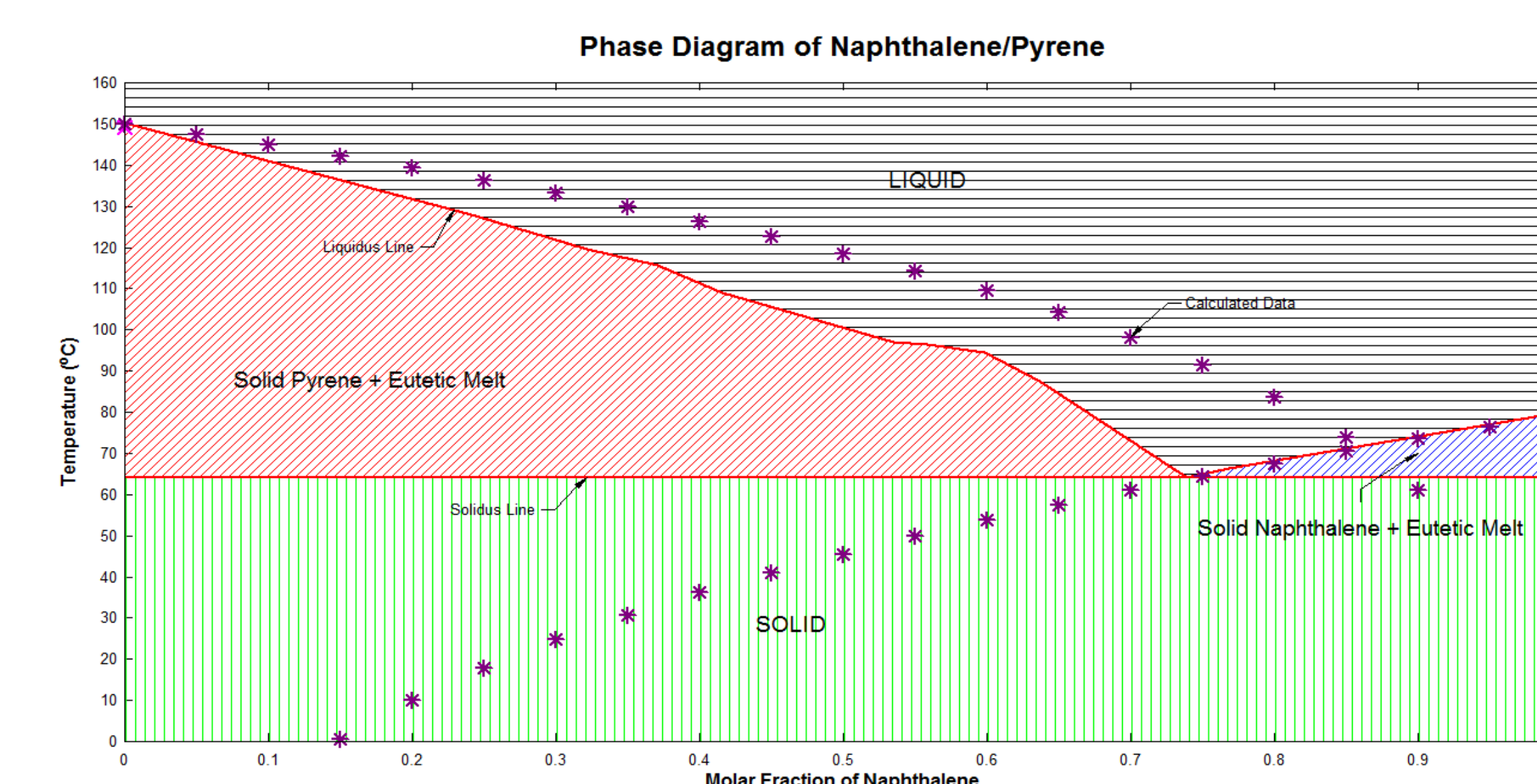


Figure 8 – Naphthalene/Pyrene Phase Diagram

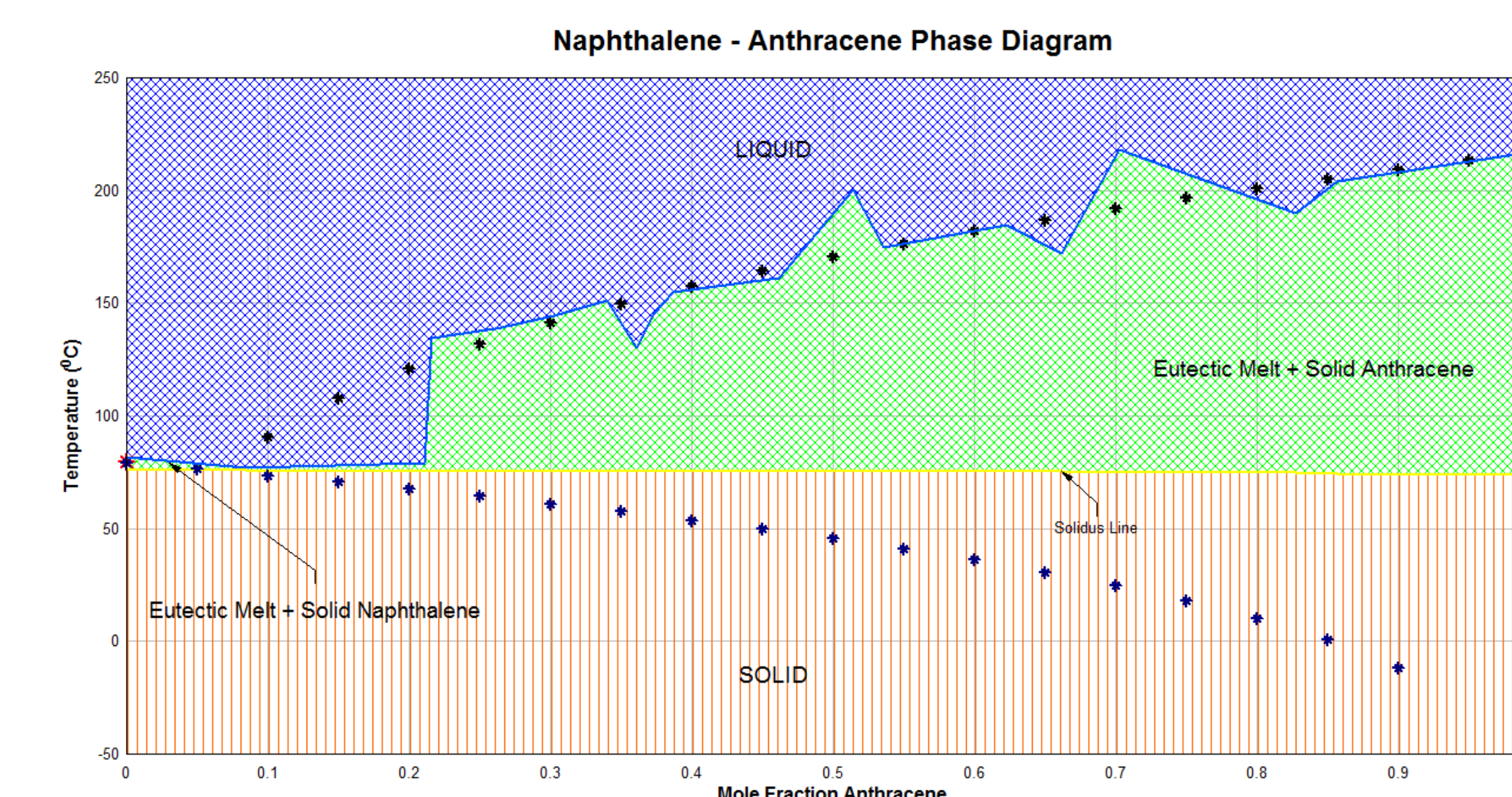


Figure 9 – Naphthalene/Anthracene Phase Diagram

