The action of tetramethylurea and hexamethylphosphoramide blended with other solvents on the dissolution of coal
by Timothy Lee Ward

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering
Montana State University

Abstract:
Tetramethylurea (TMU) and hexamethylphosphoramide (HMPA) were blended with a number of other solvents to determine the solvent action and effectiveness of the blends on extraction of coal as compared with that of unblended TMU/HMPA (TMU and HMPA In a 50/50 mixture).

Dissolution to more than 41% was observed using 33% tetralin blended with 67% TMU/HMPA on Kittaning coal at 320°F, compared to a maximum of 40.7% dissolution observed with unblended TMU/HMPA.

It was found that aromatic/hydroaromatic solvents such as tetralin, napthalene, and l-me-napthaIene, which are relatively inert toward coal at temperatures below 350°F, could be blended up to 80% by volume with TMU/HMPA without significantly reducing the ultimate dissolving power below that of unblended TMU/HMPA.

Use of 80% decalin and 80% limonene blended with TMU/HMPA resulted in substantially lower extraction than unblended TMU/HMPA. Isopropyl alcohol, when blended with TMU/HMPA in amounts greater than 10%, was found to result in a substantial decrease in dissolving ability.

The apparent dissolution rate for a blend of 80% tetralin and 20% TMU/HMPA is lower than for unblended TMU/HMPA, however the ultimate dissolution attained is approximately equal. At 320°F much of the ultimately attainable dissolution with TMU/HMPA and 80% tetralin blended with TMU/HMPA occurs within 5 minutes, with slow or even retrogressive dissolution after that.

Solubility parameters were considered and found to be helpful in correlating dissolution effectiveness of solvent blends tested.

TMU and HMPA are retained in the extraction residue in the amount of, typically, 5-15% by weight and tetralin retention of 8-10% was indicated for a pure tetralin extraction at 320°F. Relation of solvent retention to extraction variables was discussed.

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Timothy Lee Ward

This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

Feb 15/84 — Date

John T. Sears — Chairperson, Graduate Committee

Approved for the Major Department

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ABSTRACT

Tetramethylurea (TMU) and hexamethylphosphoramide (HMPA) were blended with a number of other solvents to determine the solvent action and effectiveness of the blends on extraction of coal as compared with that of unblended TMU/HMPA (TMU and HMPA in a 50/50 mixture).

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TMU and HMPA are retained in the extraction residue in the amount of, typically, 5-15% by weight and tetralin retention of 8-10% was indicated for a pure tetralin extraction at 320°F. Relation of solvent retention to extraction variables was discussed.

INTRODUCTION

Since the Arab oil embargo in 1973 demonstrated the insecurity of petroleum supplies, increased attention has been directed toward alternate sources of energy. Of the alternate sources, coal is the most promising for the near future because of the magnitude and distribution of reserves, the level of utilization technology that already exists, and its flexibility in use. Coal can be combusted directly, or converted to a gaseous or liquid product which, in turn, may be used as an energy source or chemical feedstock.

Since Bergius first demonstrated the use of solvents and hydrogenation to convert coal to a liquid product in 1913, a number of industrial coal liquefaction processes have been developed and demonstrated. There are several good summaries of current coal liquefaction technology [1,2]. These industrial processes are all thermal processes wherein the coal is primarily thermally broken down and aromatic/hydroaromatic type solvents are used to stabilize the product fragments, primarily, it is thought, by hydrogen transfer and shuttling.

A variety of organic solvents are known to swell coal

and dissolve portions of coal at temperatures well below its thermal breakdown point [3]. This solvent action has been a valuable technique for studying the structure and chemistry of coal. Low temperature extraction processes have the advantage for research that reaction rates and product species can be observed without the masking effects of severe conditions. Low temperature processes might also be able to substantially avoid many of the problems that confront current high temperature industrial liquefaction technologies, eg. lower thermal efficiency, hydrogen utilization efficiency, solids separation, high temperature and pressure equipment, etc. Tetramethylurea (TMU) and hexamethylphosphoramide (HMPA), the solvents of interest in this work, are two examples of a class of solvents that show promise as coal solvents at low temperatures and pressure [4].

TMU and HMPA

Tetramethylurea (TMU) and hexamethylphosphoramide (HMPA) are both members of a class of solvents called dipolar aprotic solvents. Dipolar aprotic solvents are characterized by the ability to accept, but not donate, hydrogen or hydrogen bonds, moderate to high dielectric constants (20-50) and dipole moments, and often a wide liquid-state

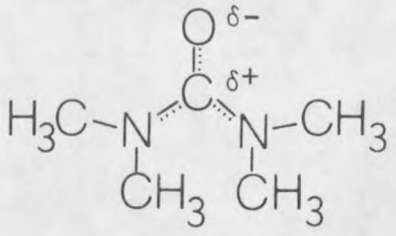
temperature range. Other examples of dipolar aprotic solvents are dimethylformamide, dimethylacetamide, and dimethylsulfoxide [5,6].

