

PREDICTION OF MESOPHASE FORMATION IN CARBONACEOUS PITCHES

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Abstract

As originally developed, the Statistical Associating Fluid Theory (SAFT) equation of state cannot predict liquid crystalline behavior. However, by adding an orientational free energy term based on Maier–Saupe theory, we have developed an equation of state that can be used to predict the phase behavior of carbonaceous, oligomeric pitches over a wide range of conditions, where either excess free energy or orientational free energy effects dominate, both with and without solvents. For example, SAFT–liquid crystal (LC) can be used to identify supercritical solvent extraction conditions for producing pitch fractions that, upon solvent removal, consist of 100% liquid crystalline mesophase. In addition, SAFT–LC can predict the experimentally observed ability of discotic, nematic mesophases of carbonaceous pitches to dissolve significant amounts of solvent while still maintaining their 100% mesophase character.

Introduction

Carbonaceous pitches are polycyclic aromatic, oligomeric materials that have a broad molecular weight distribution (MWD), ranging from about 250 to 2000 g/mol. They are produced via the thermal polymerization of decant oil, a by-product of the fluid catalytic cracking (FCC) of crude oil fractions.

It is often necessary to process carbonaceous pitches in the liquid crystalline state. Such is the case when the pitches serve as precursors for advanced carbon materials such as high thermal conductivity carbon fibers. On the other hand, isotropic pitches are appropriate when the desired product is the matrix phase for a carbon/carbon composite. Thus, the degree to which a potential precursor material forms mesophase at processing conditions strongly influences its suitability for a given use.

With both temperature and molecular composition affecting the isotropic/nematic phase behavior of pitches, a predictive model is of significant interest to researchers. Recently, we presented the development of such an equation, the Statistical Associated Fluid Theory – Liquid Crystal equation of state, or SAFT–LC (Burgess and Thies, 2007; Burgess et al., 2007). This model accounts not only for the nonideal free energy of mixing (via SAFT), but it also accounts for the orientational free energy exhibited by liquid crystalline systems (via Maier–Saupe theory).

Near critical and supercritical extraction (SCE) processes are of interest for the fractionation of carbonaceous pitches into cuts with a range of mesophase-forming tendencies. In this paper, we use SAFT–LC to explore the effect of SCE operating conditions on the molecular composition of pitch fractions and on isotropic–nematic phase equilibria.

Supercritical Extraction for Producing Mesophase Pitch

A schematic illustrating the production of mesophase pitch via the solvent extraction of carbonaceous pitches is shown in Figure 1. Note that the process is divided into two steps. The first step is an extraction in which an isotropic feed pitch and a solvent are fed into an extractor, which is simply a single-stage flash vessel. Over the range of temperatures, pressures, and solvent-to-pitch (S/P) ratios shown in Figure 1, two phases form in the extractor: a lighter, solvent-rich phase (denoted by V) and a heavier, pitch-rich liquid phase (denoted by L). Lower molecular weight pitch components concentrate in the top V phase, while the heavier pitch components tend to concentrate in the bottom L phase. In the second step of the process, the L phase is dried to remove all solvent, yielding the final product. Depending on the experimental conditions and the feed pitch used, this final product can range from being completely isotropic to being 100% mesophase.

Application of SAFT–LC to Carbonaceous Pitches

In order to apply SAFT–LC to a poorly defined system such as carbonaceous pitch, the pitch must be represented as a mixture of discrete pseudocomponents. To this end, the MWD of a pitch obtained from Conoco (denoted by the company as PB35A/B; CAS 68187-58-6) was obtained by matrix-assisted laser desorption/ionization, time-of-flight mass spectrometry (MALDI-TOF-MS). Details of the application of this analytical method to carbonaceous pitches are presented elsewhere (Edwards and Thies, 2003). In Figure 2, the MALDI spectrum obtained is presented in terms of the normalized intensity of

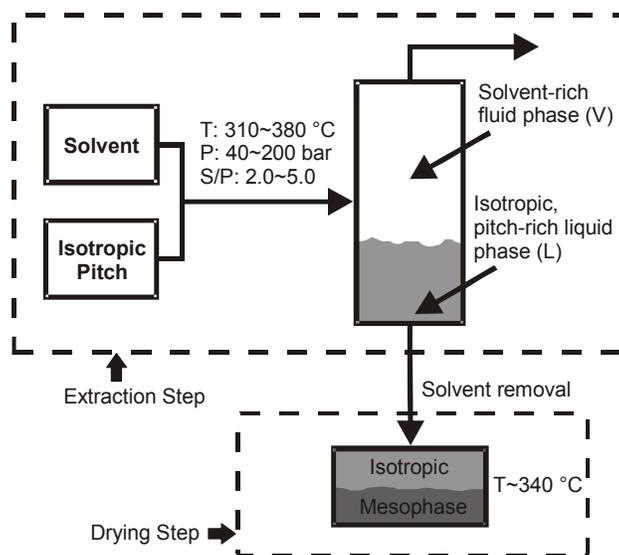


Figure 1. The supercritical extraction process for producing mesophase pitch consists of an extraction and a drying step.

