

Solubility and Viscosity Studies of Coal-Derived Preasphaltenes

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INTRODUCTION

The high viscosity and poor solubility of coal-derived preasphaltenes (PA) are detrimental to the utility of those materials as fuel sources. These physical properties have been widely studied and may be ascribed to non-covalent interactions such as hydrogen bonding and charge transfer (1). For that reason, several researchers have examined dissolvability of coal-derived liquids or extraction and swelling of coal as a function of solvent parameters (2-11) and viscosity as a function of polarity and molecular weight (12-19).

Roy and coworkers (2) have studied extractability of coal at 35°C as a function of the dielectric constant of dipolar aprotic solvents. The results, however, were ambiguous: dimethylsulfoxide (DMSO, $\epsilon = 46.6$) was comparable to pyridine ($\epsilon = 12.3$) and better than ethylenediamine ($\epsilon = 14.2$). Hombach (3) determined solubility parameters for coals of differing ranks by measuring the spectrophotometric absorbance of extracts obtained by treating the coals with binary solvent mixtures. The parameters ranged from ca. 20.4 to 23.0 $J^{1/2} \text{ cm}^{-3/2}$ and, as expected, showed little dependence on the chemical nature of the solvents in the mixture. Likewise, Weinberg and Yen (4) determined solubility parameters for a high volatile bituminous (hvb) coal by swelling measurements and for hvb coal liquefaction products by dissolvability in various solvents and solvent mixtures. Two maxima were observed in the swelling spectrum of the coal at 22.5 and 28.6 $J^{1/2} \text{ cm}^{-3/2}$. Benzene-soluble liquefaction products (asphaltenes) exhibited maximum dissolvability in solvents (pure or mixtures) with δ values of ca. 19-26 $J^{1/2} \text{ cm}^{-3/2}$. Benzene-insoluble liquefaction products (preasphaltenes) were dissolved to the greatest extent in solvents with δ values of ca. 23.5 $J^{1/2} \text{ cm}^{-3/2}$. Marzec, et al. investigated possible correlations of solvent acceptor and donor numbers (AN and DN, respectively) with extractability (5-7) and swelling (7,8) of hvb coal at ambient temperatures. Both the extract yield and the swelling ratio increased with increases in the DN or DN-AN values of solvents.

Bockrath and coworkers have reported that aggregation of asphaltenes and preasphaltenes significantly contributes to the viscosity of coal-derived liquids (14). Further studies demonstrated that phenolic content, representative of intermolecular hydrogen bonding, was relatively more important than molecular weight to the viscosity of coal-derived asphaltenes (15). Likewise, Tewari, et al., from studies of coal liquids (16, 17) and model compounds (17), have shown that hydrogen bonding, primarily involving phenolic OH and nitrogen bases, is largely responsible for the viscosity of the coal liquids. Additional evidence for the importance of hydrogen bonding was provided by derivatization experiments. Gould, et al., found that silylation of coal liquefaction bottoms resulted in a four- to seven-fold reduction in viscosity (13). Patel, et al. reported a substantial increase in the dissolvability of solvent-refined lignite in nonpolar solvents after silylation or acetylation (20), attributable to disruption of intermolecular hydrogen bonding.

In connection with a study of intermolecular attractive forces in coal-derived liquids, we have measured the quantitative dissolvability of coal preasphaltenes in various solvents. Described herein are the results of those measurements and correlation of the data to five solvent parameters: δ , net hydrogen bonding index (θ), DN, DN-AN, and DN/AN. In addition, we have determined relative viscosities (η_{rel}) of native and acetylated PA samples of narrow molecular weight ranges and various model compounds. These measurements were carried out in an effort to determine the relative importance of molecular weight, hydrogen bonding and charge transfer to overall viscosity.

EXPERIMENTAL

The solvents employed in this study were reagent grade, obtained from commercial suppliers, and were used without further purification. A modified version of the solvent extraction procedure of Steffgen, et al. (21) was used to separate the preasphaltenes (THF soluble, toluene insoluble) from total liquefaction samples obtained from the University of North Dakota Energy Research Center. Room temperature acetylation of a sample of PA from run 80 was accomplished following the method of Baltisberger, et al. (22). Both acetylated and native PA-80 samples were separated into narrow molecular size fractions by preparative gel permeation chromatography on Biobeads S-X3 or S-X8.