TMU and HMPA have many similar physical and chemical characteristics. Their structures, shown in Figure 1, both have $-N(CH_3)_2$ groups symmetrically oriented about a central atom which is bonded to an oxygen atom. For both molecules, the oxygen atom carries a negative charge density and a positive charge density is delocalized over the central atom and the nitrogen atoms. Also, in both compounds the N atoms and the central atom, and hence the region of positive charge, are effectively shielded by the methyl groups; but the O atom is exposed and available as an electron donor or hydrogen acceptor [7,8].

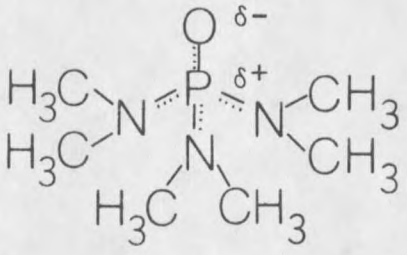
The physical properties of TMU and HMPA, given in Table 1, show characteristics typical of dipolar aprotic solvents. Their boiling points and viscosities make them logical choices for low to moderate temperature experiments at low pressure.

As would be expected from their similar properties, TMU and HMPA have several similarities in their chemistry. The important relevant similarities are [7,8]:

1. Both are miscible in a variety of organic, inorganic,polar, and non-polar solutions.
2. Both act as hydrogen bond acceptors, but not as



TMU



HMPA

Figure 1. Structure of TMU and HMPA.

hydrogen bond donors or hydrogen donors.

3. Both are good electron donors.
4. Both solvate cations well, but not anions.
5. Both promote and accelerate reactions that involve anion reactivity, eg. SN2 and E2 reactions.
6. Both are relatively stable to nucleophilic attack.
7. Both are poor electron acceptors and are relatively unstable as radical anions.

Table 1. Physical Constants of TMU and HMPA

	TMU	HMPA
M.P.(C)	-1.2 [7]	7.20 [8]
B.P. (C)	177/760 mm [15]	235/760 mm [8]
Density (20°C/4°C)	0.9687 [7]	1.0253 [8]
Dielectric Const.	23.1 [7]	30/20 C [8]
Dipole Moment	3.37 [7]	4.31-5.37 [8]
M.W.	116.16	179.20

There are also several notable differences in the action of TMU and HMPA, though they are primarily differences of degree. The electron density on the oxygen atom of HMPA is considerably higher than TMU, hence it is significantly stronger as a hydrogen bond acceptor,

electron donor, cation solvator and anion reaction promoter. HMPA is also more stable toward nucleophilic attack due to more delocalization of the positive charge and is somewhat more stable as an electron acceptor [7,8].

HMPA, probably because of its unusually high electron donating ability, is known to be very apt to form coordinate complexes and adducts with inorganic and organic species [8,9]. The same behavior may be true with TMU, but is considerably less dramatic. Of note also is the larger molecular size of HMPA which, Gutmann pointed out [9], could give rise to interesting stereochemistry in a highly coordinated solvent-solute complex.

Some carboxylic acids and alcohols have been observed to give stable adducts with HMPA at 150°C [10]. Among the compounds which formed stable adducts were phthalic, isophthalic, and terephthalic acid, benzyl alcohol, hydroquinone, benzidine, ethylene glycol, and aniline. HMPA was also observed to form adducts with unsaturated hydrocarbons, eg. 1,3 butadiene and styrene, though the structure is not certain [10].

A variety of carboxylic acids will cause amide displacement on HMPA at 180°C-200°C, as follows [11,12]:

$$OP(N(CH_3)_2)_3 + 3\ RCO_2H = OP(OH)_3 + 3\ RCO\text{-}N(CH_3)$$

The chemistry of HMPA has been covered in some detail

by Normant [8], and that of TMU by Luttringhaus and Dirksen [7]. The reader is referred to those sources for further discussion of the chemistry of these compounds.

The solubility characteristics of TMU for a variety of materials were reported by Luttringhaus and Dirksen [7], and later reviewed by Barker [13]. The reported solubilities for organic compounds and macromolecules in TMU are tabulated in Appendix D and general observations discussed below.

The dissolving power for hydrocarbons can probably be credited to the methyl group shell of the TMU molecule. The high dissolving power of TMU for aromatics is, according to Luttringhaus, "probably derived from the van der Waals forces due to the methyl groups, from the interactions between the resonance systems of the solvent and the solute, and from a favorable molecular structure of tetramethylurea" [7].

Due to coal's many polymer-like properties and the fact that coal's macrostructure is now generally considered to be that of a crosslinked polymer [14], solvent behavior towards polymers is of particular interest. TMU exhibits high solubility for cellulose esters and most aromatic polymers, which would indicate potential suitability as a coal solvent, given knowledge of the structure of coal and its chemical precursors [15].

Such a comprehensive listing of HMPA solubilities has not been made to the author's knowledge. But the similar methyl group shell and resonance structure would indicate similar solvent behavior toward hydrocarbons and aromatics. More vigorous interaction, and possibly complexing, might occur with polar compounds.

