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EVALUATION OF INTERMOLECULAR ATTRACTIVE FORCES IN COAL-DERIVED LIQUIDS

Final Report for the Period August 1983—July 1987

By
Martin B. Jones

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I EXECUTIVE SUMMARY

The effect of structural features (hence types of intermolecular interactions) on the physical properties of coal-derived preasphaltenes was studied by comparing (1) the solubility of several model compounds of known structure with the dissolvability of preasphaltene samples as a function of solvent parameters and (2) intrinsic viscosities of model compounds of known structure with intrinsic viscosities of preasphaltene samples.

The quantitative dissolvabilities of nine model compounds and nine preasphaltene samples isolated from different liquefaction runs in 12 solvents were measured. The dissolvabilities were correlated with five solvent parameters: Hidebrand solubility parameter (δ), net hydrogen-bonding index (θ), donor number (DN), donor number minus acceptor number (DN-AN), and donor number divided by acceptor number (DN/AN). For each parameter tested, the model compounds behaved differently from the preasphaltene samples, likely because of the lack of hydrogen-bond donor functionalities in the models. The value of DN/AN for solvents was more reliable as a predictor of solvent effectiveness for preasphaltene dissolvability, coal extractability or coal swelling than were δ, θ, DN, or DN-AN. These results suggest that more than one type of intermolecular interaction are important in the dissolution of preasphaltenes.

The intrinsic viscosities of 66 model compounds and 38 size-separated preasphaltene samples were determined in THF solution. The model compounds were divided into three subsets: (1) models which were primarily hydrocarbon, with dispersion and π-π interactions as the dominant intermolecular forces, (2) models which contained polar groups, such as etheral oxygen and heterocyclic amine, but which exhibited the same general types of interactions as group 1, and (3) models which contained hydrogen-bond donor functionalities. The preasphaltene samples were isolated from different liquefaction runs and were separated into narrow molecular weight fractions by preparative gel permeation chromatography.

The viscosity measurements support the conclusion that hydrogen-bonding contributions are more important than contributions of π-π interactions or molecular weight (dispersion forces) to intrinsic viscosity of model compounds. For coal-derived preasphaltenes, molecular weight (hence nonpolar, nonspecific interactions) and hydrogen-bonding are equally important. Pi-pi associations should not be disregarded, although they seem to have a secondary influence on intrinsic viscosity. To minimize the viscosity of coal liquids, cracking (to decrease molecular weight), derivatization (to mask H-bond donor groups) and reduction (to increase alkyl content) should be carried out.

II. 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[2-14] and viscosity as a function of polarity and molecular weight.[15-23]

Roy and coworkers[4] studied the extractability of coal at 35°C as a function of the dielectric constant of dipolar aprotic solvents. The results were ambiguous: dimethyl sulfoxide (DMSO, ε = 46.6) was comparable in extracting ability to pyridine (ε = 12.3) and better than ethylenediamine (ε = 14.2). Angelovich *et al.*[5] found that solvents with a Hildebrand solubility parameter δ of ca. 19.4 $J^{0.5}\,cm^{-1.5}$ were most effective in the conversion of subbituminous coal to benzene-soluble products from liquid-phase catalytic hydrogenation. Hombach[6] 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 $J^{0.5}\,cm^{-1.5}$ and, as expected, showed little dependence on the chemical nature of the solvents in the mixture. Likewise, Weinberg and Yen[7] 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 ovserved in the swelling spectrum of the coal at 22.5 and 28.6 $J^{0.5}\,cm^{-1.5}$. Benzene-insoluble liquefaction products exhibited maximum dissolvability in solvents (pure or mixtures) with δ values of ca. 23.5 $J^{0.5}\,cm^{-1.5}$. Marzec and coworkers investigated possible correlations of solvent acceptor and donor numbers (AN and DN, respectively) with extractability[8-10] and swelling[10,11] of hvb coal at ambient temperatures. Both the extract yield and the swelling ratio increased with increases in the DN or DN minus AN values of solvents.

Bockrath *et al.* reported that aggregatrion of asphaltenes and preasphaltenes significantly contributes to the viscosity of of coal-derived liquids.[16] 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.[17] Likewise, Li and coworkers, from studies of coal-derived liquids[18,19] and model compounds,[19] have shown that hydrogen-bonding, primarily involving phenolic OH and nitrogen bases, is largely responsible for the

viscosity of the coal-derived liquids. Preasphaltenes have a greater impact on viscosity than do asphaltenes,[16,20,22] but whether this is attibutable to the larger molecular weight of the former[20] or to differences in concentrations of phenolic functionalities is not clear.

Additional evidence for the contribution of hydrogen-bonding to reduced solubilities and increased viscosities has been provided by derivatization studies. Patel *et al.* reported a substantial increase in the dissolvability of solvent-refined lignite in nonpolar solvents after silylation or acetylation.[24] Gould *et al.* found that silylation of coal liquefaction bottoms resulted in a four- to seven-fold reduction in viscosity.[23] The results of both investigations were interpreted in terms of disruption of intermolecular hydrogen-bonding. There can be little doubt of the importance of hydrogen-bonding to solublility and viscosity.

The contribution of charge transfer interactions, particularly π-π interactions, to physical properties of coal and coal-derived liquids is less clear. Aromatic stack formation in coal crystallites leading to inhibited flexibility, decreased solubility, and increased apparent molecular weight has been attributed to π-π interactions.[25] Speight has shown that the solvent dielectric strength affects the apparent molecular weight of asphaltene fractions.[26] This effect has been ascribed to π-π interactions.[26,27] Disruption of charge transfer stacks has been given credit for an increase in the solubility of coal and coal-derived liquids upon alkylation.[28]

The original objective of this research project was to examine intermolecular attractive forces for both model and actual coal-derived liquids. The primary emphasis was to discern contributions of hydrogen-bonding and π-π interactions to physical properties, particularly solubility and viscosity, of model and coal-derived liquids. Accordingly, model compounds were chosen on the basis of structural similarities to coal-derived liquids. They were principally aromatic in nature with substituents (oxygen, nitrogen, aliphatic carbon) attached to the ring or bridging between two rings. To distinguish between H-bonding and π-π interactions, functionalities of both models and actual coal-derived liquids were modified.

III. SOLUBILITY STUDY

As mentioned previously, several researchers have investigated the solubility of coal-derived liquids and the extractability/swellability of coal in various solvents. Correlations of solvent parameters, particularly the Hildebrand solubility parameter (δ) and the donor number, acceptor number (DN, AN) concept, with the behavior of the coal and coal-derived samples in the solvents have been carried out. In our study, an effort to evaluate the effect of structural features on the dissolvability of coal-derived preasphaltenes was made by comparing the solubility of several model compounds of known structure with the dissolvability of preasphaltene samples.

Experimental

The solvents employed in this study were reagent grade, obtained from commercial suppliers and were used without further purification. The model compounds employed for this study are illustrated in Figure 1 and listed in Table 1. Compounds **1-5** were synthesized by condensation of the appropriate lithioaromatic (from treatment of the bromoaromatic with *n*-butyllithium) with the appropriate aromatic aldehyde. The resulting diaryl carbinols were reduced to the corresponding hydrocarbons with lithium aluminum hydride/aluminum chloride.[29] For example, **1** was prepared from condensation of 1-lithionaphthalene with 1-naphthaldehyde followed by reduction. Compound **6** was prepared by condensation of 1-lithionaphthalene with 6-methoxy-1-tetralone, followed by acid-catalyzed dehydration of the resulting alcohol. Compound **7** was synthesized by a modified Ullmann procedure, in which potassium carbonate, 4,4'-dihydroxybiphenyl, 1-bromonaphthalene and cuprous iodide were refluxed in pyridine for 96 hours.[30] Likewise the same technique afforded compound **8** from 2-naphthol and 1,4'-dibromobenzene and compound **9** from phenol and 1,4-dibromonaphthalene.

A modified version of the solvent extraction procedure of Steffgen *et al.*[31] was used to separate the preasphaltenes (THF-soluble, toluene-insoluble) from total liquefaction samples obtained from the University of North Dakota Energy and Minerals Research Center (EMRC). Liquefaction conditions and yield data are presented in Table 2. Analytical data for the preasphaltenes are given in Table 3.

Quantitative solubility measurements of the model compounds in various solvents were made by dissolving 100 mg of compound in a minimum measured amount of solvent (not exceeding 10

ml), using ultrasound for mixing. If not all the compound dissolved in 10 ml, the suspension was vacuum filtered and the insoluble residue was weighed. The quantitative dissolvability of the preasphaltene samples was determined by mixing 30 mg of preasphaltene with 3 ml of solvent in a stoppered test tube in an ultrasonic bath for one minute. Vacuum filtration of the suspension 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.

Results and Discusion

The model compounds emcompass a molecular weight range of 268-540 g/mole, with a percentage of oxygen from 0-10% and a degree of condensation (H_{aru}/C_{ar}) of 0.69-0.91 (Table 1). A major difference between these models and lower molecular weight fractions of coal-derived liquids is the oxygen functionality. Hydroxyl groups (as phenolic OH) account for the bulk of the oxygen present in coal-derived liquids,[32] whereas only model compound **5** possesses hydroxyl oxygen. Thus, the models, except for **5**, would not be expected to exhibit significant hydrogen-bonding interactions with the solvents. Rather, π-π or n-π interactions would be expected to be the dominant specific type of solvent-solute attraction.

The quantitative solubilities of the model compounds in twelve solvents are given in Table 4. The solvents can be separated into three groups: poor (methanol, hexane, DMSO), intermediate (acetone, DMF, diethyl ether, cyclohexanone), and good (pyridine, cyclopentanone, toluene, methylene chloride, THF). In general, THF is the best solvent for the model compounds. The quantitative dissolvabilities of the freshly isolated preasphaltene samples are presented in Table 5. Again, the solvents can be separated into three groups: poor (methanol, hexane, diethyl ether, toluene), intermediate (methylene chloride, cyclohexanone, acetone, DMSO) and good (THF, pyridine, cyclopentanone, DMF). The similar behavior of each of the PA samples in the same solvent suggests that the coal processing conditions have a minimal influence on the structural features which govern the dissolvability of the preasphaltenes, although these conditions have a profound effect on preasphaltene yield. Also included in this table are data for a preasphaltene sample aged in air for 48 days. The aged sample is less soluble than is the sample stored under nitrogen (the usual storage for the PA samples), particularly in toluene, methanol and acetone. This behavior is not unexpected; aging of coal-derived liquids has been shown to result in substantially increased molecular weights of preasphaltenes.[20,33] Oxidative coupling of phenols has been

suggested as a mechanism for the observed increase in molecular weight.[33] The overall effect is to increase the viscosity[20,33-35] and, from our data, reduce the dissolvability of the coal-derived liquid. The similar behavior of the PA samples suggests that processing conditions have a minimal influence on the structural features which govern the dissolvability.

Figure 2 contains a plot of the solubilities of the model compounds vs. the Hildebrand solubility parameter of the solvents. Various solvent parameters are given in Table 6. The maximum solubilities are attained in solvents with δ values of 18.5-20 $J^{0.5}\,cm^{-1.5}$, lower than that reported for coal-derived liquids.[6,7] A comparable plot for preasphaltene samples is shown in figure 3. The PA samples exhibit maximum dissolvabilities in solvents with δ values which range from 18.5-24.7 $J^{0.5}\,cm^{-1.5}$, in agreement with previously reported values for preasphaltenes. However, three of the eight solvents tested which have δ values within that range (methylene chloride, acetone and dimethyl sulfoxide) dissolve 50% or less of the PA and cannot be considered good solvents for the PA samples. These results suggest that the predominantly non-polar (and nonspecific) Hildebrand solubility parameter is insufficient for predicting the ability of solvents to dissolve preasphaltenes. Thus, specific solvent-solute interactions must play a role in the dissolution of PA. Larsen *et al.*[12] observed similar off-line solvent behavior in a study of swellability of pyridine-extracted Illinois #6 coal versus δ for different solvents. Excess swelling was obtained with solvents capable of hydrogen-bonding. Excellent correlation was obtained between excess swelling and the heat of hydrogen-bonding of the solvents with *p*-fluorophenol. From these results, then, one may ascertain the importance of hydrogen-bonding to solvent swelling of coal (and infer its importance to dissolution processes as well).