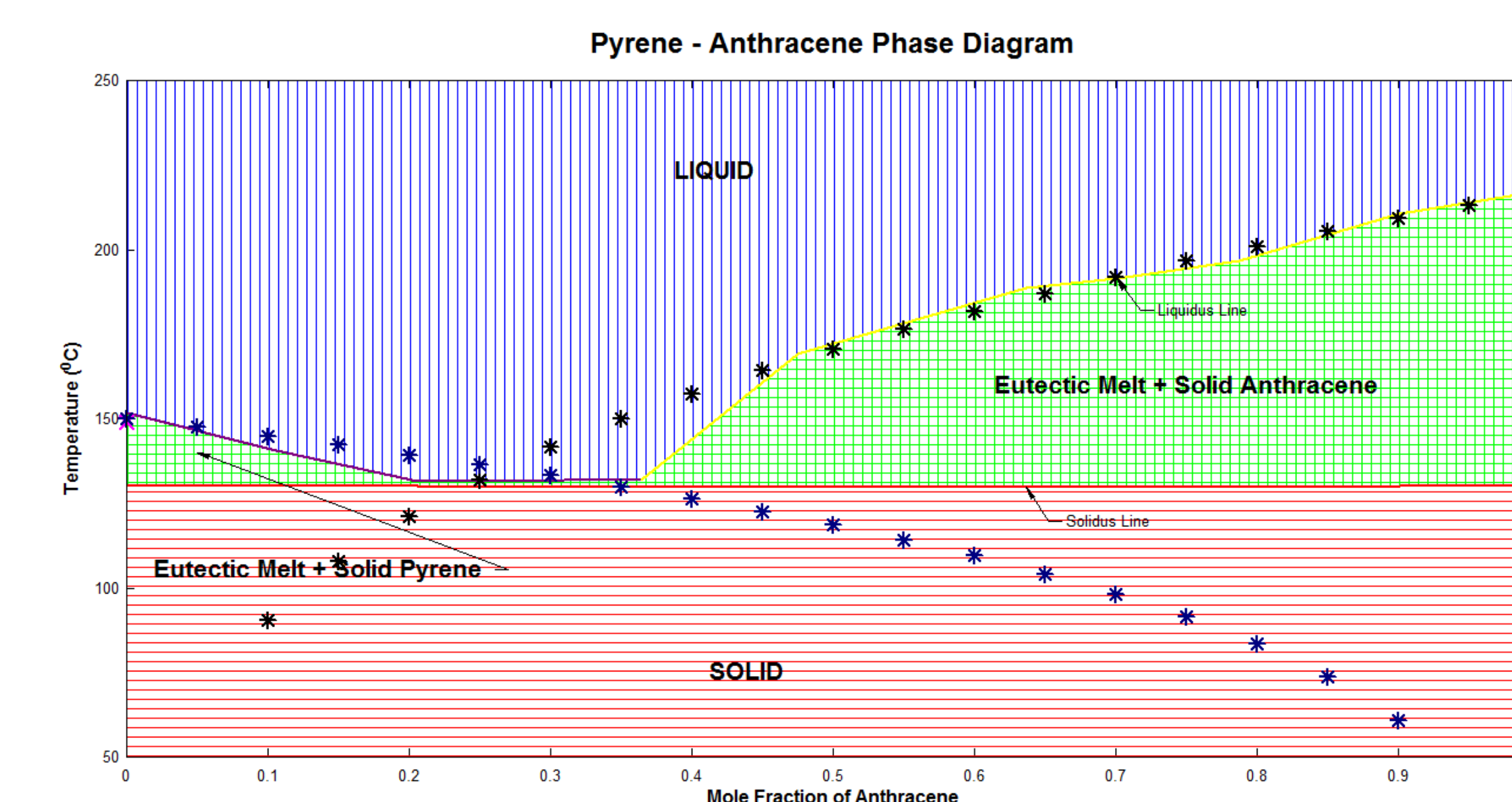


Figure 10 –Pyrene/Anthracene Phase Diagram

- Further work under different conditions is required to fully understand these and other PAH systems.
- Investigation of interactions between these molecules and inorganic mineralogical components is also being carried out.