A final note should be made about the handling of TMU and, especially, HMPA. Their high affinity for materials of all kinds deems them potentially dangerous biologically. HMPA, in particular, is suspected as a skin-contact carcinogen [16].

Solvent Theory

There have been several approaches taken toward correlating solvent characteristics with solvent activity. Hildebrand's solubility parameter, δ, which is a thermodynamic parameter defined as the square root of the solvent's energy of vaporization divided by the liquid molar volume, has proven to be very useful in accounting for solvent action [17,18,19]. The thermodynamics of the mixing process dictate that for maximum miscibility the solubility parameter of the solvent and solute should be equal.

Application of the solubility parameter concept to

non-polar materials is straightforward, but the concept must be refined to apply to solvents that have polar or hydrogen-bonding interactions. Crowley, Teague, and Lowe [20], Hansen [21],and Hansen and Skaarup [22] have proposed a three-dimensional solubility parameter which breaks up the overall solubility parameter into three components resulting from the three main types of intermolecular forces that affect solubility: dispersion forces, dipole forces, and hydrogen bonding. The relationship between the three component solubility parameters and the overall solubility parameter is:

$$\delta_O^2 = \delta_D^2 + \delta_P^2 + \delta_H^2$$

where δ_O = overall solubility parameter
δ_D = dispersion component
δ_P = polar component
δ_H = hydrogen bonding component

The solubility parameter for a mixture of solvents is determined by: $\delta_{mixt} = \Sigma\ \phi_i \delta_i$

where ϕ_i = volume fraction of component i
δ_i = solubility parameter of component i

A good summary of the solubility parameter concept

and an extensive list of values of δ_O, δ_P, δ_D, and δ_H has been compiled for solvents and polymer materials by Hansen and Beerbower [23] and Burrel [18].

Another scheme, similar in some ways to the Hildebrand solubility parameter, for classification of solvents was proposed by Snyder [24]. He defined an overall parameter (P'), called polarity or chromatographic strength, and three selectivity parameters (x_e,x_d,x_n) which represent the fraction of P' contributed by interaction with ethanol, dioxane, anf nitromethane. The x_e, x_d and x_n values can be roughly interpreted as the relative abilities to act as a proton acceptor, proton donor, and strong dipole, respectively. P' can be interpreted as a solubility parameter that includes only non-dispersion interactions. Snyder [25] has discussed the relationship between P' and δ.

In both Snyder's and Hildebrand's schemes both the overall parameter and the individual selectivity parameters can be varied, by using solvent blends, to find optimum characteristics for a particular solvent job.

The electron donor and acceptor concept, formally developed by Gutmann and others [26,27,28,9], is another important theory to account for solvent behavior and selectivity. According to this theory solvation results from interaction and coordination between donor and

acceptor groups of the solvent and solute. The solvent-solute interaction may lead to ionization or formation of a coordinate bond. In any case, Gutmann pointed out, adjacent sigma bonds in both the acceptor and donor species are weakened and structural changes induced [28].

The electron donor and acceptor properties have been quantitatively characterized by Gutmann et al. [9,27,28] in two parameters called the electron donor number (DN) or donicity and electron acceptor number (AN). The DN is defined as the negative ΔH value for interaction of the solvent with antimony pentachloride. The AN is determined from solvent interaction with triethylphosphineoxide, as measured with ^{31}P NMR, and referenced to antimony pentachloride.

Related Work on Solvent Extraction of Coal

Pullen categorized liquid solvents for coal into four groups: non-specific solvents, specific solvents, degrading solvents, and reactive solvents [29]. Degrading solvents are active at high temperature and act to stabilize thermally produced coal fragments. They can be recovered almost totally, and substantially unchanged. They are thought to stabilize fragments by dispersion forces and hydrogen shuttling.

Reactive solvents react chemically with coal and coal fragments, resulting in a chemically changed solvent. They act, usually at high temperature, primarily by either chemically attacking and degrading the coal and/or by reacting with thermally generated fragments, eg. by hydrogen donation. Nitrogen-containing hydrogen donors are especially active. Adduction of hydrocarbon and nitrogen-containing solvents into coal liquids has been reported by McNeil et al. [30].

Non-specific solvents will dissolve up to a few percent of coal at low temperatures (less than 100°C). The material extracted by non-specific solvents is believed to be resins and waxes that are occluded from the coal matrix, and is of minor importance.

Specific solvents dissolve 20-40% of coal at temperatures below 200°C. They tend to extract substances which are chemically similar to the parent coal. Solvents in this category may be aromatic or not and typically contain one or more polar groups, eg. amines and pyridine. Also in this group, Pullen suggests, are dipolar aprotic solvents.

The class of specific solvents was first referred to by Dryden [3] in a study which involved evaluating the solvent power of a number of solvents for coal. He found that solvent activity could not be accounted for by

internal pressure, surface tension, dielectric constant, or dipole moment of the solvent. He made the following important observations about solvent effectiveness on coal:

1. Electron donating power is important to dissolving power.
2. Better solvents contain an unshared electron pair and are able to form coordinate complexes.
3. Hydrogen bonding in the liquid phase reduces solvent power.
4. Large molecular size and high viscosity decrease solvent power at low temperatures.