The quantitative dissolvability of the preasphaltene samples was determined by mixing 30 mg of PA with 3 ml of solvent in a stoppered test tube in an ultrasonic bath for 1 minute. Vacuum filtration of the solution through either ordinary filter paper or 5.0 μm type LS Millipore filters yielded the insoluble residue. Increasing the mixing time to 5 minutes did not increase the amount of preasphaltene dissolved.

Relative viscosities (η_{rel}) of the PA samples and model compounds were measured at 20°C in Canon-Fenske flow-type viscosimeters.

RESULTS AND DISCUSSION

Typical solubility parameter curves are obtained when the dissolvabilities of representative preasphaltenes are plotted as a function of Hildebrand solubility parameters (δ). The preasphaltenes exhibit maximum dissolvability in solvents with δ ca. 22-23 $\text{J}^{1/2} \text{cm}^{-3/2}$, in good agreement with the data of Hombach (3) and Weinberg and Yen (4). However, individual solvents with a range of solubility parameters from 18.4 to 24.5 $\text{J}^{1/2} \text{cm}^{-3/2}$ are good solvents (i.e., > 80% dissolvability) for the preasphaltenes. Two solvents, THF and DMF, are consistently well above the smooth curve that may be drawn through the solubility parameter data, reflecting the inability of the predominantly nonpolar Hildebrand solubility parameter to adequately account for their behavior as solvents for preasphaltenes. These results are not unexpected. Larsen, et al. (9) have observed that the swelling of pyridine extracted Illinois No. 6 coal by solvents capable of hydrogen bonding interactions cannot be accounted for solely by the nonpolar δ value. Excellent correlation was obtained between excess swelling (i.e., swelling beyond that expected on the basis of δ) and the heat of hydrogen bonding of the solvents with *p*-fluorophenol (9).

The net hydrogen bonding index (θ) (23) takes into account both the formation of new solvent-solute hydrogen bonds and the cleavage of existent solvent-solvent hydrogen bonds. Thus, methanol, a strongly hydrogen-bonded solvent, has a negative value of θ , indicating its tendency to maintain solvent-solvent hydrogen bonds rather than form new solvent-solute hydrogen bonds. The aprotic solvent DMF behaves in just the opposite fashion, since it cannot hydrogen bond to itself. Plots of PA dissolvability versus θ reveal a general trend of increasing dissolvability with increasing θ . However, this parameter may not be used as a reliable predictor of individual solvent effectiveness due to the excessive scatter of the data. For example, on the basis of θ values, acetone would be forecast to be comparable in dissolving power to THF, a prediction that is not borne out experimentally.

Other researchers have noted that dissolvability of coal-derived liquids is a function of more than one structural feature of the materials. For example, Snape and Bartle (24) have found that an empirically derived solubility parameter which incorporates terms for OH concentration (representing hydrogen bonding and acid-base complexation), ratio of bridgehead aromatic to total carbons (representing π - π complexation), and molecular weight clearly distinguishes solubility categories of oils, asphaltenes, and preasphaltenes. Baltisberger, et al. (25) have obtained good distinction between asphaltenes and preasphaltenes employing a two term parameter based on OH concentration (representing hydrogen bonding) and molar density of hydrogen (moles H/100 g sample) (representing π - π and dispersive interactions). Since

coal-deriv. liquids exhibit more than one type of solute-solute interaction (vide supra), solvents which completely dissolve these materials must be capable of more than one type of solute-solvent interaction. Undoubtedly, this is the reason for the failure of solubility parameters such as δ or θ , which are based primarily on one type of interaction, to adequately predict solvent effectiveness for dissolution of preasphaltenes.

Gutmann's donor-acceptor theory of solvent-solute interactions is nonspecific in nature (26). All types of interactions - hydrogen bonding, π - π charge transfer, n - π charge transfer, acid-base complexation, and others are included in the donor number (DN)-acceptor number (AN) concept. Thus, this theory is potentially more useful for predicting the extent of preasphaltene dissolvability in various solvents.