A solvent parameter which directly addresses the issue of hydrogen-bonding is the net hydrogen-bonding index (θ), which takes into account both the formation of new solvent-solute hydrogen-bonds and the cleavage of existing solvent-solvent hydrogen-bonds.[36] 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 dimethylformamide (DMF) behaves in exactly the opposite manner, since it cannot hydrogen-bond to itself. A plot of the solubilities of the model compounds vs θ is shown in figure 4. There does not appear to be a significant trend in this plot. Methylene chloride (θ = 1.5), toluene (θ = 4.2), and THF (θ = 12.0) are all good solvents for the model compounds, but acetone, which has a θ value of 12.5, similar to THF, is a mediocre solvent. Furthermore, DMF, with a

substantially greater θ value than THF (18.9 vs. 12.0, respectively), is a poorer solvent than THF for the model compounds. These results argue against the importance of hydrogen-bonding for dissolution of the model compounds. This should not be surprising, since only one of the model compounds (**5**) has a functional group capable of donating H-bonds to the solvent. The model compounds containing ether functional groups (**6-9**) could accept H-bonds from the solvents, but only methanol, of the solvents employed, is a hydrogen-bond donor solvent and it is too polar to effectively dissolve even the ethers.

On the other hand, a distinct trend is observed in the plot of dissolvabilities of preasphaltene samples vs. θ (Figure 5). As the value of θ increases, the dissolvabilities of the PA samples increase. There are two major exceptions to this trend. On the basis of θ values, toluene would be predicted to be a better solvent for PA samples than methylene chloride and acetone would be predicted to be at least comparable or better than THF in dissolving power. In fact, neither of these cases are observed. Certainly the data support the general contention that hydrogen-bonding interactions between solute and solvent are vital for preasphaltene dissolvability. However, the data also suggest that a simple solvent parameter which focuses on primarily one aspect or type of intermolecular interaction may not be sufficient to model or predict solvent behavior for such a complex mixture as coal or coal-derived liquids.

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[37] 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) amd molecular weight clearly distinguishes solubility categories of oils asphaltenes and preasphaltenes. Baltisberger *et al.*[38] have obtained good distinction between asphaltenes and preasphaltenes by employing a two-term parameter based on OH concentration (representing hydrogen-bonding) and molar density of hydrogen (mole H/100 g sample) (representing π-π and dispersive interactions). Since coal-derived liquids exhibit more than one type of solute-solute interaction, solvents which completely dissolve these materials must be capable of more than one type of solute-solvent interaction. This is undoubtedly the reason for the less-than-satisfactory ability of solubility parameters such as δ and θ, which are based primarily on one type of interaction, to predict solvent effectiveness for dissolution of preasphaltenes.

Gutmann's donor-acceptor theory of solvent-solute interactions is nonspecific in nature.[39] 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. Solvent donor numbers are determined from calorimetric measurements of the molar enthalpy of the reaction of the solvent with $SbCl_5$ in dilute dichloroethane solution. Solvent acceptor numbers are obtained from ^{31}P NMR chemical shifts of triethylphosphine oxide in the given solvent relative to the ^{31}P chemical shift of the complex Et_3PO-$SbCl_5$. Although the AN values are dimensionless, good correlation has been found between these values and thermodynamic parameters such as Kosower's Z values or the E_T values of Dimroth and Reichardt.[39]

Figure 6 contains a plot of the solubilities of model compounds versus the solvent DN values. No identifiable trend is observed, although the lack of DN values for every solvent tested makes the interpretation less convincing. The plot is reminiscent of the Hildebrand solubility parameter plot, with a maximum in solubility at a DN value of 20.

The dissolvability of the preasphaltene samples tends to increase with increasing donor number values (Figure 7), as observed by Marzec and coworkers.[8-11] However, considerable scatter exists in plots of DN vs. dissolvability. For example, DMSO has a substantially larger DN value than does THF (29.8 and 20.0, respectively), but it is a much poorer solvent for these preasphaltenes than is THF. Thus, DN values should not be used as the sole predictor of utility of a given solvent for preasphaltene dissolvability.

The results of Marzec and coworkers[8-11] 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 structure). Although no correlation between extractability and solvent AN values was found, these values were important in determining solvent efficiency. Solvents with large values of both DN and AN, eg. water and methanol, were incapable of extracting the coal, presumably because solvent donor acceptor interactions were greater than solvent-donor-coal-acceptor or solvent-acceptor-coal-donor interactions. To incorporate the acceptor properties of the solvents, Marzec *et al.* plotted extractability of coal against values or solvent donor number minus solvent acceptor number (DN-AN). Increased extractability was noted with increasing DN-AN values. However, the scatter of data in this plot was greater than in the plot of extractability vs. DN values, particularly at larger DN-AN values, suggesting that solvent acceptor characteristics (hence coal donor characteristics) are less important for extraction

of coal than solvent donor characteristics (hence coal acceptor characteristics).

Analogous plots of solubility of model compounds and dissolvability of PA samples vs. DN-AN values are shown in figures 8 and 9. These plots are similar to the DN graphs. For the model compounds, the plot resembles the solubility parameter plot, with maximum solubility at DN-AN of 12. For the preasphaltene samples, a slight trend of increased dissolvability with increased DN-AN is observed. However, as with Marzec's results, the scatter in this plot is significant and limits the utility of this parameter for prediction of individual solvent effectiveness in dissolvability of preasphaltenes.

A second parameter for assessing the relative importance of solvent donor 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 a donor versus acting as an 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 the solubilities of model compounds and the dissolvabilities of PA samples against DN/AN values of solvents are shown in figures 10 and 11. These plots resemble solubility parameter plots in general shape. However, smooth curves with narrower maxima can be drawn through the data without significant off-line points, unlike the solubility parameter plots. The most effective DN/AN ratio for dissolution of the model compounds was 2.5 (THF). The DN/AN ratio can also be correlated with swelling or extractability of coal, as illustrated in figures 12 and 13. As expected, the maximum extractability or swelling of coal and the maximum dissolvability of preasphaltene samples were exhibited by solvents with similar DN/AN ratios (ca. 2). This similar trend in preasphaltene dissolvability and coal extractability or swelling lends further credence to the suggestion of Weinberg and Yen that molecules similar to those found in liquefaction products exist in virgin coal, probably within a macromolecular pore structure.[7] The maximum of 2 ovserved 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 contribution by electron acceptor sites (electron-deficient aromatic systems, phenolic protons). Whether this is the result of the relative numbers of donor and acceptor sites or the strength of the sites as electron donors or acceptors is unclear. The model compounds have primarily donor sites (electron-rich aromatic rings, ether oxygens) rather than acceptor sites and

would thus be expected to be more soluble in solvents with greater donor characteristics. Thus, it is not surprising that the maximum solubility of the model compounds is in a solvent with a DN/AN ratio of 2.5.

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[37] and Baltisberger *et al.*,[38] since the DN/AN parameter encompasses more than one type of intermolecularinteraction.

For each parameter tested, the model compounds behaved differently from the preasphaltene samples. This must be ascribed to differences in structural features, notably the lack of hydroxyl oxygen and the presence of highly condensed aromatic nuclei in the model compounds.

IV. VISCOSITY STUDY

Because of the nonspecificity of the DN/AN parameter (the most useful predictor of solvent effectiveness for preasphaltene dissolvability), little information concerning the relative contributions of hydrogen-bonding and charge transfer to the total intermolecular interactions of coal-derived preasphaltene samples was gleaned from the dissolvability study. Previous researchers have demonstrated that viscosity measurements can provide useful data concerning intermolecular interactions, particularly hydrogen-bonding.[15-23] Therefore, a study focusing on viscosity measurements of model compounds and preasphaltene samples was undertaken. A much larger set of model compounds (shown in figure 14) was chosen for this study. These model compounds can roughly be divided into three subsets: (1) models which are primarily hydrocarbon, with dispersion and π-π interactions as the dominant solute-solute intermolecular forces, (2) models which contain polar groups, such as etheral oxygen and heterocyclic amine, but which exhibit the same general types of interactions as group 1, and (3) models which contain hydrogen-bond donor functionalities. Differences in the viscosity characteristics of these subsets were used in the evaluation of the preasphaltene samples.

Experimental

The model compounds were, in general, available commercially or prepared by standard literature reactions. They are listed in Table 7 and illustrated in figure 14. The preasphaltene samples employed for this study were the same ones as for the dissolvability study (Tables 2 and 3). Room temperature acetylations of preasphaltenes from runs 80 and 99 were accomplished following the method of Baltisberger, *et al.*[40] Both native and acetylated preasphaltene samples were separated into narrow molecular size fractions by preparative gel permeation chromatography (GPC) on Biobeads S-X3 or S-X8. Molecular weights of the PA samples were determined from analytical GPC measurements (three 100 Å and one 500 Å μStyragel columns in series, THF as mobile phase), using a calibration curve prepared from polystyrene standards.

Specific viscosities of the preasphaltene samples and model compounds were measured in THF solution at 20°C in Canon-Fenske flow-type viscosimeters. Similar experiments were carried out with different solvents and at increased temperatures. Intrinsic viscosities were calculated by

extrapolation of plots of specific viscosities/concentration vs. concentration to infinite dilution.

Results and Discussion

Intrinsic viscosities were determined for THF solutions of lignite-derived preasphaltenes from six different liquefaction runs (Table 8). The values are similar, despite the differences in processing. The two samples with the highest viscosity have the largest molecular weight (by GPC) and the highest S + O content (Table 4). These data could then be interpreted in terms of the influence on viscosity of (1) polar oxygen groups (particularly OH), hence hydrogen-bonding or (2) the molecular weight, hence nonspecific interactions such as van der Waals forces. Recent work by White and Schmidt has demonstrated a linear relationship of average molar polarizability and mid-boiling point of Wilsonville and H-Coal liquefaction product distillates.[41] Since the mid-boiling point is representative of the total intermolecular forces and polarizability is directly related to van der Waals forces, White and Schmidt concluded that the dominant intermolecular force in these distillates was van der Waals forces. We did not measure molar polarizabilities or mid-boiling points for the preasphaltene samples. Thus, we could not determine if a linear relationship exists between intrinsic viscosity and boiling point or molar polarizability of coal-derived liquids. However, boiling point data for the model compounds was available. Figure 15 illustrates the relationship of boiling point and intrinsic viscosity. There is a general increase in boiling point with increasing viscosity, suggesting that, like boiling point, intrinsic viscosity is a measure of the total intermolecular forces of a material. The data may be separated into three groups, corresponding to nonpolar models, models which contain polar groups but without H-bond donor functionality, and models which contain H-bond donor functionality. Each of these groups has a slightly different linear relationship between boiling point and intrinsic viscosity. For two molecules with the same boiling point, the species with H-bond donor groups has the higher intrinsic viscosity than the nonpolar molecule. Thus, hydrogen-bonding may have a disproportionately larger influence on intrinsic viscosity than on boiling point.

What about the influence of molecular weight on viscosity? Pertinent data from the viscosity measurements of the model compounds and the preasphaltene samples are given in Table 9. Plots of log intrinsic viscosity vs log molecular weight are presented in figures 16 and 17. Logarithmic plots were employed because of the Mark-Houwink equation ($[n] = KM^a$ or $\log[n] = \log K + a \log M$), which is commonly used in polymer science to calculate molecular weights of known

polymers from viscosity measurements. As with the boiling point, there is a trend of increasing intrinsic viscosity with increasing molecular weight. The model compounds (Figure 16) may be divided into three groups, depending on the presence of polar and/or hydrogen-bond donor functionalities. Note that each class of models has a different linear response. The least-squares lines for the nonpolar and polar models are reasonable, but the least-squares line for the hydrogen-bond donor molecules has a poor R value. Examination of the individual points indicates that the line should probably have a much greater slope. The probable reason for the poor line is that an insufficient number of high molecular weight models with hydrogen-bond donor groups was available. With the assumption that the H-bond line should have a much greater slope, the nonpolar models then provide the line with the smallest slope (corresponding to the "a" constant in the Mark-Houwink equation). The results suggest that hydrogen-bonding plays a more significant role in determining the intrinsic viscosity of model compounds than does molecular weight, at least for those models which can participate in hydrogen-bonding.

Plots of log intrinsic viscosity versus log molecular weight of size-separated preasphaltene (PA) samples are given in Figure 17. Comparison of the data for native and acetylated PA samples from the same liquefaction run reveals least-squares lines which have similar slope ("a" in the Mark-Houwink eq.), but differ in intercept ("log K" in the Mark-Houwink eq.). Acetylation converts H-bond donor groups such as OH and NH into polar esters and amides which are not capable of hydrogen-bond donation to the solvent. Interestingly, the behavior of the PA samples is not like those of the model compounds, which had much different slopes of the least-squares lines. This suggests that hydrogen-bonding may be less influential in the overall determination of intrinsic viscosity for coal-derived preasphaltenes than for model compounds. However, there is no question that minimization of hydrogen-bonding by derivatization of coal-derived liquids is beneficial to reduction of viscosity. For more complete viscosity reduction however, molecular weight must also be reduced.