Hydrogen bonding and electron donor-acceptor interaction are suggested as important factors in solvent action on coal.

Dryden's observations about the apparent importance of electron donating and coordinate forming ability strongly suggest the applicability of Gutmann's electron donor acceptor theory, discussed earlier. Marzec et al. [31] used a number of solvents, including several dipolar aprotic solvents, to extract coal at ambient temperature and attempted to correlate their effectiveness with Hildebrand's solubility parameter and the various component solubility parameters, Snyder's polarity P' and the associated selectivity indexes, internal pressure, and Gutmann's donor and acceptor numbers. They found that

internal pressure and the various interactions upon which the Hildebrand and Snyder parameters are based did not correlate with the solvent effectiveness in coal extraction. Electron donor and acceptor properties did, however, appear to influence solvent effectiveness. Based on the electron donor-acceptor interaction concept, a model of coal extraction was developed and evaluated against the experimental results. Both the model and the data indicate that donor number (DN) and acceptor number (AN) of the solvent must lie in a particular range relative to that of the coal in order to be effective. The solvents studied were grouped according to the DN and AN groups predicted by the model. The resulting groups are shown below in Table 2.

Though TMU and HMPA were not among the solvents evaluated by Marzec et al., their DN and AN values would put them in the high extract yield group.

Roy et al. [32] studied the action of some dipolar aprotic solvents on coal. They found, at 35°C, that dimethylsulfoxide (DMSO) was as good as pyridine and better than ethylene diamine and that N-methyl-2-pyrollidone was better than DMSO. The effectiveness of N-methyl-2-pyrollidone was attributed to the presence of both oxygen and nitrogen atoms with their electron pairs.

Table 2. Solvent Groups According to Donor-Acceptor Model [31]

Solvent Group	Extract Yields Expected	Observed
Group A: Diethyl ether, tetrahydrofuran, pyridine, dimethylsulfoxide, N-methyl-2-pyrolidinone, ethylene diamine $DN_S > 19$; $AN_S < 21$	High	10-20 wt.%
Group F Dioxane, acetone $17 > DN_S > 15$; $AN_S < 21$	Low	1-2 wt.%
Group D Hexane, benzene, nitromethane, acetonitrile $DN_S < 14$; $AN_S < 21$	No extract	< 0.1 wt.%
Group E Methanol, water, ethanol, isopropanol, formamide $DN_S > 19$; $AN_S > 33$	No extract	< 0.2 wt.%

Several people have applied the Hildebrand solubility parameter concept to coal extraction. Van Krevelen [33] applied the solubility parameter theory to coal, determined solubility parameters for different classes of coals and predicted potentially suitable solvents for different coal classes on the basis of solubility parameters. Hombach [34] treated different rank coals with several solvents to evaluate the solubility parameter of the coals. He found a dependence of solubility

parameter on coal rank and found that the solubility parameter concept could explain the solvent power of chemically diverse solvents on coal and, especially, that the concept could explain the effectiveness of mixtures of otherwise poor solvents. Hombach also reported HMPA to be neither a good solvent for coal nor a good reducing medium, and mentioned evidence of HMPA solvent fragment incorporation into reduced coal. Weinberg and Yen [35] and Kirov et al. [36] have also applied the solubility parameter concept to coal-solvent interaction.

HMPA has been used successfully by Sternberg et.al. [37] and Ouchi et al. [38] as a medium for reductively alkylating coal, resulting in increased coal solubility. Sternberg et al. [37] reported the production of a "coal anion" by treatment of coal with alkali metal in HMPA. This "coal anion" then reacts with alkyl iodide to produce alkylated coal. Ouchi et al. [38] performed the alkylation using sodium and t-butyl alcohol in HMPA.

Research Objective

The objective of this research was to evaluate the action of carrier solvent blends with TMU and HMPA on coal dissolution as compared to pure TMU and HMPA. Solvent blends were chosen which were expected to give

useful insights into the action of TMU and HMPA on coal at temperatures below its thermal breakdown point. Evaluation and comparison of solvent blends was to be made on the basis of dissolution rate and temperature dependence, ultimate dissolution, and elemental analyses of the product and residue.

EXPERIMENTAL

Materials

The coal used was a lower Kittaning, high volatile bituminous coal. The specific part of the Kittaning formation that the coal was obtained from is not known. The time and treatment since removal from the mine is also not certain. This Kittaning coal was chosen for these experiments because it yielded satisfactory dissolution results, whereas several other coals tried did not dissolve significantly in TMU/HMPA.

The chunk coal was ground and sized to pass 150 mesh, but not 200 mesh, then was stored under nitrogen until use. Several different grinding batches were utilized in the coarse of the experiments. The elemental analyses, ash contents, and appropriate run numbers for all the coal used are listed in Table 3. For the second-chunk second-batch, ash, N, C, O, and H percentages add to 99 %. The sulfur content of the coal used was not determined. Because the ash content of the second-chunk third-batch was significantly higher than the other batches, the ash-containing basis percentages were significantly different. However, the ash-free basis

percentages, given in parentheses in Table 3, are very close to the other batches. The two experiments conducted with the second-chunk third-batch coal were replicated with the third-chunk first-batch coal and percent dissolution results were within 3% absolute.