The dissolvability of the PA samples tends to increase with increasing DN values of the solvents, consistent with the results of Marzec and coworkers (5-8). However, considerable data scatter exists in plots of DN versus dissolvability. For example, even though DMSO has a substantially larger DN value than does THF (29.8 vs. 20.0, respectively), it is a poorer solvent than THF for the preasphaltenes. Thus, DN values may not be employed as the sole predictor of utility of a given solvent for preasphaltene dissolvability.

The results of Marzec, et al. (5-8) were interpreted in terms of the importance of solvent donor interactions with coal acceptor species (which are either part of the macromolecular network or molecules within the pore structures). Although no correlation between extractability and solvent AN values was found, these values were important in determining solvent efficiency. Solvents with large values for both DN and AN, e.g. water and methanol, were incapable of extracting the coal, presumably because solvent donor-acceptor interactions were greater than solvent donor-coal acceptor interactions. To incorporate the acceptor properties of the solvents, Marzec, et al. plotted extractability of coal vs. donor number minus acceptor number (DN-AN) values (5). The spread of data in the resulting graphs was substantial, particularly at larger DN-AN values. Our results for analogous plots, i.e., PA dissolvability vs. solvent DN-AN values, also disclosed an unsatisfactory amount of scatter. These values are, therefore, no more reliable for use in predicting solvent effectiveness for PA dissolution than are DN values.

A second parameter for assessing the relative importance of solvent donor numbers and acceptor numbers is the ratio of DN to AN. Qualitatively, at least, this ratio measures the strength of the solvent-solute interaction for the solvent acting as donor vs. acting as acceptor. For dissolution to occur, the solvent donor and acceptor sites must replace the solute donor and acceptor sites. Thus, this ratio may also be interpreted as giving information regarding the relative contributions of the donor sites and the acceptor sites in the solute to the overall intermolecular interactions. Plots of DN/AN vs. preasphaltene dissolvability are presented in Figure 1. They are similar in appearance to the Hildebrand solubility parameter plots, but with less scatter of data than the latter graphs. Furthermore, the range of values exhibited by good solvents (> 80% dissolvability) is smaller for the DN/AN plots (1.7-2.5) than for the solubility parameter plots (18.4-24.5 $J^{1/2} \text{ cm}^{-3/2}$). Figure 2 illustrates that DN/AN values may also be correlated to extractability or swelling of coal. As anticipated, the maximum extractability or swelling of coal and the maximum dissolvability of PA samples were exhibited by solvents with similar DN/AN values (ca. 2). This similar trend in preasphaltene dissolvability and coal extractability or swelling lends further credence to the suggestion of Weinberg and Yen (4) that molecules similar to those found in liquefaction products exist in virgin coal, probably within a macromolecular pore structure. The maximum of 2 observed in the DN/AN plot suggests that the contribution to the total intermolecular attractions of the preasphaltenes by electron donor sites (e.g. oxygen functionalities, electron-rich aromatic systems) outweighs the contributions by electron acceptor sites (e.g. electron deficient aromatic systems, phenolic protons). Whether this is the result of the relative number of donor vs. acceptor sites or the strength of the sites as electron donors or acceptors is unclear.

The value of DN/AN for solvents seems to be more reliable as a predictor of solvent effectiveness for preasphaltene dissolvability, coal extractability or coal swelling than are DN, DN-AN, θ , or δ . These results, then, are in agreement with the observations of Snape and Bartle (24) and Baltisberger, et al. (25), since the DN/AN parameter encompasses more than one type of intermolecular interaction.

Because of the nonspecificity of the DN/AN parameter, little information concerning the relative contributions of hydrogen bonding and charge transfer to the total intermolecular interactions of the PA samples may be gleaned from the dissolvability study. Previous researchers have demonstrated that viscosity measurements can provide useful data concerning intermolecular interactions, particularly hydrogen bonding (12-19). Therefore, a preliminary investigation focusing on viscosity measurements of a preasphaltene sample and model compounds was undertaken. Actual viscosities of the materials were not determined, since the preasphaltenes and most of the model compounds were solids at room temperature. Rather, viscosities of solutions of the samples in THF were measured relative to that of the pure solvent (η_{rel}).