The effect of temperature on intrinsic viscosity of certain of the model compounds was investigated (Table 10). As expected, an increase in temperature was accompanied by a decrease in viscosity. The percent change in viscosity from 20°C to 50°C was greater for the nonpolar models (e.g. 30 % for **12**) than for the models with H-bond donor groups (20% decrease for **59**). We were not, however, able to raise the temperature high enough (because of the boiling point of THF) to decrease the viscosity more than approximately 30% for any of the compounds.

The effect of solvent on intrinsic viscosity of model compounds was also examined. In most instances, THF solutions gave higher intrinsic viscosities than did methanol or toluene solutions. Tetralin, which could associate with toluene via π-π interactions, gave only a slightly higher intrinsic viscosity in toluene than in methanol. On the other hand, decalin, which has no aromaticity, had a higher intrinsic viscosity in methanol than in toluene. One could suggest that the lack of π-π interactions with the solvent decreased the intrinsic viscosity of decalin in toluene. The most interesting results from this study were from the polar models quinoline (**38**), dibenzofuran (**41**) and dibenzothiophene (**42**). These models are all aromatic and contain polar functionalities capable of accepting, but not donating hydrogen-bonds. For both quinoline and dibenzofuran, THF provided the greatest intrinsic viscosity, followed by methanol, then toluene. The data seem to indicate that the particular type of interaction which THF has with the solutes (n-π ?) is more important in determination of viscosity than is hydrogen-bonding or π-π interaction. For dibenzothiophene, however, methanol afforded a larger intrinsic viscosity than THF, with toluene again at the lowest value. This seems unusual, since sulfur is generally regarded as a poorer H-bond acceptor than either O or N. Again, the contribution of n-π interactions outweighs that of π-π association. Models which were both aromatic and capable of donating/accepting hydrogen-bonds comprised the last group. 1,2,3,4-Tetrahydroquinoline (**55**) had a higher intrinsic viscosity in toluene than in methanol, indicative of greater importance of π-π interactions than hydrogen-bonding. To assess the relative importance of solvent H-bond accepting atoms, intrinsic viscosities of 2-naphthol (**56**) and 2,7-dihydroxynaphthalene (**59**) were measured in THF (which contains O) and quinoline (which contains N). Similar values were obtained in both solvents for 2-naphthol, although THF was slightly higher. With 2,7-dihydroxynaphthalene, quinoline gave a significantly greater intrinsic viscosity that did THF. These results suggest that with increasing phenolic content, H-bonds between phenols as donors and amines as acceptors become more important that H-bonds between phenols as donors and ethers as acceptors.

In summary, the viscosity measurements support the conclusion that hydrogen-bonding contributions are more important than contributions of π-π interactions to intrinsic viscosity of model compounds. For coal-derived preasphaltenes, molecular weight (hence nonpolar, nonspecific interactions) and hydrogen-bonding are equally important. Pi-pi associations should not be disregarded, although they seem to have a secondary influence on intrinsic viscosity. To minimize the viscosity of coal liquids, cracking (to decrease molecular weight), derivatization (to mask H-bond donor groups) and reduction (to increase alkyl content) should be carried out.

Finally, data pertaining to a measure of the relative importance of hydrogen-bonding versus π-π interaction was obtained from gel permeation chromatographic (GPC) determinations (THF solvent) of molecular weight of model compounds (Table 12). Model compounds which contained large planar aromatic nuclei which were not highly substituted (**22**, **25**, **26**, **27**, **29**, **30**, **31**, **52**) all exhibited GPC molecular weights which were much lower than their actual molecular weights. This arose from retardation on the GPC columns due to π-π association of the compound with the polystyrene-divinylbenzene packing material. Molecules with smaller aromatic nuclei such as naphthalene (12) and 2-phenoxynaphthalene (**45**) had GPC molecular weights that were similar to their actual weights. Association with the packing material was not as important for these models. Compounds which could hydrogen-bond to the solvent (THF) gave GPC molecular weights that were much higher than actual. This can be explained by strong association with the solvent, resulting in the formation of a solvent-solute complex which was larger than the pure solute itself, hence passed through the column more rapidly

Both π-π association and hydrogen-bonding do, then, play a role in the GPC separation. Is one more important than the other? Contrast the results of 2-phenoxynaphthalene (**45**) with those of 2-naphthol (**56**). For either molecule, the degree of π-π association with the column material should be similar, since the ring sizes and substituents are similar. However, of the two, only **56** can hydrogen-bond with the solvent. The observed behavior of **56**, i.e., higher GPC molecular weight than actual, is consistent with hydrogen-bonding being more influential than π-π association. Thus, as with viscosity, the GPC results for model compounds indicate that hydrogen-bonding is a more important intermolecular interaction than is π-π association.

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VI. TABLES

Table 1. Model compounds employed in solubility study.

Compound	MW (g/mol)	H_{aru}/C_{ar} [a]	F_a [b]	% O (total)	% O (as OH)
1-(1-Naphthalenylmethyl)-naphthalene (1)	268	0.80	0.95	0	0
1-(2-Naphthalenylmethyl)-pyrene (2)	342	0.69	0.96	0	0
1,4-Bis(phenylmethyl)naphthalene(3)	308	0.91	0.92	0	0
1,4-Bis(9-phenanthrenylmethyl)-naphthalene (4)	508	0.74	0.95	0	0
1,4-Bis(9-phenanthrenylhydroxy-methyl)naphthalene(5)	540	0.74	0.95	5.9	5.9
1-(1-Naphthyl)-6-methoxy-3,4-dihydronaphthalene (6)	286	0.75	0.76	5.6	0
1,4-Bis(1-Naphthoxy)biphenyl (7)	438	0.88	1.00	7.3	0
1,4-Bis(2-Naphthoxy)benzene (8)	362	0.85	1.00	8.8	0
1,4-Diphenoxynaphthalene (9)	312	0.91	1.00	10.3	0

[a]Degree of aromatic condensation
[b]Fraction of aromatic carbons

Table 2. Preasphaltenes (PA) employed in solubility and viscosity studies.

Run #[a]	Coal[b]	Reducing Gas	Temp (°C)	Press (MPa)	Gas flow (m^3/h)	Additive	Yield PA (%)[c]
41	B3	H_2-CO	459	26.6	1.25	-	9.4
53	POW1	H_2	469	13.9	0.91	-	7.4
58	BB2	H_2	459	18.4	1.16	-	7.3
80	BB2	H_2-CO	456	22	1.13	H_2S	10.7
89	BB2	H_2-CO	436	19	0.99	H_2S	9.0
90	BB2	H_2-CO	436	15	0.93	-	11.2
93	BB2	H_2-CO	440	15	0.88	S	8.6
98	BB2	H_2-CO	440	14	0.93	H_2S + pyrite	6.2
99	BB2	H_2-CO	400	16	0.96	-	19.6

[a]All runs were carried out under bottoms-recycle operation at the University of North Dakota Energy and Minerals Research Center.

[b]B3, Beulah 3 lignite; POW1, Powhattan bituminous coal; BB2, Big Brown lignite.

[c]Hexane- and toluene-insoluble, THF-soluble; yield based on starting weight of coal liquefaction product.

Table 3. Analytical data for the preasphaltenes.

	Elemental Analysis (wt %)					
Run #	C	H	N	S + O	H_{aru}/C_{ar}	F_a
41	85.5	5.3	2.1	7.1	0.71	0.78
53	87.4	5.1	2.6	4.9	-	-
58	86.0	5.2	2.6	6.2	0.68	0.83
80	77.8	6.1	2.1	14.0	0.90	0.64
89	81.6	5.6	2.6	10.2	0.77	0.73
90	83.8	5.4	2.3	8.5	0.70	0.78
93	81.9	5.5	2.5	10.1	-	-
98	81.2	5.7	2.6	10.5	0.78	0.70
99	80.1	5.7	2.1	12.1	0.83	0.72

[a]By difference

Table 4. Dissolvability of model compounds in various solvents.

	mg indicated compound dissolved in 10 ml solvent								
Solvent	1	2	3	4	5	6	7	8	9
Methanol	5.5	4.5	6.2	1.2	3.7	3.3	2.6	4.2	4.6
Hexane	7.6	7.7	9.0	2.9	3.7	4.2	0.9	9.2	4.3
DMSO	35	8.4	7.5	-	9.9	3.9	1.2	8.9	7.6
Acetone	106	25	107	-	7.1	51	3.2	14	202
DMF	225	33	32	-	16	112	5.4	34	229
Diethylether	131	29	198	-	3.0	101	3.5	41	22
Cyclohexanone	222	72	160	33	8.8	189	13	35	138
Pyridine	97	79	269	-	123	189	10	157	420
Cyclopentanone	720	124	412	82	7.0	424	17	178	350
Toluene	770	182	487	104	5.2	350	8.6	185	74
CH_2Cl_2	622	481	783	28	5.8	1000	22	228	713
THF	1000	883	1050	143	163	1000	97	303	500

Table 5. Dissolvability of preasphaltenes in various solvents.

	% indicated sample dissolved in solvent[a]									
Solvent	41	53	58	80	80[b]	89	90	93	98	99
Methanol	22.9	11.8	20.1	28.2	19.0	28.9	26.4	29.7	25.9	25.2
Hexane	7.6	6.8	6.7	6.0	-	6.0	7.0	7.2	6.4	5.9
DMSO	43.4	20.5	30.4	55.3	-	37.7	35.3	37.5	43.1	34.7
Acetone	46.4	30.3	33.7	45.6	32.7	48.4	48.2	49.4	46.5	45.3
DMF	94.9	93.7	95.0	96.8	87.0	94.0	94.1	95.5	94.8	96.1
Diethylether	28.7	21.6	22.6	24.2	-	24.4	31.1	28.2	26.1	24.9
Cyclohexanone	87.6	85.9	80.1	65.6	-	75.2	82.0	85.7	67.2	62.5
Pyridine	95.8	95.3	95.5	96.2	94.4	95.4	95.1	95.4	95.9	96.2
Cyclopentanone	89.1	88.5	88.1	81.0	76.2	85.8	87.0	88.9	85.4	86.3
Toluene	33.4	31.2	27.4	21.5	9.1	20.6	26.7	23.5	23.2	21.9
CH_2Cl_2	49.9	50.4	43.8	30.1	-	35.7	40.6	40.3	35.9	28.4
THF	87.5	85.5	84.7	85.4	85.8	81.0	83.5	81.0	84.5	87.5

[a]Percentage of 30 mg sample dissolved in 3 ml solvent.
[b]Preasphaltene sample exposed to air for 48 days.

Table 6. Solvent parameters.

Solvent	δ^a	θ^b	DN[c]	DN-AN[d]	DN/AN[e]
Methanol	29.7	-19.8	19.0	-22.3	0.5
Hexane	14.9	0.0	0.0	0.0	0.0
DMSO	24.5	-	29.8	10.5	1.5
Acetone	20.5	12.5	17.0	4.5	1.4
DMF	24.7	18.9	26.6	10.6	1.7
Diethylether	15.1	-	19.2	15.3	4.9
Cyclohexanone	20.3	13.7	-	-	-
Pyridine	21.9	-	33.1	18.9	2.3
Cyclopentanone	21.3	-	-	-	-
Toluene	18.2	4.2	-	-	-
CH_2Cl_2	19.8	1.5	-	-	-
THF	18.6	12.0	20.0	12.0	2.5

[a]Hildebrand solubility parameter, $J^{0.5}\,cm^{-1.5}$. Values taken from reference 42.
[b]Net hydrogen-bonding index. Values taken from reference 36.
[c]Donor number. Values taken from reference 43.
[d]Donor number minus acceptor number. Calculated from data in reference 43.
[e]Donor number divided by acceptor number. Calculated from data in reference 43.

Table 7. Model compounds employed in viscosity study.