Table 3. Analyses of Coals Used *

Coal	%Ash Con	%N	%C	%H	%O	Runs
Second chunk Second batch	8.9	1.31 (1.44)	77.86 (85.47)	5.18 (5.69)	5.74 (6.30)	T1-T22
Second Chunk Third batch	13.9	1.25 (1.45)	73.19 (84.97)	4.89 (5.68)		T23,T24
Third Chunk First batch	8.3	1.34 (1.46)	78.49 (85.61)	5.24 (5.72)		T26,T28, T30

* values in parentheses are % on an ash-free moisture-containing basis, other values are on an ash-containing moisture-containing basis

The moisture content of the second chunk of Kittaning coal was determined by a coworker to be 0.6%. The procedure used for the moisture content determination was to measure weight loss after drying a sample of ground coal overnight at 100 °C. The moisture content of the coal will vary according to the humidity of the atmosphere it is exposed to. As a basis for estimating the magnitude of moisture content changes in the coal due to humidity changes, sorption studies on coal reported by Anderson

et al. were consulted. For a relative H_2O pressure of 0.035, which corresponds roughly to saturation at 75°F, water adsorption of < 10 c.c.(STP) per gram coal was reported for two bituminous coals (adsorption experiments were run at 30 and 35°C). Ten c.c.(STP) per gram coal corresponds to 0.80 weight percent of the coal. If this is considered a reasonable estimate of the variability of coal moisture content due to humidity, then the coal moisture content should be in the 0.0 to 1.40 percent range.

The solvents used, sources, and grade are listed in Table 4. Wash liquids, acetone and ethanol, were laboratory grade.

Table 4. Solvents Used

Solvent	Source	Grade
TMU	Aldrich Chemical	99%
HMPA	Aldrich	99%
Tetralin	Aldrich	99%
Decalin	Sargent-Welch	Practical
Napthalene	Baker	Baker Analyzed
1-Methyl Napthalene	Eastman Kodak	(?)
Isopropanol	(?)	Lab
Pyridine	Baker	Baker Analyzed

The apparatus, shown in Figure 2, was a continuosly stirred batch reactor, fitted with a condenser to reflux solvent vapors. A nitrogen purge was maintained in the reactor vessel during solvent heat up and reaction. A combination magnetic stirrer-hotplate was used to stir and heat the reactor vessel. Experiments were run at room temperature (65-77°F), 200°F, and 320°F. Experimental limitations restricted the maximum temperature to 320°F.

Experimental Procedure

For all experiments, 200 ml total solvent was used and approximately 4 grams coal was used, giving a solvent:coal ratio of approximately 50:1. The solvent was added to the reaction vessel and heated to the desired stable temperature with the condenser, mixer, and nitrogen purge in operation. The condenser was then lifted momentarily, the preweighed coal sample introduced, and the condenser refit. The experiment was then allowed to proceed the desired time, with temperature variations recorded, and the reaction mixture was removed and filtered hot. Due to time required for filtration, typically 3-5 minutes, very short reaction time experiments were removed and filtration begun about 1.5

