

## HYDROGEN BONDING AND COAL SOLUBILITY AND SWELLING

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Most descriptions of the thermodynamic properties of coal solutions and the swelling of coal are based on models that in their original form only dealt with simple van der Waals or London dispersion forces. It is now well-known that such descriptions are inadequate when applied to systems where there are strong specific interactions such as hydrogen bonds. In part, this is because for weak forces random contacts between unlike segments can be assumed, allowing interactions to be formulated in a mean field form,  $\Delta E_{int} \phi_A \phi_B$ , where  $\Delta E_{int}$  is an exchange interaction term;  $\phi_A \phi_B$  are the volume fractions of the components A and B and their product is proportional to the number of unlike contacts in a solution where there is random mixing. Hydrogen bonds are different and cannot be dealt with by means of a simple approximation. Polymer segments and solvent molecules that interact in this manner are truly associated and above the  $T_g$  there is a dynamic equilibrium distribution of hydrogen bonded species. There is a non-random arrangement of the hydrogen bonding functional groups (relative to one another) and this leads to modifications in the entropy of mixing. Theories that deal only with the enthalpy of hydrogen bonding interactions are thus inadequate.

In recent work (1-4) we have developed an association model that essentially consist of a Flory-Huggins type of equation with an additional term ( $\Delta G_H$ ) describing the free energy changes associated with the changing pattern of hydrogen bonding that occurs as a function of composition:

$$\frac{\Delta G_M}{RT} = \frac{\phi_A}{N_A} \ln \phi_A + \frac{\phi_B}{N_B} \ln \phi_B + \phi_A \phi_B \chi + \frac{\Delta G_H}{RT}$$

Although it may appear that we have arbitrarily added a term accounting for non-random contacts to a random mixing theory, association models are more subtle than that and it can be shown that the above equation can be derived directly from a lattice model (2). The  $\Delta G_H$  term has a complex appearance (but once you get used to it has an easily understandable structure), but it is important to note that all terms in this equation are determined from experimental FTIR measurements and the equations describing the stoichiometry of hydrogen bond formation. (Space does not permit a reproduction of these equations here, and the interested reader should consult the literature.) Accordingly, given a knowledge of  $\chi$ , or a reasonable way of estimating this parameter, we could predict the free energy of mixing coal with hydrogen bonding solvents. It is relatively easy to show that the  $\Delta G_H$  term is either zero or negative, the  $\chi$  term is positive for purely van der Waals or London dispersion interactions, while the combinatorial entropy term of course favours mixing. The  $\chi$  and  $\Delta G_H$  terms have very different temperature dependencies and the balance between these forces leads to the prediction of a rich variety of phase behaviors (2, 4, 5-7). In initial work on coal solutions we have determined general trends, through a calculation of the free energy of mixing pyridine with model coal structures (4).

These initial results provide some fundamental insight, but there now remains the more difficult task of calculating the behavior of specific systems and determine expressions for the chemical potentials, so that the model can be extended to swelling and molecular weight

measurements. Here we consider the first part of this task and we will commence by first defining an average coal structure per OH group. This sounds as if we are arbitrarily classifying a coal molecule as a set of "average" repeat units. In a certain sense we are, but this is not a fallacious approach, as we will show. In the classic work of Scott (8), performed more than thirty years ago, it was demonstrated that the "physical" (ie. non-hydrogen bonded) interactions of a copolymer of any degree of heterogeneity could be described by a solubility parameter that is a volume fraction average of the contributions of its constituents. We can therefore use the method of van Krevelen (9) to determine the parameter  $\delta_{\text{coal}}$ . This requires first of all a knowledge of the coal composition and the relative proportions of aromatic and aliphatic carbon, which have been determined directly for many coals by  $^{13}\text{C}$  nmr, or can be estimated from FTIR measurements of the relative proportions of aromatic and aliphatic CH groups. In addition, we also need to define a reference volume for the coal that can correspond to any arbitrarily defined segment (because we will simply calculate the free energy change per segment upon mixing). Van Krevelen (9) calculated his solubility parameter in terms of the molar volume of a coal "molecule" per carbon atom,  $V_M/C$ , using:

$$\frac{V_M}{C} = \frac{1200}{C \cdot d}$$

where  $C$  is the weight percent carbon in the sample and  $d$  is the density. In the same fashion we define a molar volume per OH group as:

$$\frac{V_M}{O_{\text{OH}}^1} = \frac{1600}{O_{\text{OH}}^1 \cdot d}$$

where  $O_{\text{OH}}^1$  is the weight percent oxygen in the sample that is present as OH groups ( $O_{\text{OH}}^1$  and  $d$  are known or measurable quantities). This allows us to calculate the free energy contribution from hydrogen bonding interactions per molar volume of the average coal segment containing one OH group.