Compound	MW (g/mol)	H_{aru}/C_{ar} [a]	F_a [b]	% O or N (total)	% O or N (as OH or NH)
Benzene (**10**)	78	1.00	1.00	0	0
Toluene (**11**)	92	1.00	0.86	0	0
Naphthalene (**12**)	128	0.80	1.00	0	0
Tetralin (**13**)	132	0.67	0.60	0	0
Decalin (**14**)	138	-	0	0	0
1-Methylnaphthalene (**15**)	142	0.80	0.91	0	0
Biphenyl (**16**)	154	0.83	1.00	0	0
2-Ethylnaphthalene (**17**)	156	0.80	0.83	0	0
2,6-Dimethylnaphthalene (**18**)	156	0.80	0.83	0	0
2,3-Dimethylnaphthalene (**19**)	156	0.80	0.83	0	0
Fluorene (**20**)	166	0.67	0.92	0	0
Diphenylmethane (**21**)	168	0.83	0.92	0	0
Phenanthrene (**22**)	178	0.71	1.00	0	0
Anthracene (**23**)	178	0.71	1.00	0	0
1,2-Diphenylethane (**24**)	182	0.83	0.86	0	0
Pyrene (**25**)	202	0.62	1.00	0	0
Chrysene (**26**)	228	0.67	1.00	0	0
Triphenylene (**27**)	228	0.67	1.00	0	0
p-Terphenyl (**28**)	230	0.78	1.00	0	0
Perylene (**29**)	252	0.60	1.00	0	0
2,2'-Binaphthyl (**30**)	254	0.70	1.00	0	0
1,1'-Binaphthyl (**31**)	254	0.70	1.00	0	0
1,3,6,8-Tetraethylpyrene (**32**)	314	0.63	0.67	0	0
9,10-Diphenylanthracene (**33**)	330	0.65	1.00	0	0
1-(2-Naphthalenylmethyl)-pyrene (**2**)	342	0.69	0.96	0	0
1,2,3,4-Tetraphenyl-1,3-cyclo-pentadiene (**34**)	370	0.83	0.83	0	0
2,3,4,5,6-Pentaphenyltoluene (**35**)	472	0.69	0.97	0	0
Polystyrene (**36a**)	615	1.00	0.75	0	0
Polystyrene (**36b**)	1140	1.00	0.75	0	0
Polystyrene (**36c**)	2500	1.00	0.75	0	0
Poly(2-vinylnaphthalene) (**37a**)	570	0.80	0.83	0	0
Poly(2-vinylnaphthalene) (**37b**)	780	0.80	0.83	0	0
Poly(2-vinylnaphthalene) (**37c**)	850	0.80	0.83	0	0

Table 7 cont.

Compound	MW (g/mol)	H_{aru}/C_{ar} [a]	F_a [b]	% O or N (total)	% O or N (as OH or NH)
Poly(2-vinylnaphthalene) (**37d**)	1150	0.80	0.83	0	0
Poly(2-vinylnaphthalene) (**37e**)	1450	0.80	0.83	0	0
Quinoline (**38**)	129	0.78	1.00	10.9	0
5,6,7,8-Tetrahydroquinoline (**39**)	133	0.60	0.56	10.5	0
2-Methoxynaphthalene (**40**)	158	0.80	0.91	10.0	0
Dibenzofuran (**41**)	168	0.67	1.00	0	0
Dibenzothiophene (**42**)	184	0.67	1.00	0	0
2-Acetoxynaphthalene (**43**)	186	0.80	0.83	17.1	0
1,5-Dinitronaphthalene (**44**)	218	0.80	1.00	0	0
2-Phenoxynaphthalene (**45**)	220	0.80	1.00	7.3	0
4-Acetoxydiphenylmethane (**46**)	226	1.00	0.80	14.2	0
1-Methoxypyrene (**47**)	232	0.63	0.94	6.9	0
2,7-Diacetoxynaphthalene (**48**)	244	0.80	0.71	26.2	0
4,4'-Diacetoxybiphenyl (**49**)	270	0.83	0.75	23.7	0
4,4'-Diacetoxydiphenylmethane (**50**)	284	1.00	0.71	22.5	0
1,9-Diphenyl-1,3,6,8-nonatetraen-5-one (**51**)	286	1.00	0.57	5.5	0
1-Phenoxypyrene (**52**)	294	0.63	1.00	5.4	0
Pentaphenyl ether (**53**)	446	1.00	1.00	14.3	0
m-Cresol (**54**)	108	1.00	0.86	14.3	14.3
1,2,3,4-Tetrahydroquinoline (**55**)	133	0.60	0.56	10.5	10.5
2-Hydroxynaphthalene (**56**)	144	0.80	1.00	11.1	11.1
8-Hydroxyquinoline (**57**)	145	0.78	1.00	20.7	11.0
5,6,7,8-Tetrahydro-1-naphthol (**58**)	148	0.67	0.60	10.8	10.8
2,7-Dihydroxynaphthalene (**59**)	160	0.80	1.00	20.0	20.0
Carbazole (**60**)	167	0.67	1.00	8.4	8.4
2-Hydroxycarbazole (**61**)	183	0.67	1.00	16.4	16.4
2-Hydroxydiphenylmethane (**62**)	184	1.00	0.92	8.7	8.7
4,4'-Dihydroxybiphenyl (**63**)	186	0.83	1.00	17.2	17.2
9-Hydroxyphenanthrene (**64**)	194	0.71	1.00	8.2	8.2
4,4'-Dihydroxydiphenylmethane (**65**)	200	1.00	0.92	16.0	16.0
1-Hydroxypyrene (**66**)	218	0.63	1.00	7.7	7.7
1,1,2-Triphenylethanol (**67**)	274	1.00	0.90	5.8	5.8

Table 7 cont.

Compound	MW (g/mol)	H_{aru}/C_{ar} [a]	F_a [b]	% O or N (total)	% O or N (as OH or NH)
1,4-Bis(9-phenanthrenylhydroxy-methyl)naphthalene(**5**)	540	0.74	0.95	5.9	5.9

[a]Degree of aromatic condensation
[b]Fraction of aromatic carbons

Table 8. Viscosity data for unseparated preasphaltene samples in THF.

Sample	MW[a]	Intrinsic viscosity
PA-80	1119	3.95
PA-89	940	3.88
PA-90	709	3.73
PA-93	824	3.66
PA-98	931	3.61
PA-99	1126	4.15

[a]Determined by GPC analysis with polystyrene calibration standards.

Table 9. Viscosity data for model compounds and separated preasphaltene samples in THF.[a]

Sample	MW[b]	Intrinsic viscosity	Molar volume[c]	Molar volume[d]	# of associated THF molecules
Benzene (**10**)	78	0.24	91	99	0.1
Toluene (**11**)	92	0.32	103	115	0.2
Naphthalene (**12**)	128	1.43	119	192	1.0
Tetralin (**13**)	132	1.15	134	195	0.9
Decalin (**14**)	138	1.02	153	212	0.8
1-Methylnaphthalene (**15**)	142	1.22	141	214	1.0
Biphenyl (**16**)	154	1.54	144	239	1.3
2-Ethylnaphthalene (**17**)	156	1.30	156	239	1.2
2,6-Dimethylnaphthalene (**18**)	156	1.30	153	235	1.1
2,3-Dimethylnaphthalene (**19**)	156	1.42	154	244	1.3
Fluorene (**20**)	166	1.64	158	267	1.5
Diphenylmethane (**21**)	168	1.40	164	259	1.3
Phenanthrene (**22**)	178	1.94	144	283	1.9
Anthracene (**23**)	178	1.93	158	298	1.9
1,2-Diphenylethane (**24**)	182	1.58	180	298	1.6
Pyrene (**25**)	202	2.19	166	346	2.5
Chrysene (**26**)	228	2.34	167	381	2.9
Triphenylene (**27**)	228	2.16	182	377	2.7
p-Terphenyl (**28**)	230	2.19	217	418	2.8
Perylene (**29**)	252	2.64	103	368	3.7
2,2'-Binaphthyl (**30**)	254	2.40	219	459	3.3
1,1'-Binaphthyl (**31**)	254	2.30	211	442	3.2
1,3,6,8-Tetraethylpyrene (**32**)	314	1.93	287	534	3.5.
9,10-Diphenylanthracene (**33**)	330	2.56	267	600	4.6
1-(2-Naphthalenylmethyl)-pyrene (**2**)	342	2.91	254	648	5.4
1,2,3,4-Tetraphenyl-1,3-cyclo-pentadiene (**34**)	370	2.55	312	689	5.2
2,3,4,5,6-Pentaphenyltoluene (**35**)	472	2.70	383	900	7.2
Polystyrene (**36a**)	615	2.68	646	1309	9.3
Polystyrene (**36b**)	1140	3.45	1032	2650	22.4
Polystyrene (**36c**)	2500	4.90	2500	7400	69.0
Poly(2-vinylnaphthalene) (**37a**)	570	3.20	517	1230	9.8
Poly(2-vinylnaphthalene) (**37b**)	780	3.12	684	1700	14.0
Poly(2-vinylnaphthalene) (**37c**)	850	3.88	742	2075	18.4
Poly(2-vinylnaphthalene) (**37d**)	1150	4.00		2350	25.1

Table 9 cont.

Sample	MW[b]	Intrinsic viscosity	Molar volume[c]	Molar volume[d]	# of associated THF molecules
Poly(2-vinylnaphthalene) (**37e**)	1450	3.50	1385	3500	29.5
Quinoline (**38**)	129	1.51	114	192	1.1
5,6,7,8-Tetrahydroquinoline (**39**)	133	1.20	126	190	0.9
2-Methoxynaphthalene (**40**)	158	1.60	137	238	1.4
Dibenzofuran (**41**)	168	1.80	145	266	1.7
Dibenzothiophene (**42**)	184	1.99	147	293	2.0
2-Acetoxynaphthalene (**43**)	186	1.61	170	292	1.7
1,5-Dinitronaphthalene (**44**)	218	1.71	204	370	2.3
2-Phenoxynaphthalene (**45**)	220	1.92	184	357	2.4
4-Acetoxydiphenylmethane (**46**)	226	1.80	204	368	2.3
1-Methoxypyrene (**47**)	232	2.13	181	380	2.7
2,7-Diacetoxynaphthalene (**48**)	244	2.11	192	400	2.8
4,4'-Diacetoxybiphenyl (**49**)	270	2.35	215	473	3.4
4,4'-Diacetoxydiphenylmethane (**50**)	284	2.25	238	495	3.5
1,9-Diphenyl-1,3,6,8-nonatetraen-5-one (**51**)	286	2.95	224	565	4.7
1-Phenoxypyrene (**52**)	294	2.26	225	494	3.7
Pentaphenyl ether (**53**)	446	2.77	396	888	6.8
m-Cresol (**54**)	108	1.58	100	183	1.2
1,2,3,4-Tetrahydroquinoline (**55**)	133	1.81	130	225	1.3
2-Hydroxynaphthalene (**56**)	144	2.58	112	260	2.0
8-Hydroxyquinoline (**57**)	145	1.81	122	230	1.5
5,6,7,8-Tetrahydro-1-naphthol (**58**)	148	2.25	131	266	1.9
2,7-Dihydroxynaphthalene (**59**)	160	4.11	102	360	3.6
Carbazole (**60**)	167	2.13	142	290	2.0
2-Hydroxycarbazole (**61**)	183	3.31	131	374	3.4
2-Hydroxydiphenylmethane (**62**)	184	2.44	168	352	2.6
4,4'-Dihydroxybiphenyl (**63**)	186	4.22	121	435	4.3
9-Hydroxyphenanthrene (**64**)	194	2.81	158	381	3.0
4,4'-Dihydroxydiphenylmethane (**65**)	200	3.81	170	470	4.1
1-Hydroxypyrene (**66**)	218	2.88	151	405	3.5
1,1,2-Triphenylethanol (**67**)	274	2.34	231	495	3.6
1,4-Bis(9-phenanthrenylhydroxy-methyl)naphthalene (**5**)	540	3.60	403	1186	10.9

Table 9 cont.