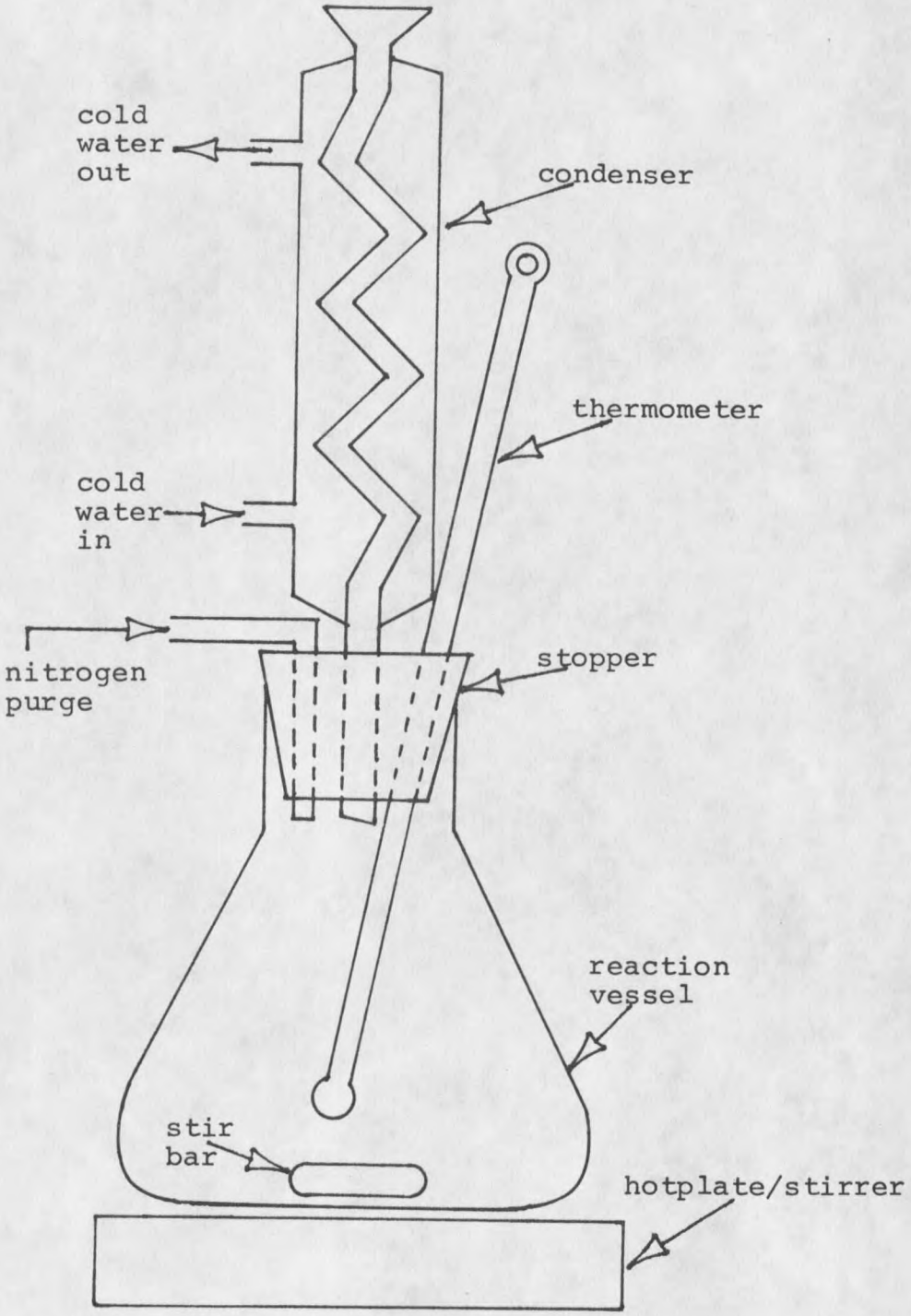


Figure 2. Experimental Apparatus

minutes before the desired reaction time.

Filtration was begun immediately after removal from the hotplate. Preweighed Whatman No 1 filter paper was fitted to a conical funnel and the filtrate was drawn by house vacuum into a filtration flask that was immersed in cold water to help quench any reaction and prevent solvent loss to the vacuum system. A cold finger type trap, immersed in cold water, was also used in the vacuum line.

After filtration was complete, the liquid product was decanted into a storage jar, the reaction vessel rinsed well with acetone and washed through the residue. The residue was washed with acetone until the filtrate appeared colorless. The residue, after the liquid was removed, was dried under a vacuum of about 0.1 torr at room temperature for approximately one week. The earlier experiments had shown that significant weight loss occurs for 4-5 days under vacuum, but is not very significant after that. Upon removal from vacuum, residues were weighed quickly then allowed enough time to moisture equilibrate with air, and elemental analyses were performed.

The experimental procedure and apparatus is such that water vapor and low boiling vapors evolved during the extraction might be carried out of the system with the nitrogen purge. Because the coal used for the experiments was only air dried, loss of moisture in the coal during

extraction could affect results. As mentioned above, the total moisture content of the coal is probably <1.4%. This corresponds to a hydrogen content of 0.17% due to moisture, which is probably detectable but not very significant.

It was thought that allowing vacuum-dried residues to moisture equilibrate with air before doing elemental analyses might help compensate for any effect of unmeasured moisture loss during extraction. No experiments were done to estimate moisture take up of residue after drying. It is therefore possible that moisture gain of the residue might be more than the original coal moisture. Because performing the elemental analyses without exposing the samples to air is not feasible, the equilibrium moisture containing basis was taken as the most reasonable for analyses. Moisture effects are not thought to affect results significantly.

Loss of some low boiling extract product vapors from the system is possible, but is probably very slight and not thought to be significant as far as results are concerned.

Analytical Procedures

Elemental analyses (C,H,N) were performed by the author on a Carlo Erba Model 1100 Elemental Analyzer, integrated with a Carlo Erba DP110 integrator and Osborne 1 computer. Sample weighings for the elemental analyses were performed on a Cahn 29 electrobalance, with sensitivity at the 0.1 microgram level. Other weighings were performed on a Mettler H80 balance, sensitive at the 0.1 milligram level.

Apparent dissolution was determined by the following relationship:

$$\text{App Diss} = \frac{\text{Coal Wt} - \text{Residue Wt}}{(1.0 - \text{A.C.})\ \text{Coal Wt}}$$

where A.C. = wt. fraction of ash in coal

Ash contents of the coal samples were determined as the remaining weight fraction after leaving coal samples in an air available oven at 700-750°C for 24 hours.