To assess the importance of molecular weight to relative viscosity, a preasphaltene from run 80 (PA80) was separated into narrow molecular weight fractions by preparative GPC on Biobeads S-X3 and S-X8. The relative viscosities of the fractions vs. concentration are illustrated in figure 3. The expected trend, i.e., an increase in relative viscosity with an increase in molecular weight, was observed (cf. curves a, f, h, i), with one exception. The fraction with the lowest molecular weight (6-N) exhibited the second largest increase in relative viscosity (curve e). This result was suggestive of a strong interaction between THF and fraction 6-N. To test the nature of the interaction, PA80 was subjected to acetylation at room temperature, according to the procedure of Baltisberger, et al. (22). Following separation by preparative GPC, the relative viscosities in THF were again measured. Fractions 1 (highest molecular weight) and 6 (lowest molecular weight) exhibited the largest changes upon acetylation (cf. curves a and b, curves e and g). The intermediate molecular weight fractions evinced slight or no changes in relative viscosity. Derivatization of coal-derived liquids by acetylation has previously been demonstrated to disrupt intermolecular hydrogen bonding (20). Thus, the substantial decreases in relative viscosities for fractions 1 and 6 may be attributed to a diminution in the number of hydrogen bond donating moieties in the acetylated samples. These results argue for hydrogen bonding to be of greater importance than molecular weight for viscosity of preasphaltenes, in agreement with previous reports (15). Further evidence for this interpretation is the observation that the relative viscosity of a sample of polystyrene (which cannot hydrogen bond to THF) with $M_w = 2500$ is less than that of fraction 1-N ($M_w = 1950$).

From the preasphaltene samples, we were not able to assess the influence of charge transfer on viscosity. Thus, relative viscosities of a carefully selected set of model compounds in THF were measured (figure 4). In the ensuing discussion, all comparisons will be made at a constant concentration of 0.25 M. Charge transfer between the nonbonding electrons of the THF oxygen and the pi electron system of the model compounds does seem to play at least a minor role in determining relative viscosities. The greater relative viscosity of naphthalene (curve h) compared to tetralin (curve i) may be ascribed to the enhanced pi system of naphthalene. One might be tempted to apply the same reasoning to the observed increase in relative viscosity upon going from naphthalene (curve h) to phenanthrene (curve d) to pyrene (curve b). A plot of relative viscosity vs. reduction potentials (a measure of the ability of the aromatic molecule to act as an electron acceptor in a charge transfer complex) for naphthalene, phenanthrene and pyrene reveals a general trend of increasing relative viscosity as the reduction potential becomes more positive (i.e., as the molecule becomes easier to reduce). However, the data are scattered on either side of a least-squares line. In a homologous series, an increase in molecular weight is accompanied by an increase in viscosity, due to increased London (dispersion) forces. Thus, molecular weight should also be considered. A plot of relative viscosity vs. molecular weight for naphthalene, phenanthrene and pyrene is linear and

contains less scatter of data than does the reduction potential plot. Thus, molecular weight is probably more important in determining relative viscosity than is charge transfer.

The effect of hydrogen bonding on relative viscosity can also be seen in figure 4. 2-Naphthol (curve c) has a much greater relative viscosity than does 2-methoxy-naphthalene (curve e). The difference between the two arises from the ability of 2-naphthol to donate hydrogen bonds to THF. Furthermore, hydrogen bonding must play a more important role in determining the relative viscosity of the model compounds than does charge transfer. This can be seen by comparing the relative viscosity of quinoline (curve g) to 1,2,3,4-tetrahydroquinoline (THQ, curve f). Quinoline may be considered analogous to naphthalene, since both possess two fused aromatic rings, and THQ to tetralin, since both possess a reduced ring fused to an aromatic ring. However, unlike the naphthalene-tetralin pair, quinoline possesses a lesser relative viscosity than THQ. This result must arise from the hydrogen bond donating capability of THQ.

In summary, the greatest influence on relative viscosity of model compounds and preasphaltenes in THF appears to be hydrogen bonding. Second in influence is molecular weight, a measure of the extent of London forces. Finally, charge transfer seems to be only a minor contributor to overall relative viscosity of the samples.