Sample	MW[b]	Intrinsic viscosity	Molar volume[c]	Molar volume[d]	# of associated THF molecules
A-41-1A[e]	1250	4.37	906	3070	30.0
A-41-2A	740	3.45	541	1568	14.2
A-41-3A	640	3.31	502	1344	11.7
A-41-4A	470	2.99	380	937	7.7
A-41-5A	350	2.48	278	627	4.8
PA-41-1A	2850	5.11	2828	8611	80.0
PA-41-2A	1420	3.66	1062	3090	28.7
PA-41-3A	740	3.26	582	1540	13.2
PA-41-4A	430	2.75	341	810	6.5
PA-41-5A	290	2.85	226	556	4.6
PA-80-N (total)	675	3.95	600	1820	16.8
PA-80-1N	1202	7.53	1073	4693	50.0
PA-80-2N	470	2.90	423	1002	8.0
PA-80-3N	375	1.85	422	748	4.7
PA-80-4N	272	1.88	250	468	3.1
PA-80-5N	247	1.39	270	410	2.0
PA-80-6N	150	2.70	155	345	2.6
PA-80-A (total)	858	3.70	963	2315	19.1
PA-80-1A	1077	5.31	973	3311	32.4
PA-80-2A	605	2.58	570	1245	9.3
PA-80-3A	520	2.38	512	1070	7.7
PA-80-4A	313	1.55	324	560	3.2
PA-80-5A	265	.055	331	441	1.5
PA-80-6A	187	1.98	238	410	2.4
PA-99-N (total)	762	4.15	695	1950	17.5
PA-99-1N	1382	5.35	1331	4195	40.0
PA-99-2N	584	4.13	473	1424	13.1
PA-99-3N	443	3.84	405	1077	9.3
PA-99-4N	337	3.64	330	824	6.8
PA-99-5N	277	3.14	263	615	4.9
PA-99-6N	189	3.00	192	437	3.4
PA-99-A (total)	936	3.72	864	2291	19.8
PA-99-1A	1080	4.43	1066	3074	28.2
PA-99-2A	614	3.46	588	1436	11.8
PA-99-3A	478	2.92	457	1015	7.7
PA-99-4A	370	2.76	359	764	5.6

Table 9 cont.

Sample	MW[b]	Intrinsic viscosity	Molar volume[c]	Molar volume[d]	# of associated THF molecules
PA-99-5A	260	2.54	266	530	3.7
PA-99-6A	228	2.74	251	503	3.5

[a]Molecular weight in g/mole. Values for pure model compounds are calculated from atomic masses; values for polymers were determined from NMR measurements; values for preasphaltene samples were determined from VPO measurements.

[b]Measured at room temperature.

[c]Calculated from density measurements.

[d]Calculated from viscosity measurements.

[e]Example abbreviations: Asphaltene from run 41, 1st fraction from preparative GPC separation, Acetylated; Preasphaltene from run 80, Native(nonacetylated)

Table 10. Effect of temperature on intrinsic viscosity.[a]

Sample	Temperature (°C)	Intrinsic viscosity	Molar volume[b]	Molar volume[c]	# of associated THF molecules
12	20	1.43	119	192	1.0
12	40	1.03	126	182	0.7
12	50	0.99	122	175	0.7
14	20	1.02	153	212	0.8
14	40	0.77	162	208	0.6
14	50	0.86	158	206	0.7
36c	20	4.90	2500	7400	69.0
36c	40	3.84	2400	6500	55.0
36c	50	4.07	2415	6350	54.0
43	20	1.61	170	292	1.7
43	40	1.31	170	270	1.4
43	50	1.38	160	265	1.4
56	20	2.58	112	260	2.0
56	40	1.89	125	240	1.6
56	50	2.00	114	232	1.6
59	20	4.11	102	360	3.6
59	40	3.10	115	321	2.8
59	50	3.25	108	310	2.8

[a]Measured in THF.
[b]Calculated from density measurements.
[c]Calculated from viscosity measurements.

Table 11. Effect of solvent on intrinsic viscosity of model compounds.

Sample	Solvent	Intrinsic viscosity	Molar volume[a]	Molar volume[b]	# of associated solvent molecules
13	Methanol	0.94	134	184	1.5
13	THF	1.15	134	195	0.9
13	Toluene	0.99	143	189	0.5
15	Methanol	1.18	132	196	1.9
15	THF	1.22	141	219	1.0
15	Toluene	0.99	148	205	0.6
38	Methanol	1.39	110	178	2.1
38	THF	1.51	114	192	1.1
38	Toluene	1.28	121	186	0.7
41	Methanol	1.62	131	232	3.1
41	THF	1.80	145	266	1.7
41	Toluene	1.34	154	241	0.9
42	Methanol	2.16	135	290	4.7
42	THF	1.99	147	293	2.0
42	Toluene	1.59	152	265	1.2
55	Methanol	1.28	123	190	2.0
55	THF	1.81	130	225	1.3
55	Toluene	1.53	128	205	0.8
56	THF	2.58	112	260	2.0
56	Quinoline	2.47	118	250	1.0
59	THF	4.11	102	360	3.6
59	Quinoline	5.82	115	423	2.4

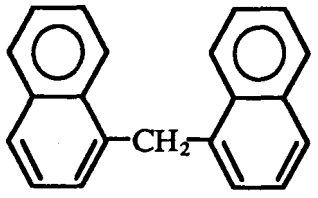
[a]Calculated from density measurements.
[b]Calculated from viscosity measurements.

Table 12. Molecular weights of model compounds by GPC measurements.

Model compound	MW actual	Intrinsic viscosity	Retention volume (ml)	MW by GPC[a]	No. of assoc. THF[b]
12	128	1.43	39.3	130	0
13	132	1.15	39.8	115	0
18	156	1.30	36.5	215	0.8
22	178	1.94	38.9	140	-
25	202	2.19	39.8	115	-
26	228	2.34	37.9	167	-
27	228	2.16	38.3	155	-
29	252	2.64	39.9	113	-
30	254	2.40	36.4	215	-
31	254	2.30	37.2	190	-
32	314	1.93	33.9	335	0.3
34	370	2.55	32.9	405	0.5
35	472	2.70	31.1	555	1.1
45	220	1.92	36.2	225	0
51	286	2.95	31.6	515	3.2
52	294	2.26	36.5	215	-
56	144	2.58	35.3	262	1.6
59	160	4.11	32.8	410	3.5

[a]Based on polystyrene calibration standards.
[b]Based on difference between observed molecular weight and actual molecular weight.

VII. FIGURES



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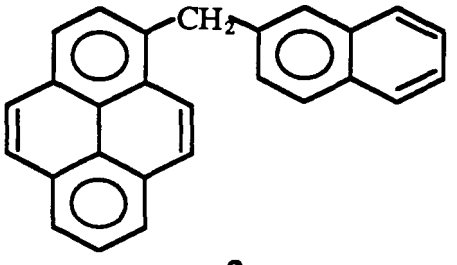

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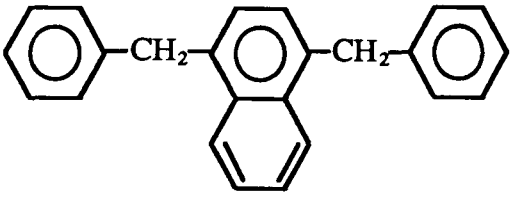

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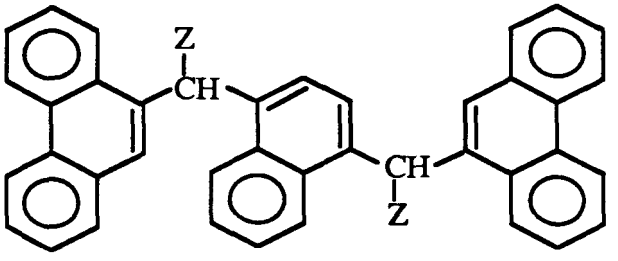

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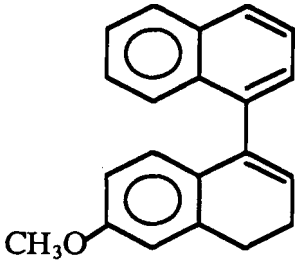
5 Z = OH



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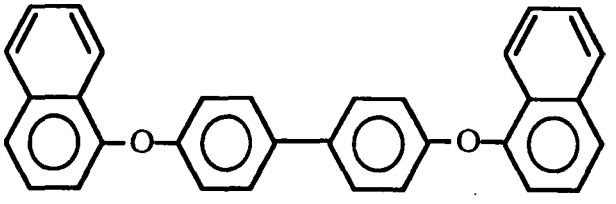

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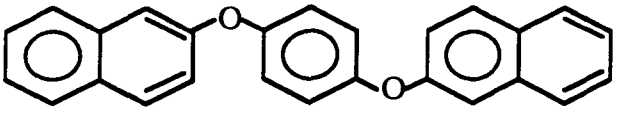

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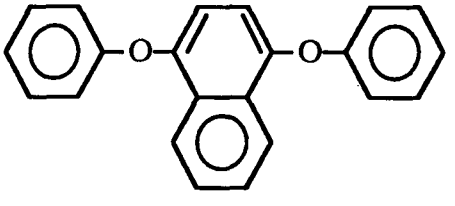


9

Figure 1. Model compounds employed in the solubility study.

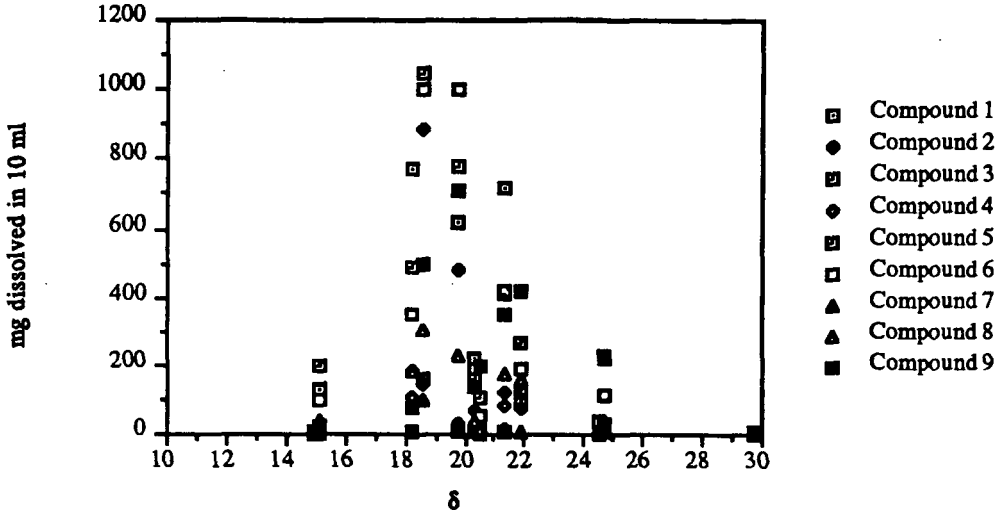


Figure 2. Plot of solubility of model compounds vs. Hildebrand solubility parameter (δ) of solvents.

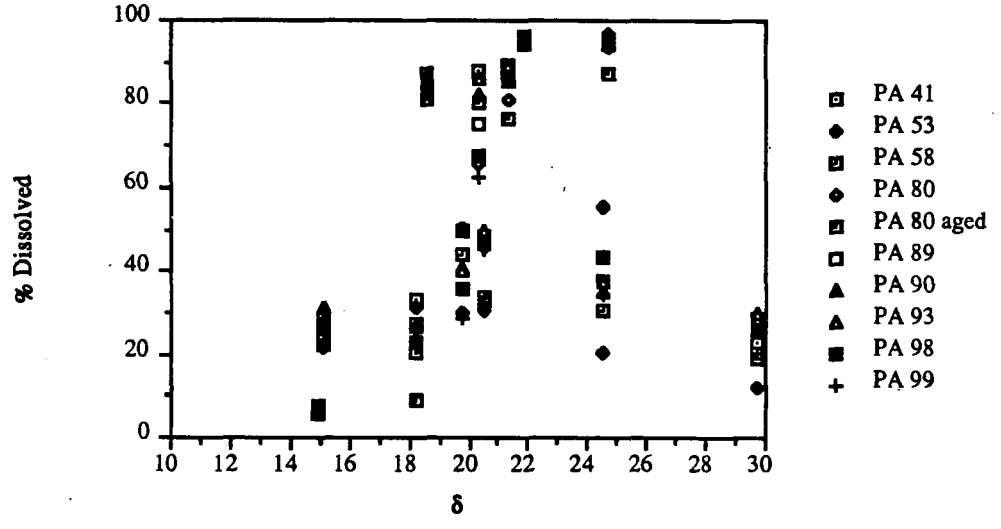


Figure 3. Plot of dissolvability of preasphaltene samples vs. Hildebrand solubility parameter (δ) of solvents.