High nitrogen content in the residue indicated that substantial solvent retention was taking place and masking the true dissolution levels. Solvent retention and true dissolution were then estimated based on the following assumptions and calculation method. The solvent-free residue was assumed to have the same percent nitrogen as

the coal. The nitrogen containing solvents were assumed to be retained in the same ratio as they were present in the solvent mixture. This assumption is not critical because of very similar nitrogen contents in TMU and HMPA. Solvent molecules were also assumed to be retained unfragmented. Attar et al.[39] reported the nitrogen content of aromatic solvent extracts to be very close to the nitrogen content of the parent coal and that of polar solvent extracts to be significantly less. Given the solvent varieties being used in these experiments, the assumption of equal nitrogen content in residue and coal seemed most reasonable. Potential magnitude of error in results due to this assumption is considered in the Error and Reproducibility section. McNeil et al. [30] reported quinoline adduction to coal liquids primarily by hydrogen bonding for extractions run at 450°C. It seems likely, then, that, for our low temperature extractions, solvent molecules are retained unfragmented.

Based on these assumptions, a nitrogen balance allowed calculation of the amount of nitrogen containing solvent retained. A solvent free residue weight could then be calculated and the true dissolution estimated. The true solvent free residue hydrogen and carbon percentages were also estimated by subtracting out the hydrogen and carbon due to the solvent from the elemental

analyses of the solvent containing residue. A copy of the Fortran program used to calculate the solvent free residue values and a set of sample calculations based on the assumptions just mentioned is included in Appendix C.

Error and Reproducibility

The precision of weight measurements has already been noted. The accuracy of elemental analyses is approximately ±1.1% of measured value for carbon, ±2.1% of measured value for hydrogen and ±1.5% of measured value for nitrogen, based on standard deviations of measured values from theoretical values for numerous standard compounds run.

Some temperature variations about the nominal temperature occurred during runs due to the nature of the equipment. The maximum variation observed during each run is included in the experimental data in Appendix A. The largest temperature variation observed was 30°F during a 4.5 hour run at 320°F. It was quickly returned to the proper level and, due to length of the run, was not thought to have affected the results significantly. For one hour and shorter runs, the maximum variation observed was 12°F. Temperature variations were normally both plus and minus during a run, and hence expected to more or less

average out over the course of the run.

For longer experiments (20 minutes or more), uncertainty in run time length, due to variability in filtration time, is not thought to contribute error as far as results are concerned. Because the dissolution reaction appears to be rapid in the first 10 minutes, filtration time variability could affect the results for short time runs. For these short time runs the extraction time was taken to be the sum of the actual time on the hotplate-stirrer and approximately one third of the filtration time. One third was used because the filtration is typically faster initially and slows down as filter cake accumulates.

Several extraction experiments were replicated to check reproducibility. The results of these experiments, presented in Table 5, indicate that reproducibility for dissolution is approximately plus or minus 3% absolute about the average. The variability for solvent retention values and H/C ratios, however, is very high in some cases. The reproducibility on solvent retention values is approximately ± 0.0250 g solvent/g coal. The potential reasons for this high variability in solvent retention are discussed in more detail in the Solvent Retention section of this thesis. It seems likely that the variation is due to either: (1) errors in the

Table 5. Replicate Experiments to Observe Reproducibility

Run#	Temp (F)	Time (min)	%Diss	Sol Ret (g/g coal)	H/C (mol/mol)
T23 (80% Tet)	320	10	23.1	0.0776	0.82
T31	320	10	25.5	0.1335	0.81
T24 (80% Tet)	320	5	20.2	0.0614	0.80
T32	320	5	23.3	0.1134	0.80
T33 (TMU/HMPA)	320	20	40.7	0.1870	0.82
#20*	320	20	33.7	0.1418	0.79
#14* (TMU/HMPA)	200	20	6.1	0.0413	0.77
#19*	200	20	11.6	0.0626	0.77
#12* (TMU/HMPA)	200	60	12.6	0.0703	0.79
#27*	200	60	13.5	0.0619	0.81
#15* (TMU/HMPA)	200	720	34.2	0.1213	0.78
#34*	200	720	27.9	0.0673	0.82

* Experiment conducted by coworker C. Ichioka.

solvent retention assumptions, or (2) experimental error introduced by inconsistency in the residue washing and/or drying procedure. Residue washing was continued until an apparently colorless filtrate was obtained. However the filtrate collection flask was not changed during filtration, which made the "colorless" observation subjective.

It should also be noted that some of the anomalous H/C ratios observed might be partially due to error in elemental analyses. An error of 3.2% for a H/C value of 0.79 corresponds to an absolute error of 0.025, which is significant. Most of the time hydrogen and carbon error in the elemental analyses occurs in the same direction, which would give a H/C error much less than 3.2%. However, there are occasional cases when hydrogen and carbon errors are in the opposite direction, giving an atypically large error in H/C.

Error bars have been placed on the total dissolution and solvent retention plots in the Results and Discussion section. The magnitude of the error bars was based on reproducibility observations from Table 5 and on calculations of the potential error due to the assumption of equal nitrogen percentage in the coal and extraction residue. Calculations of the potential error due to the nitrogen assumption are presented in Appendix C, and are summarized in Table 6.