The  $\chi$  parameter is then calculated from solubility parameters in the usual fashion, while  $\Delta G_H$ , the free energy of hydrogen bonding interactions, can be calculated in a straightforward manner by methods we will describe below. The definition of a "segment" of a coal molecular per OH group, therefore merely serves to place the calculations of  $\chi$  and  $\Delta G_H$  on a common scale of unit volume. As long as the OH groups in coal are more or less randomly distributed our definition of an arbitrary segment is conceptually sound.

The quantity  $\Delta G_H$  is calculated from a knowledge of the number of OH groups present in a sample (more precisely, the molar volume per OH group) and equilibrium constants describing the free energy change per hydrogen bond (the equation describing  $\Delta G_H$  is then a simple counting of the change in the number of hydrogen bonds of various types upon mixing). These are determined by FTIR. Fortunately, we do not have to measure these directly on coal. It is a consequence of the lattice model (2) that equilibrium constants for a particular functional group determined in one molecule can be transferred to a different molecule with the same functional group by simply adjusting according to the molar volume

$$\text{ie. } K_B^1 V_B^1 = K_B^2 V_B^2$$

Using values determined for phenol and cresols ( $K_B^1 V_B^1$ ) we can thus calculate appropriate values for a coal segment defined by  $V_B^2$ . (This result has worked extremely well in predicting the phase behavior of blends of polyvinyl phenol with various polyethers and polyesters (6). The values of the equilibrium constants describing the self-association of phenol have been determined by Whetsel and Lady (10). (This splendid paper, published in Spectrometry of Fuels a number of years ago, anticipates our use of association models for coal and has the almost forgotten virtue of tabulating all data obtained, in this case in both the near and mid IR. We were thus able to check all calculations and determine the appropriate values of the equilibrium constants.) We have expanded our treatment of self association to

also account for the hydrogen bonds that can form intramolecularly between coal OH and ether oxygens. This is conceptually straightforward and comes at the expense of a minor increase in the algebraic complexity of the equations. The equilibrium constants describing interactions between phenolic OH groups and ethers, and indeed between OH and most of the functional groups found in solvents commonly used to swell coals, are tabulated in the literature (eg see the review by Murthy and Rao (11)). We are fortunate that interactions involving both alkyl and phenolic OH groups have been so widely studied. The parameters used in the calculations are listed in table 1 and our computational procedures are described elsewhere (2-4, 6).

Typical results are shown in figure 1. The data points represent spinodals and were calculated for various coal-pyridine mixtures. This naturally requires that the structural parameters of the coals have been determined and we used a data set compiled for a set of vitrinite concentrates (12). In the accessible range of temperature (up to about the boiling point of pyridine) we determine a classic inverted U shape coexistence curve characterized by an upper critical solution temperature near 0°C, for a coal of 78.3% carbon content. As the carbon content of coal increases the calculated solubility parameter decreases to a minimum near a carbon content of 88% C (9).

For the three coals from which we have performed detailed calculations, with carbon contents of 78.3%, 84.7% and 90.1%, the value of  $\chi$  thus decreases with increasing carbon content, favoring mixing. At the same time, however, the number of OH groups systematically decreases, thus decreasing the favorable contribution of hydrogen bonding. This latter effect dominates, so as the carbon content of the coal increases we predict that the upper critical solution temperature shifts to higher temperature and for a coal of 90.1% carbon content we calculate spinodals characteristic of a phase separated system throughout the accessible temperature range.

At first sight these results might seem inconsistent with some of the known characteristics of coal (13-18), where swelling reaches a maximum in about the middle range of carbon contents we have considered. It should be kept in mind, however, that in our calculations we have assumed that the chains are not cross-linked (The phase diagrams in figure 1 were determined for a coal molecule of "degree of polymerization" 100, relative to the molar volume of a pyridine molecule). Such molecules are predicted to be soluble at room temperature for a low carbon content coal, and to phase separate into a dilute coal solution and a solvent swollen coal gel at higher carbon contents. The degree of swelling depends not only on the phase behavior of these systems as defined by their chemical potentials, but also upon the degree of cross-linking. We have obtained appropriate expressions for the contribution of hydrogen bonding interactions to the chemical potentials and plan to incorporate these into theories of swelling. Of more interest to us here, however, is the overall effect of hydrogen bonding interactions on phase behavior. Pyridine forms relatively strong bonds with phenolic OH groups, so we would like predict that for solvents that hydrogen bond less strongly, such as THF, the contribution of  $\Delta G_H$  would be smaller. It must be kept in mind that hydrogen bonding alone does not determine phase behavior, the contribution of the "physical" (usually repulsive) forces measured by  $\chi$ , together with the combinatorial entropy of mixing, all contribute to the balance. As it happens, the  $\chi$  value for the coal-THF mixtures considered here are larger than their coalpyridine counterparts and this combined with the smaller contributions to  $\Delta G_H$  from hydrogen bonding results in the spinodals shown in figure 2, which indicate that the coals are less soluble and would swell less in this solvent.

