

# A UNIFIED MODEL OF SOLVENT EXTRACTION AND MESOPHASE FORMATION IN PITCH MATERIALS

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## Introduction

Mesophase-containing pitches from petroleum, coal tar, or naphthalene polymers are important feedstocks for advanced carbon materials, including fibers, foams, binders, and microbeads. Some important mesophase technologies employ solvent extraction to produce pitch fractions whose properties are more desirable than the whole pitch. In some cases the pitch is spun to fibers in the presence of solvent, under conditions where it is desirable to maintain 100% anisotropic content. For these reasons there is interest in developing models of both the pitch / solvent phase equilibrium and the formation of orientationally ordered liquid (mesophase).

There have been two theories to describe the formation of mesophase: (1) high-MW pitch fractions have limited solubility in the lower MW fractions, leading to precipitation of the high-MW mesophase, and (2) the free energy of the high-MW pitch molecules is reduced by a concerted molecular orientation. These two theories are based on different chemical principles and are described by different classes of models. The second theory is the basis for the first quantitative model of mesophase formation by Shishido et al. [1] based on liquid crystal theory .

Recently a model of mesophase formation has been proposed [2] that unified these two approaches by integrating a submodel for non-ideal mixing with a submodel derived from the statistical molecular theories of the liquid crystalline state [3]. The model describes mesophase formation in a variety of pitches, but does not rigorously consider the effect of low-molecular weight solvents. Other work has treated solvent extraction of pitches under supercritical conditions using the Statistical Associating Fluid Theory (SAFT) approach [4,5], but does not treat molecular orientation as needed to identify mesophase. The present paper combines the SAFT approach with the statistical liquid crystal theory to develop a new model capable of describing both solvent processing and mesophase formation with a single thermodynamic formulation.

## Model Development

The current model is based on a free energy expansion of the form:

$$a^{\text{res}} = a^{\text{SAFT}} + a^{\text{orient}} \quad (1)$$

where  $a^{\text{res}}$  is the residual free energy. The SAFT approach describes non-ideal mixing in complex liquids by modeling the molecules as chains of Lennard-Jones spheres bonded by covalent linkages. The individual segments on a chain will interact with other chains through association "bonds," leading to the expansion:

$$a^{\text{SAFT}} = a^{\text{seg}} + a^{\text{chain}} + a^{\text{assoc}} \quad (2)$$

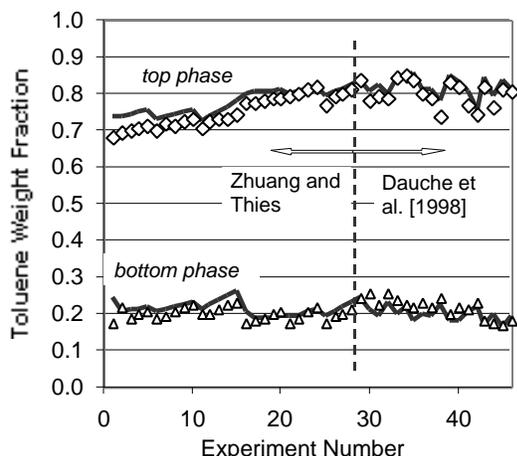
The orientational term in Eq. (1) is modeled using the statistical theory of liquid crystal mixtures of Luckhurst and coworkers [3], following Shishido [1] and our previous work [2]. The primary relation is:

$$a^{\text{orient}} = -\frac{N}{2} \sum_{i,j} x_i x_j e_{ij} \bar{P}_i \bar{P}_j - RT \sum_i x_i \ln Z_i \quad (3)$$