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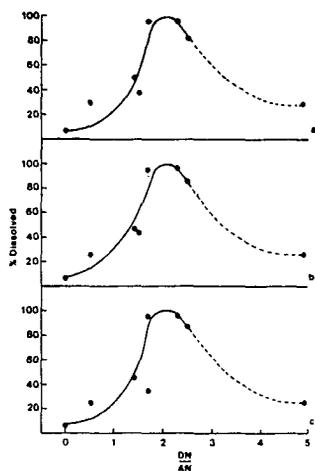


Figure 1. Dissolvability of pressphthalenes as a function of donor number divided by acceptor number (DN/AN) values of solvents. (a) Run 93; (b) Run 98; (c) Run 99.

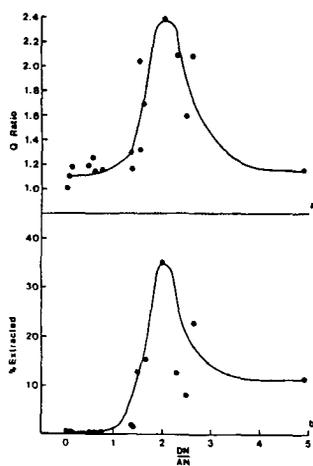


Figure 2. (a) Swelling of coal as a function of DN/AN values of solvents. Data from Reference 8. (b) Extractability of coal as a function of DN/AN values of solvents. Data from Reference 5.

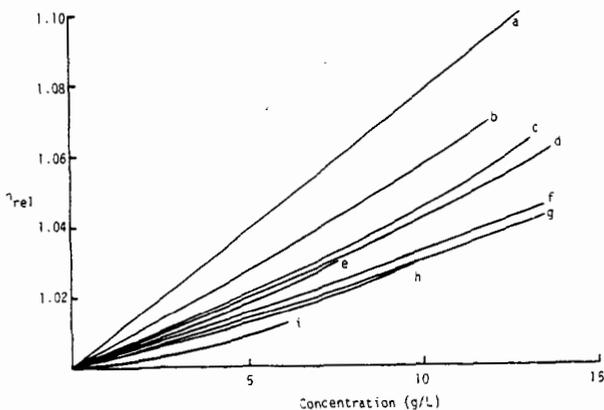


Figure 3. Relative viscosity of fractionated PABO (native, N, and acetylated, A) as a function of concentration. Molecular weights were determined by GPC. (a) fraction 1-N, $\bar{M}_w = 1950$; (b) fraction 1-A, $\bar{M}_w = 1800$; (c) unfractionated PABO-N; (d) unfractionated PABO-A; (e) Fraction 6-N, $\bar{M}_w = 135$; (f) fractions 2-N, $\bar{M}_w = 1050$ and 2-A, $\bar{M}_w = 950$; (g) fractions 3-A, $\bar{M}_w = 670$ and 6-A, $\bar{M}_w = 120$; (h) fraction 3-N, $\bar{M}_w = 720$; (i) fractions 5-N, $\bar{M}_w = 260$ and 5-A, $\bar{M}_w = 240$.

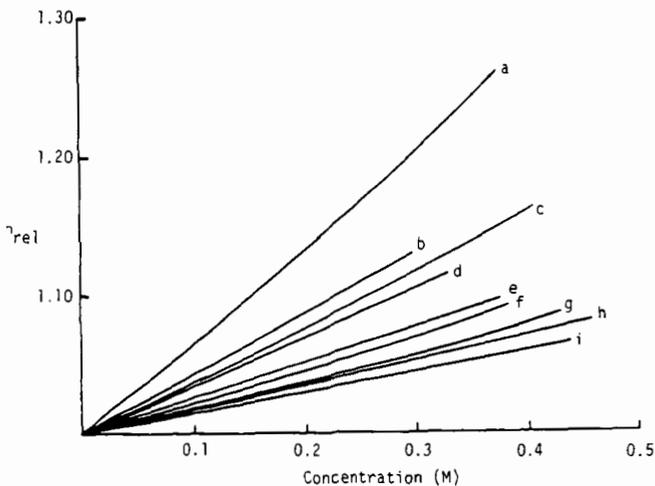


Figure 4. Relative viscosity of model compounds as a function of concentration. (a) 2,7-dihydroxynaphthalene; (b) pyrene; (c) 2-naphthol; (d) phenanthrene; (e) 2-methoxynaphthalene; (f) 1,2,3,4-tetrahydroquinoline; (g) quinoline; (h) naphthalene; (i) tetralin.