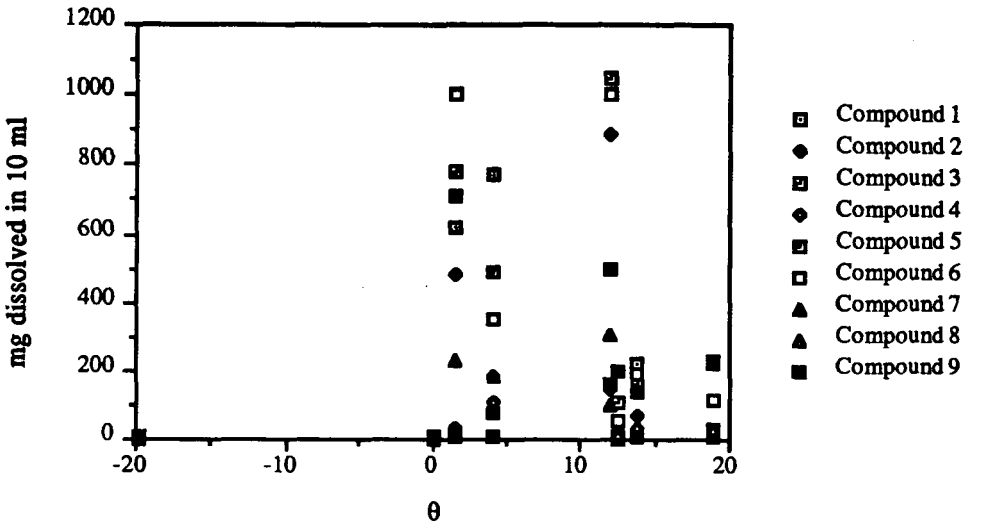


Figure 4. Plot of model compound solubility vs. net hydrogen-bonding index (θ) of solvents.

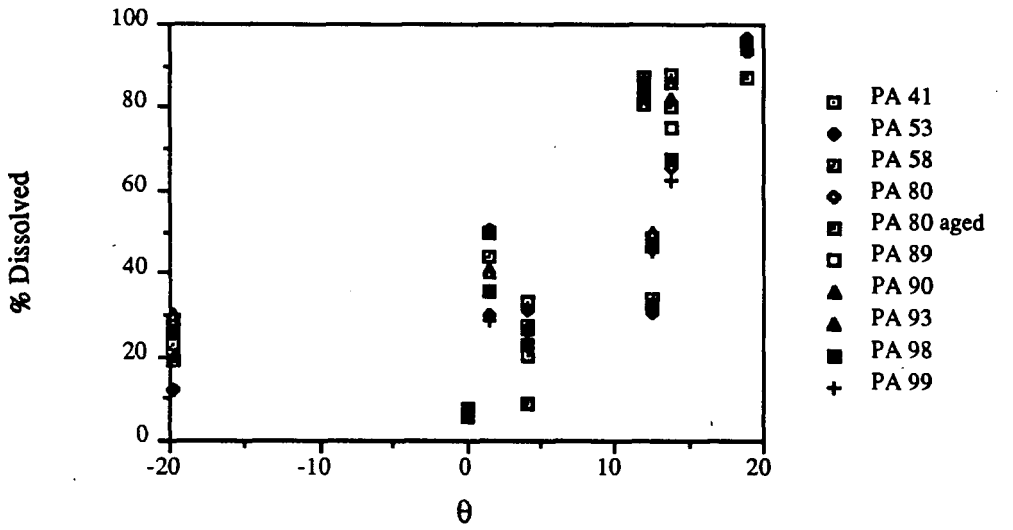


Figure 5. Plot of PA dissolvability vs. net hydrogen-bonding index (θ) of solvents.

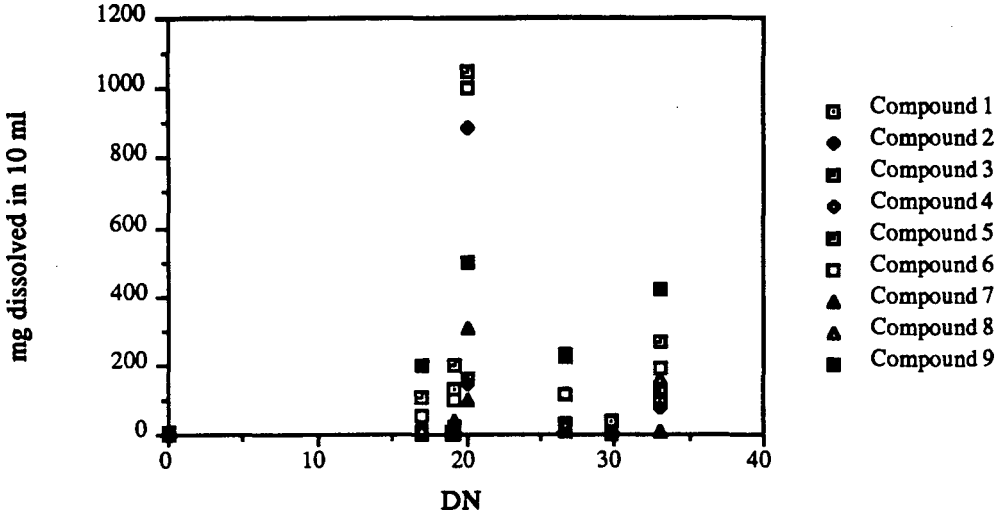


Figure 6. Plots of model compound solubilities vs. DN values of solvents.

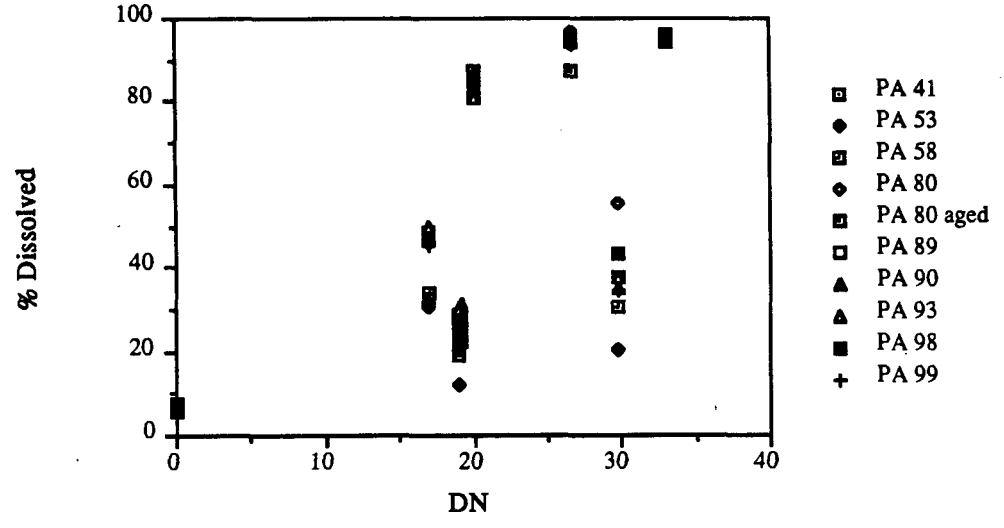


Figure 7. Plots of PA dissolvability vs. DN of solvents.

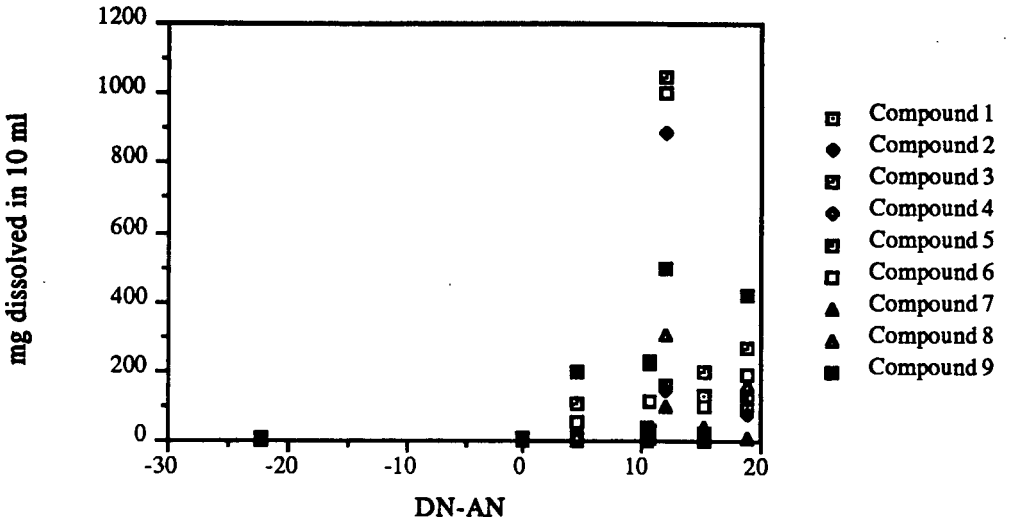


Figure 8. Plot of solubilities of model compounds vs. donor number minus acceptor number values of solvents.

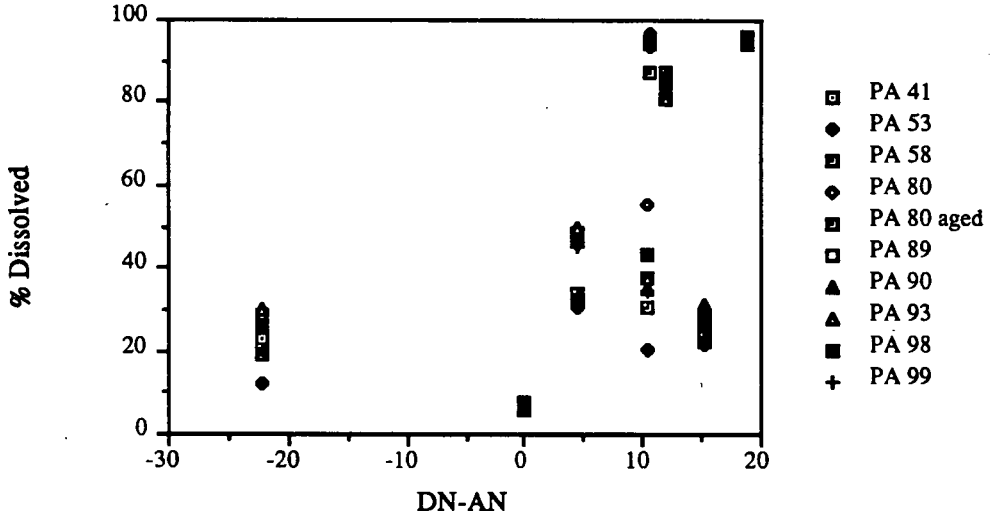


Figure 9. Plots of dissolvabilities of preasphaltene samples vs. donor number minus acceptor number values of solvents.

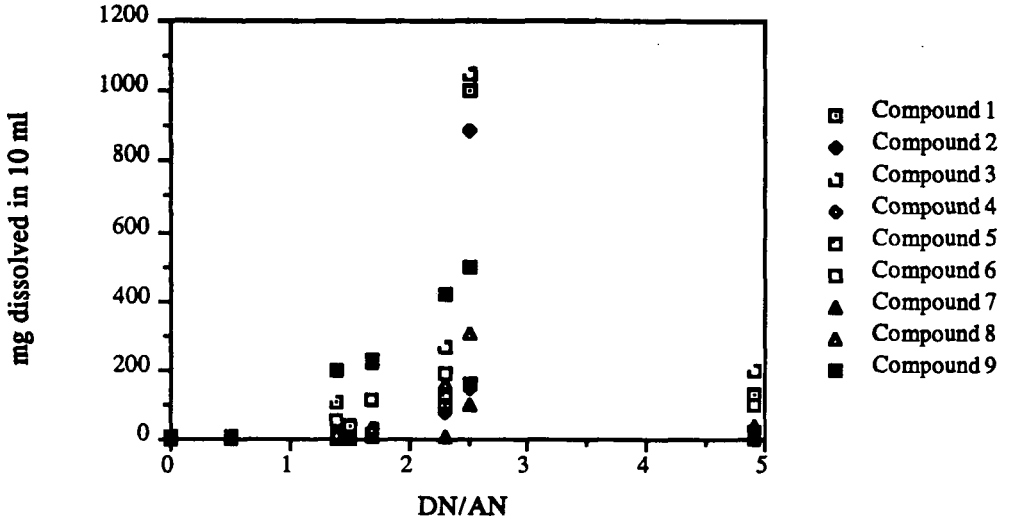


Figure 10. Plot of model compound solubility vs. DN/AN values of solvents.