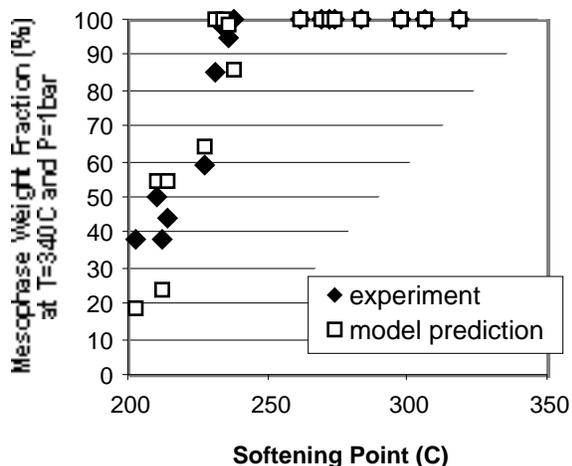
where  $\bar{P}_i$  are the single component order parameters. Previous publications present the full development of the SAFT equation [4,5] and the statistical LC theory [2,3]. A number of auxiliary relations are necessary to complete the model, which in its final form has 4 parameters: "A" and "B" which describe isotropic molecular interactions between the pitch molecules and the solvent, "C" which describes the isotropic molecular interactions between pitch molecules of differing molecular weight, and " " which describes the effect of molecular weight on the "clearing temperature" a measure of the orientational potential or liquid crystal forming tendency of a disotic.

## Model Validation and Application

The new model was fit to previously published data of Thies and coworkers [4,5] and the results summarized in Figs. 1, 2, and Table 1. The model was able to fit the extraction compositions (Fig. 1) and the mesophase contents (Fig. 2) using a common optimized parameter set (Table 1).



**Figure 1.** Composition of top and bottom phases during pitch extraction with toluene under a variety of experimental conditions. Symbols are experimental data; lines show predictions of the current model.



**Figure 2.** Mesophase content in bottom phase from pitch extraction with toluene under a variety of experimental conditions. Experimental samples are ordered based on the measured softening point of the bottom phase.

Note that in the previous work by Thies and coworkers on extraction, the "C" parameter was set to zero, since pitch/pitch interactions were insignificant compared to solvent/pitch interactions. In the present work in which we also attempt to predict mesophase formation, and therefore find that the "C" parameter must be non-zero. Because the mesophase contents in Fig. 2 were determined in the absence of solvent, pitch/pitch non-ideal mixing become important for prediction of mesophase occurrence. As concluded in the previous paper in this series [2], mesophase forms (in Fig. 2) due to the combined effect of

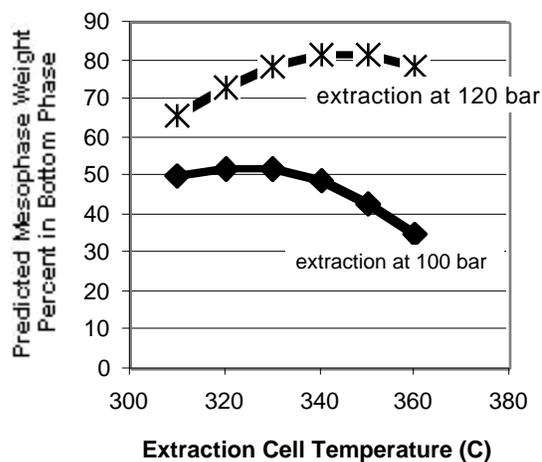
pitch/pitch non-ideal mixing (embodied here by parameter "C") and due to orientation free energy (embodied here by parameter " ").

Table 1 Model parameters used for predictions in Figs. 1 and 2.

Parameters	Previous work <sup>†</sup>	Present model
A (mol/gm)	$5.3 \cdot 10^{-3}$	$6.6 \cdot 10^{-3}$
B	$3.0 \cdot 10^{-2}$	$5.5 \cdot 10^{-2}$
C (mol/gm)	0	$5.0 \cdot 10^{-6}$
(mol-K/gm)	N/A	0.38

<sup>†</sup> used to model extraction phase equilibrium (% toluene in top / bottom) [Zhuang and Thies, 2000] using SAFT only.

Figure 3 shows one example of a parameter study carried out with the validated model. Many other parameter studies are possible, and we believe this model will have applications in the optimization of industrial pitch processing conditions.



**Figure 3.** Example parameter study with validated model. Result shows the presence of an optimal extraction temperature to maximize the mesophase mass fraction in bottom phase.

## References

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