the MALDI detector response, so that the total area under the MALDI spectra is equal to unity. In order to define pseudocomponents (PCs) for this pitch, the plot was then divided into 10 regions, with each oligomeric peak being divided into 2 sections. Next, the number average mol wt (\overline{M}_n) and the area under the curve for each region was calculated. Each region was then assumed to represent one pseudocomponent, and the area fraction of the curve in that region was assumed to equal the PC mole fraction. Work in progress in our laboratory indicates that this latter assumption is a good first approximation.

It was then necessary to determine the SAFT–LC parameters. The parameters v_{00} , m , and u/k were fixed for each pseudocomponent and were obtained using correlations developed by Huang and Radosz for bitumen (1991). Required inputs to the correlations are the PC mol wts and the atomic carbon-to-hydrogen (C/H) ratio. For each pseudocomponent, the values for the C/H ratios were predicted using a correlation developed by our group (Edwards and Thies, 2006) that relates the MALDI-determined \overline{M}_n for particular pitch fraction produced by dense-gas extraction to the C/H ratio of that fraction. The adjustable parameters in SAFT–LC (i.e., the clearing temperature parameters a and b and the intermolecular interaction parameters A , B , and C) were fit to the SCE measurements of Dauche et al. (1998) for pitch–solvent mixtures and the resultant mesophase products (see Fig. 1).

Results and Discussion

Because a long-term objective of our work on the solvent extraction of pitches is control of the MWD of carbonaceous pitches, SAFT–LC was then used to predict the impact of the extraction pressure on the PC mass distribution in the dried L phase (see Fig. 1). For a temperature of 330 °C and a S/P ratio of 3.0, pressures of 40, 77, and 155 bar were examined; these pressures correspond to the experimental work of Dauche et al. (1998). The change of the PC mass distribution with pressure is given in Figure 3.

These results reveal some interesting trends. First, for the dried residues formed at lower extraction pressures (40 and 77 bar), two phases, one isotropic and one nematic, are predicted. As the extraction pressure is increased, the PC distribution in the bottom phase shifts to the right. The effect of the denser solvent is a more aggressive extraction, with a key contribution to the increase in mesophase content being the marked decrease in the presence of PCs 1-5 as the pressure is increased from 40 to 77 bar. Even higher extraction pressures are required for the bottom L phase to consist

entirely of 100% mesophase. At 155 bar, SAFT-LC predicts that there are only trace amounts of PCs 1-4, with PC 5 being present at only about 1 wt %. Thus, the primary mesophase-forming species are the five heaviest pseudocomponents.

In the last decade, researchers observed that carbonaceous mesophase pitches can absorb up to 20 wt % solvent and still consist of 100% mesophase (Kalback et al., 1996). Therefore, we tested the ability of SAFT-LC to predict this phenomenon by generating phase diagrams that illustrate system phase behavior as a function of temperature and solvent (toluene) addition. As shown in Figure 4, a phase diagram was generated at 50 bar for the addition of toluene to dried bottom (L) phases predicted by SAFT-LC (and in agreement with the experimental work of Dauche et al.) to consist of 100% mesophase. These L phases were produced at SCE conditions of 330 °C, a S/P ratio of 3.0, and pressures of 100 bar

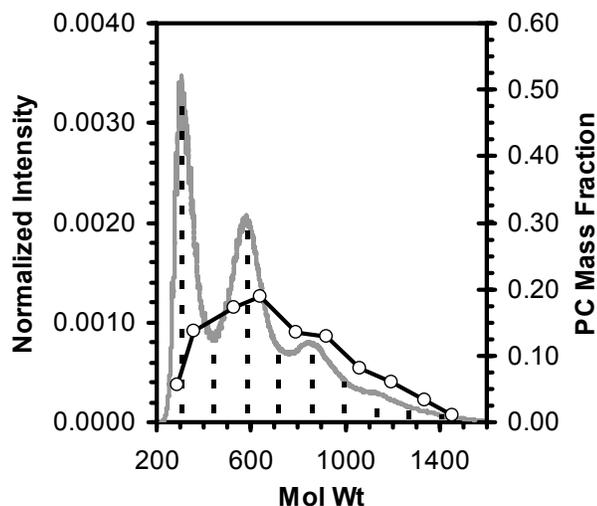


Figure 2. MALDI-TOF-MS mass spectrum (grey line, left axis) for the isotropic petroleum pitch fed to the SCE process of Fig. 1. PC mass fractions (right axis) are denoted by open circles.