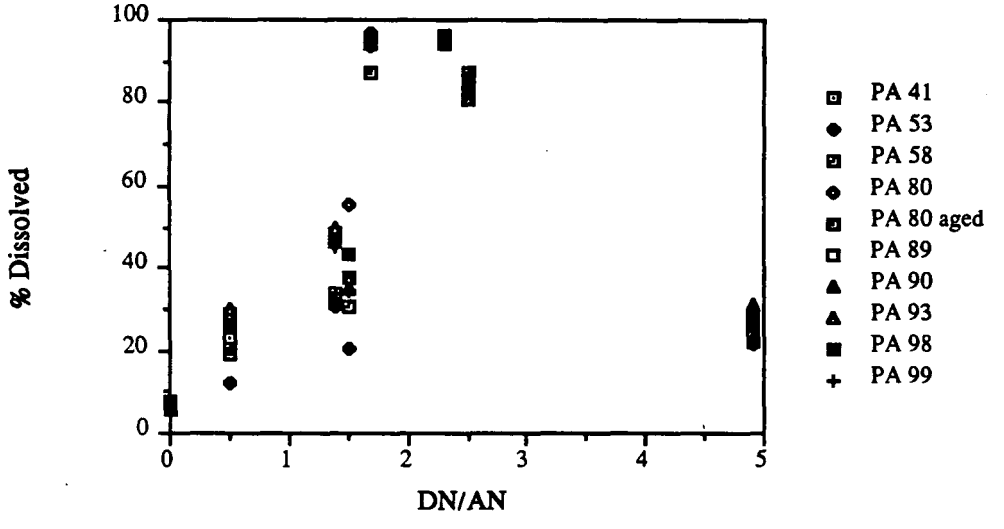


Figure 11. Plots of preasphaltene dissolvability vs. DN/AN values of solvents.

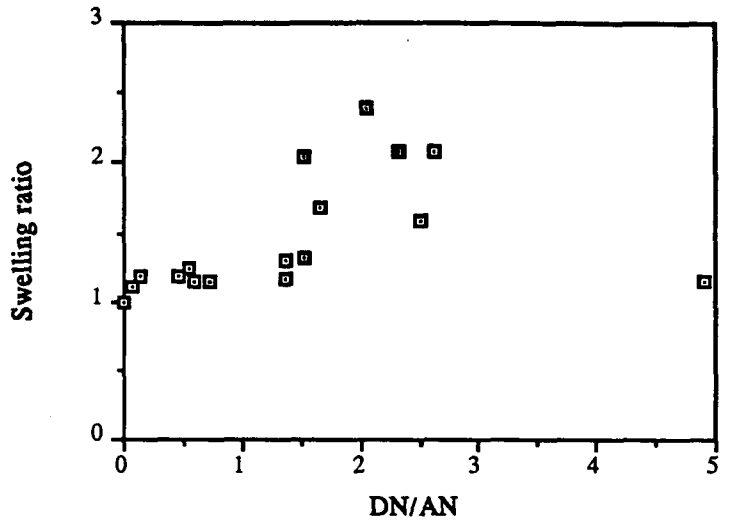


Figure 12. Swelling of coal as a function of DN/AN values of solvents. Data taken from reference 11.

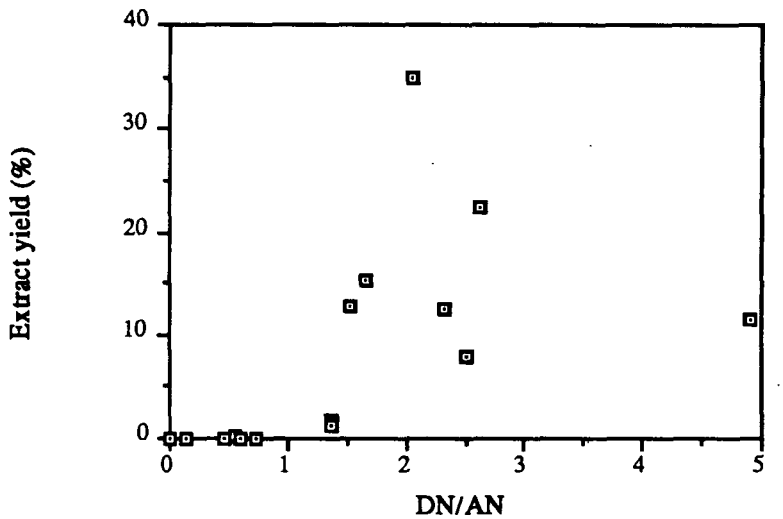


Figure 13. Extractability of coal vs. DN/AN values of solvents. Data taken from reference 8.

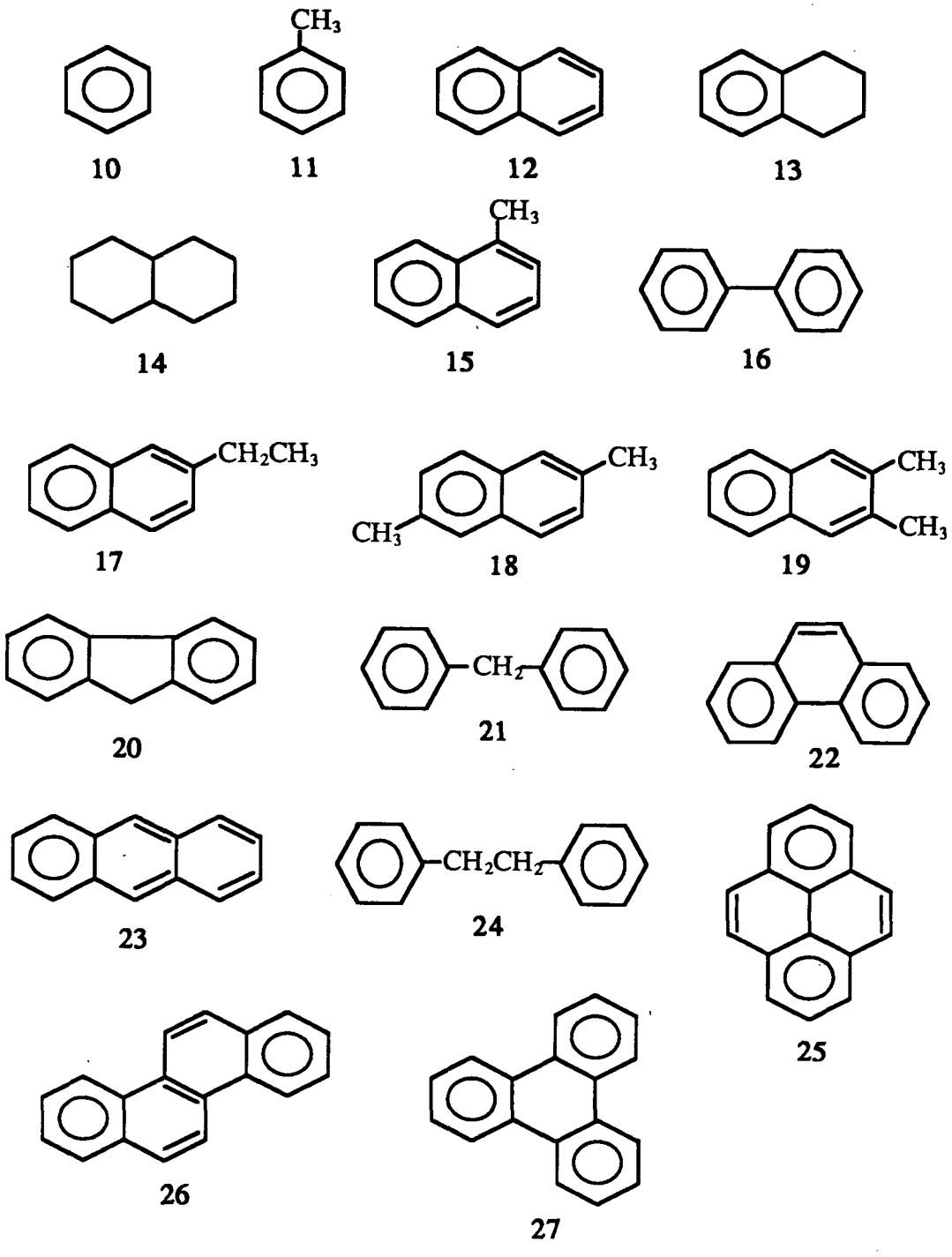


Figure 14. Model compounds employed in viscosity study.

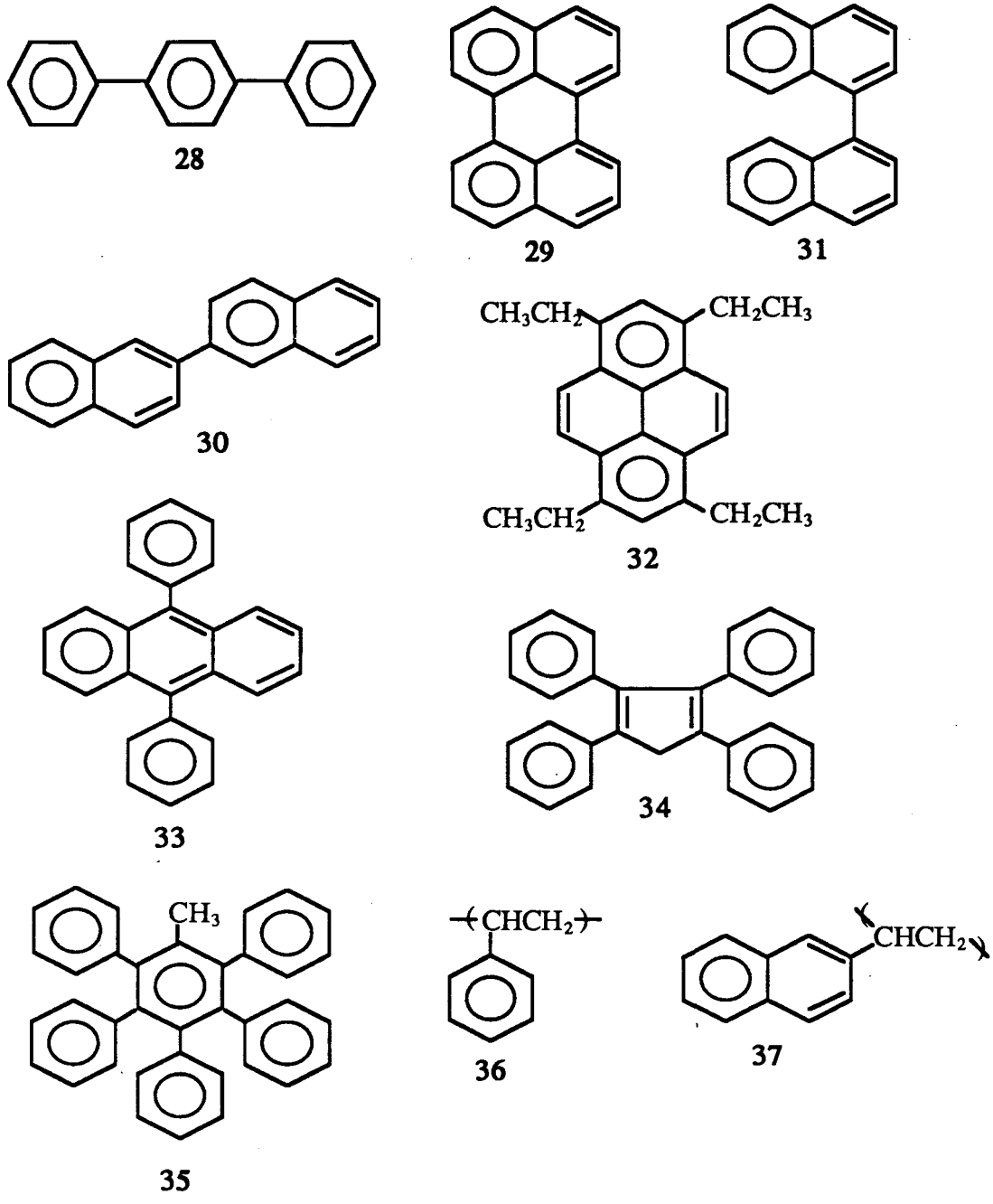
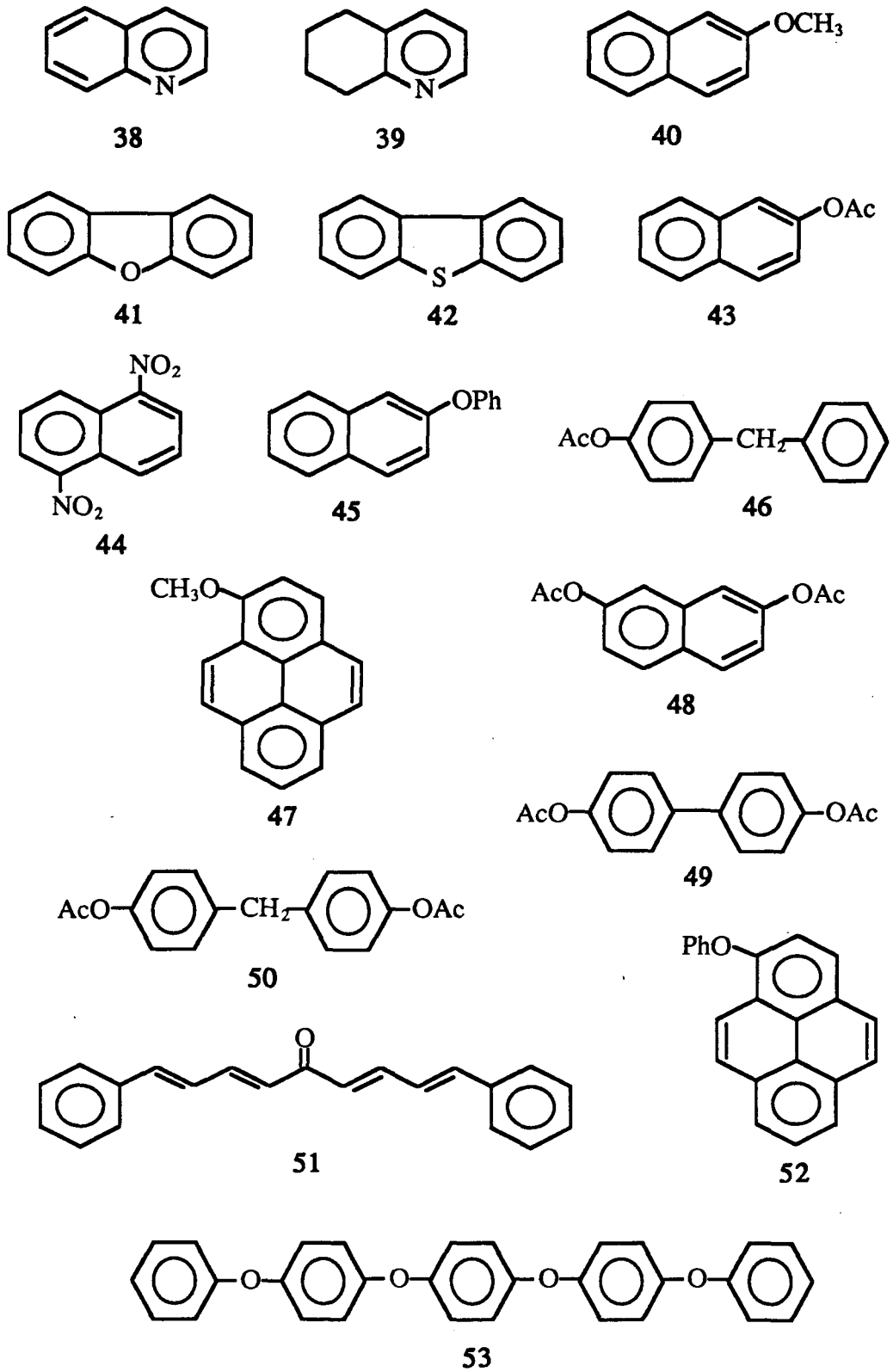