Obviously solubility is molecular weight dependent and the phase behavior of the 84.7% coal as a function of molecular weight (defined in terms of a degree of polymerization  $N_B$  relative to the molar volume of the solvent molecule) is shown in figure 3. This model predicts that for this coal fairly large molecules. ( $N_B > 30$ ) would be soluble in boiling pyridine, although some of the high molecular weight material would

precipitate out at room temperature, depending upon the concentration of the solvent. Only relatively low molecular weight material would be completely soluble in THF.

Finally, we must re-emphasize that for any specific coal the overall phase behavior is determined by the balance between hydrogen bonding and physical forces. The former is measured by the equilibrium constant for association, which we define by the symbol  $K_A$ . Values listed in the literature (11) are reproduced in Table 2, together with values of the solubility parameter. For the coals considered here we would therefore qualitatively expect that NMP and pyridine would be the best solvents (large  $K_A$ ,  $\delta_s$  in the range 10.7 to 11.5); dimethyl formamide hydrogen bonds strongly but has a somewhat larger  $\chi$  than these solvents; DMSO hydrogen bonds very strongly but would have an even larger value of  $\chi$ ; while the remaining solvents would not give comparable swelling or solubility characteristics. Obviously detailed calculations are required for quantitative predictions and these are presently being performed.

Acknowledgment. We gratefully acknowledge the support of the Office of Basic Energy Sciences, Division of Chemical Sciences, Department of Energy, under Grant No. DE-FG02-86ER13537.

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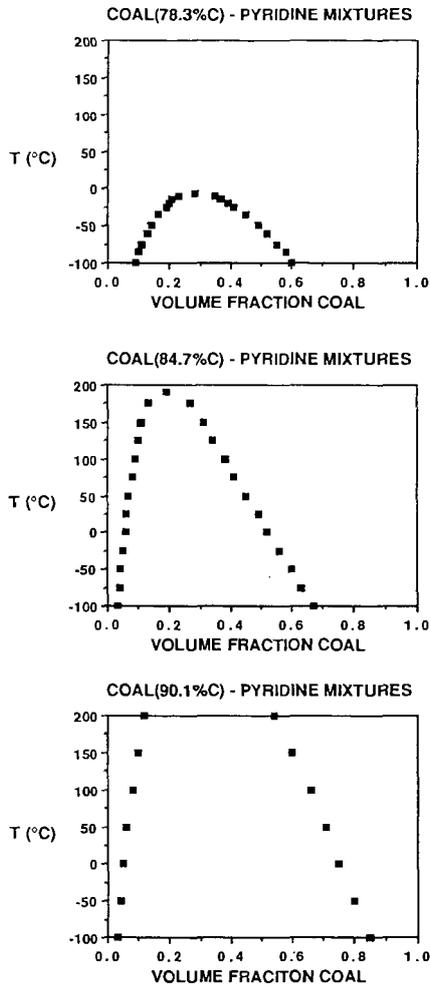


FIGURE 1. Phase diagrams (spinodals) for various coals with pyridine.