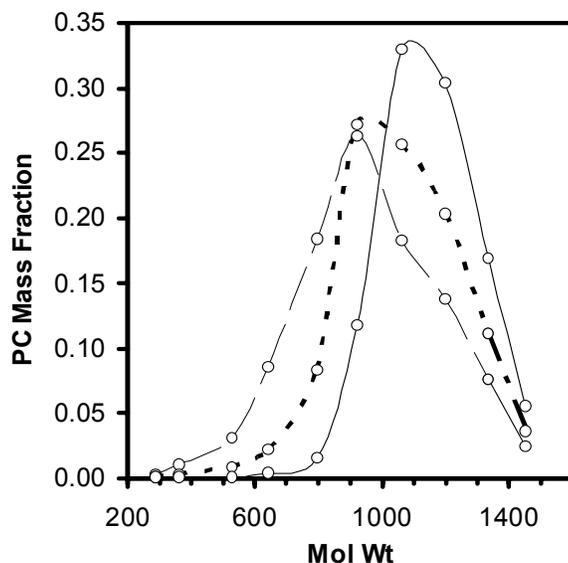


Figure 3. SAFT-LC predictions for the PC mass distribution in the bottom phase (L) for $T = 330^{\circ}\text{C}$, $S/P = 3.0$, and various extraction pressures. Mesophase content is predicted to be 32.3 wt % at $P = 40$ bar (thin dashed black line), 75.4 % at $P = 77$ bar (thick dashed black line), and 100 % at $P = 155$ bar. PC mass fractions are denoted by open circles.

(Fraction 1), 155 bar (Fraction 2), and 200 bar (Fraction 3).

Several trends are apparent from an examination of Figure 4. First, we note that for the fractions produced at higher extraction pressures, and thus with higher average mol wts, increasing amounts of toluene are required before we cross the phase boundary to create an isotropic phase (analogous to a bubble point). For example, at a temperature of 340 °C, an isotropic phase forms from Fraction 1 with the addition of only 0.5 wt % toluene; however, no phase split occurs for the higher mol wt fractions until the toluene level reaches 8.5 and 10.5 wt %, respectively.

On the other hand, a different behavior is observed at the boundary between the 2-phase region and the isotropic phase (the clearing temperature; analogous to the dew point). At low concentrations of solvent ($< \sim 0.04$ weight fraction), the behavior is as expected, with the clearing temperatures increasing with the average mol wt of the fraction. However, at solvent concentrations $> \sim 0.04$, this trend reverses itself, as Fraction 1 becomes the toluene/pitch mixture with the highest overall clearing temperature. We have no immediate explanation for this phenomenon. Finally, we note that as the extraction pressure increases, the size of the two-phase region decreases markedly. Thus, at 0 percent toluene, Fraction 1 has a “bubble point” of 380 °C and a clearing temperature of 490 °C. However, for Fraction 3 the two phase transitions differ by less than 20 °C. For all fractions, the addition of toluene greatly expands the size of the two-phase region, as expected.

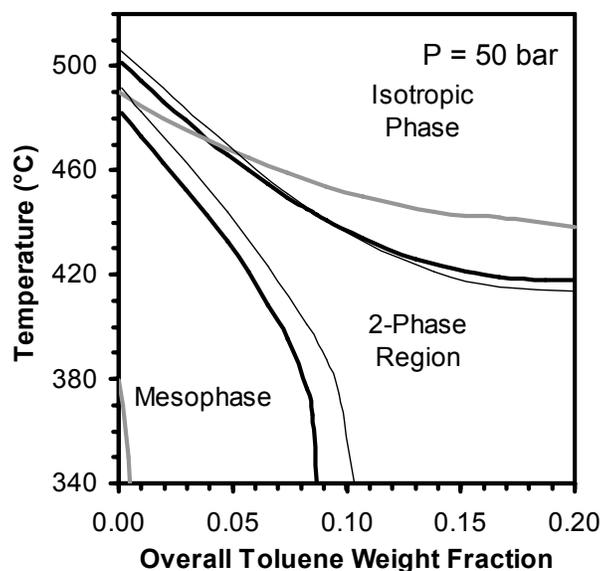


Figure 4. Calculated binary phase diagram for systems of toluene and mesophase pitch at 50 bar. Pitches were obtained from SCE conditions of $T = 330^\circ\text{C}$, S/P ratio = 3.0, and $P =$ (i) 100 bar (gray phase boundaries), (ii) 155 bar (thick black phase boundaries), and (iii) 200 bar (thin black phase boundaries).

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