Figure 14 cont.



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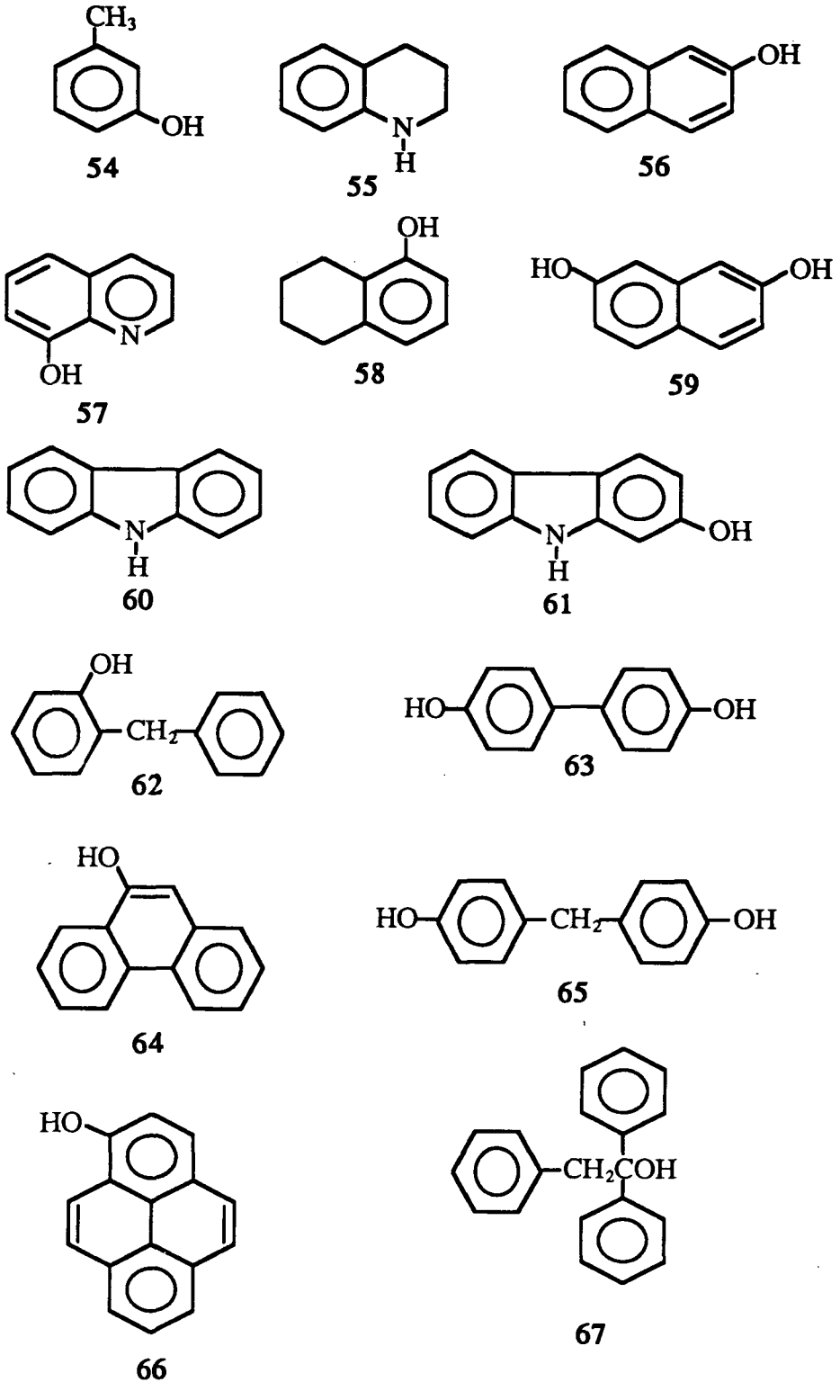

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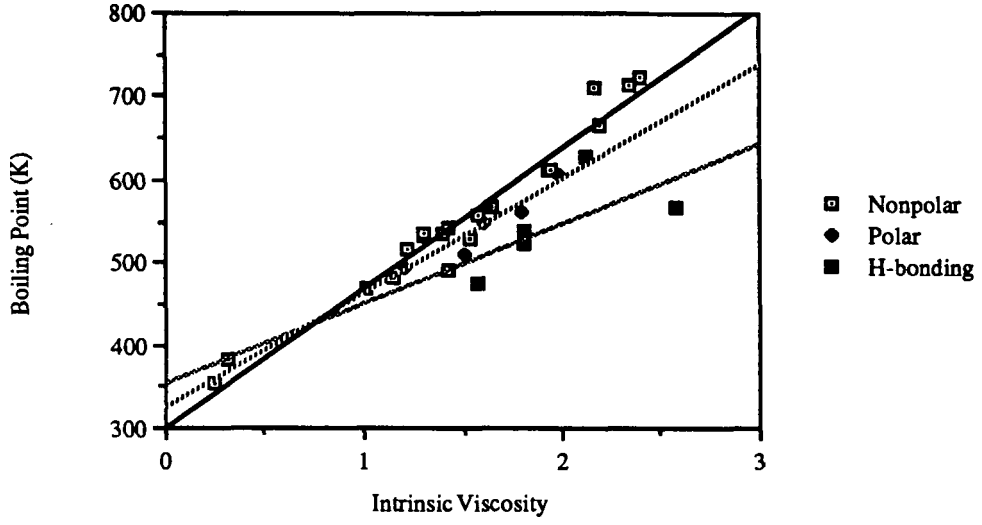

Figure 15. Intrinsic viscosity versus boiling point of model compounds. The lines in the graph are least-squares lines and the equations for the lines are given below.

——— ▫ y = 302.0234 + 168.1822x R = 0.98

····· ◆ y = 353.3498 + 97.7044x R = 0.67

——— ■ y = 324.5464 + 137.8704x R = 0.92

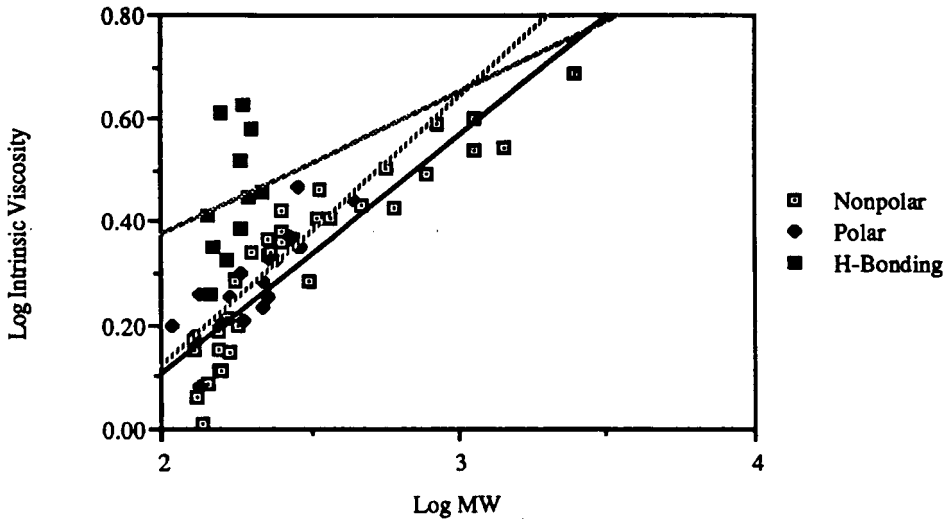

Figure 16. Plot of log of intrinsic viscosity versus log of molecular weight of model compounds. The lines in the graph are least-squares lines and the equations for the lines are given below.

——— ▫ y = - 0.8031 + 0.4571x R = 0.90

····· ● y = - 0.9119 + 0.5171x R = 0.84

——— ■ y = - 0.1742 + 0.2749x R = 0.19

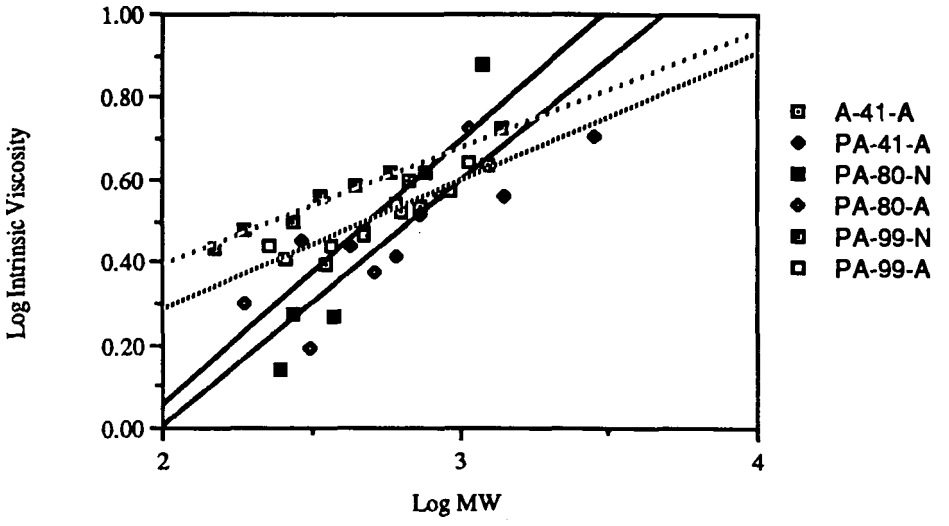

Figure 17. Plot of log intrinsic viscosity versus log molecular weight of coal-derived liquids. The lines in the graph are least-squares lines and the equations for the lines are given below.

- ■ y = - 1.2234 + 0.6396x R = 0.78
- ◆ y = - 1.1678 + 0.59x R = 0.86
- □ y = - 0.1762 + 0.2845x R = 0.98
- □ y = - 0.3455 + 0.3149x R = 0.94