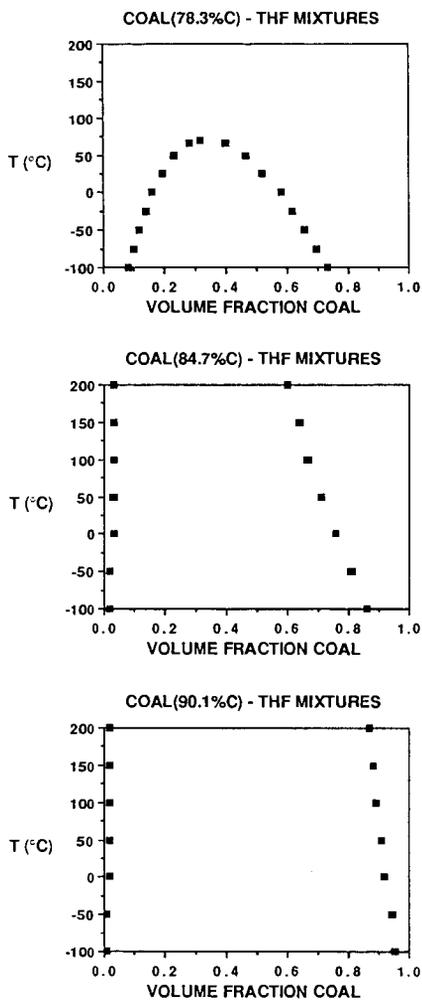
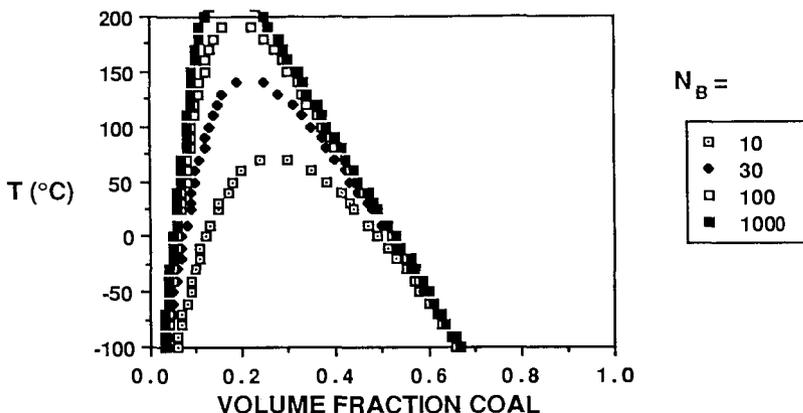


FIGURE 2. Phase diagrams (spinodals) for various coals with THF.

**COAL(84.7%C) - PYRIDINE MIXTURES**



**COAL(84.7%C) - THF MIXTURES**

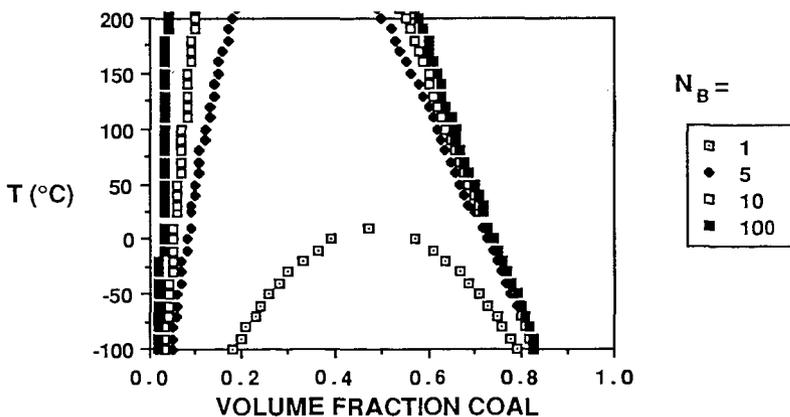


FIGURE 3. Phase diagrams (spinodals) as a function of molecular weight.

Table 1. Parameters for Coal at 25°C

	78.3%C	84.7%C	90.1%C
molar vol, ( $V_B$ ) $\text{cm}^3 \text{mol}^{-1}$	227.92	286.23	4102
molar vol, ( $V_E$ ) $\text{cm}^3 \text{mol}^{-1}$	151.95	384.62	440
$\delta_C$ , $(\text{cal cm}^{-3})^{1/2}$	11.5	11.27	10.78
$K_2$	8.33	6.64	0.46
$h_2$ , $\text{kcal mol}^{-1}$	5.6	5.6	5.6
$K_E$	19.44	15.48	1.08
$h_E$ , $\text{kcal mol}^{-1}$	5	5	5
$K_B$	26.67	21.23	1.48
$h_B$ , $\text{kcal mol}^{-1}$	5.2	5.2	5.2

Parameters for Solvents at 25°C

	pyridine	THF
molar vol, ( $V_S$ ) $\text{cm}^3 \text{mol}^{-1}$	81	74.3
$\delta_S$ , $(\text{cal cm}^{-3})^{1/2}$	10.6	9.9

Table 2

SOLVENT	$K_A$ ( $\text{l mol}^{-1}$ ) (20°C)	$\delta_S$ ( $\text{cal cm}^{-3}$ )
PYRIDINE	60	10.6
NMP	163	11.2
DIMETHYL FORMAMIDE	64	12.1
DMSO	60	10.6
THF	18.8	9.9
ACETON	12.3	9.9
DIETHYL ETHER	9.6	7.5
ACETONITRILE	5.0	11.8
BENZENE	0.3*	9.1

- \* Weak H-bonds between OH groups and  $\Pi$  electrons have been proposed.