Table 6. Potential Error Due to Assumption of Equal Nitrogen Percentage in Coal and Residue. Z = g dissolved per g coal (ash containing basis) as determined by the assumption of equal N in coal and residue.

Assumption	Result
Extraction Product %N = 2.0(Coal %N) Coal %N = 1.3 Solvent %N = 23.79 (50/50 TMU/HMPA)	True Dissolution = 1.06(Z) Absolute Error in TMU/HMPA Retention Value = 0.06(Z) g/gcoal
Extraction Product %N = 0.5(Coal %N) Coal %N = 1.3 Solvent %N = 23.79	True Dissolution = 0.97(Z) Absolute Error in TMU/HMPA Retention Value = 0.03(Z) g/g coal

The magnitude of the error bars is, then, a function of the dissolution level. For the error bars the contribution due to the N assumption was taken to be 0.06(Z)% for dissolution and 0.06(Z) g/g coal for TMU/HMPA retention. Table 7 presents a summary of the error contributions that went into the error bars placed on the plots in the Results and Discussion section. Tetralin retention was not considered in determination of the error bars. In any case tetralin retention would result in underestimation of the true dissolution.

Table 7. Error Contributions to Total Estimated Error in Total Dissolution and Solvent Retention.

Total Dissolution :

Z*	0.35	0.25	0.15	0.075
Reproducibility Error	3.0	3.0	3.0	3.0
Error due to equal %N assumption	2.1	1.5	0.9	0.5
Total Error	5.1	4.5	3.9	3.5

Solvent Retention :

Z*	0.35	0.25	0.15	0.075
Reproducibility error	0.025	0.025	0.025	0.025
Error due to equal %N assumption	0.021	0.015	0.009	0.005
Total error	0.046	0.040	0.034	0.030

* Z = g dissolved per g coal on ash containing basis as determined by assumption of equal N in coal and residue.

RESULTS AND DISCUSSION

Complete data and results for all experiments discussed in this thesis are presented for reference in Tables 12 and 13 in Appendix A and B, respectively, and discussion of results follows.

TMU/HMPA/Tetralin Blends

Tetralin was initially chosen as a suitable solvent to investigate in blends with TMU and HMPA. It was chosen because of suitable boiling point, its aromatic and aliphatic character, its well studied hydrogen transfer capabilities, and because, alone, it is relatively inert toward coal at low temperatures.

Four runs were done at 200°F to compare tetralin blended with TMU and HMPA separately with tetralin blended with both. Results from these experiments and relevant experiments conducted by a coworker are shown in Table 8. The increase in dissolution observed in Run T4 compared to Runs T1-T3 could be attributed to two effects: (1) the effect of having both TMU and HMPA present in the blend, and (2) the effect of decreasing the amount of tetralin from 50% to 33%. Previous screening experiments done by

the author and coworkers had also indicated that a 50:50 mixture of TMU/HMPA was better than either solvent alone.

Table 8. Effect of Blending TMU, HMPA and Tetralin. Extraction temp. of 200°F, time is 1 hr.

Run No	Solvent	% Diss
T1	100% Tetralin	1.9
T2	50% Tet, 50% HMPA	11.0
T3	50% Tet, 50% TMU	6.4
T4	33% Tet, 33% HMPA, 33% TMU	20.7
27*	50%HMPA, 50% TMU	13.5
23*	100% TMU	9.9

* Runs conducted by coworker C. Ichioka.

It should be noted that previous experiments attempted with HMPA alone resulted in an unfilterable, apparently colloidal mixture, hence further pure HMPA experiments were not done. In the remainder of my experiments TMU and HMPA were always utilized in a 50:50 mixture.

Dissolution Rate in Tetralin Blends

A series of experiments were made to assess the dissolution rate behavior of tetralin/TMU/HMPA blends compared with TMU/HMPA. Most of the TMU/HMPA experiments

were done by a coworker. An 80% tetralin blend was chosen to compare with TMU/HMPA. The results are shown graphically in Figure 3.

Figure 3 shows that 80% tetralin results in an apparent reduction in the initial dissolution rate. However, tetralin retention experiments, discussed in more detail later, indicate that significant retention of tetralin may occur. This effect could mask the true dissolution rates and levels of tetralin-containing blends making them appear lower. Experiments done to estimate tetralin retention indicate that as much as 8-10% retention of tetralin may occur at 320°F. The apparently lower dissolution rate for the 80% tetralin blend might also be attributed to lower TMU/HMPA concentration compared to unblended TMU/HMPA.

Notable from Figure 3 is that the pronounced decrease in the amount dissolved after 40 minutes in TMU/HMPA does not occur in the 80% tetralin blend. The decrease in dissolution for TMU/HMPA extraction at 320°F is probably due to recondensation or repolymerization of product fragments. The presence of tetralin seems to inhibit this drop in dissolution at longer times. If the drop is, in fact, due to product repolymerization, tetralin may be functioning to stabilize reactive product fragments.

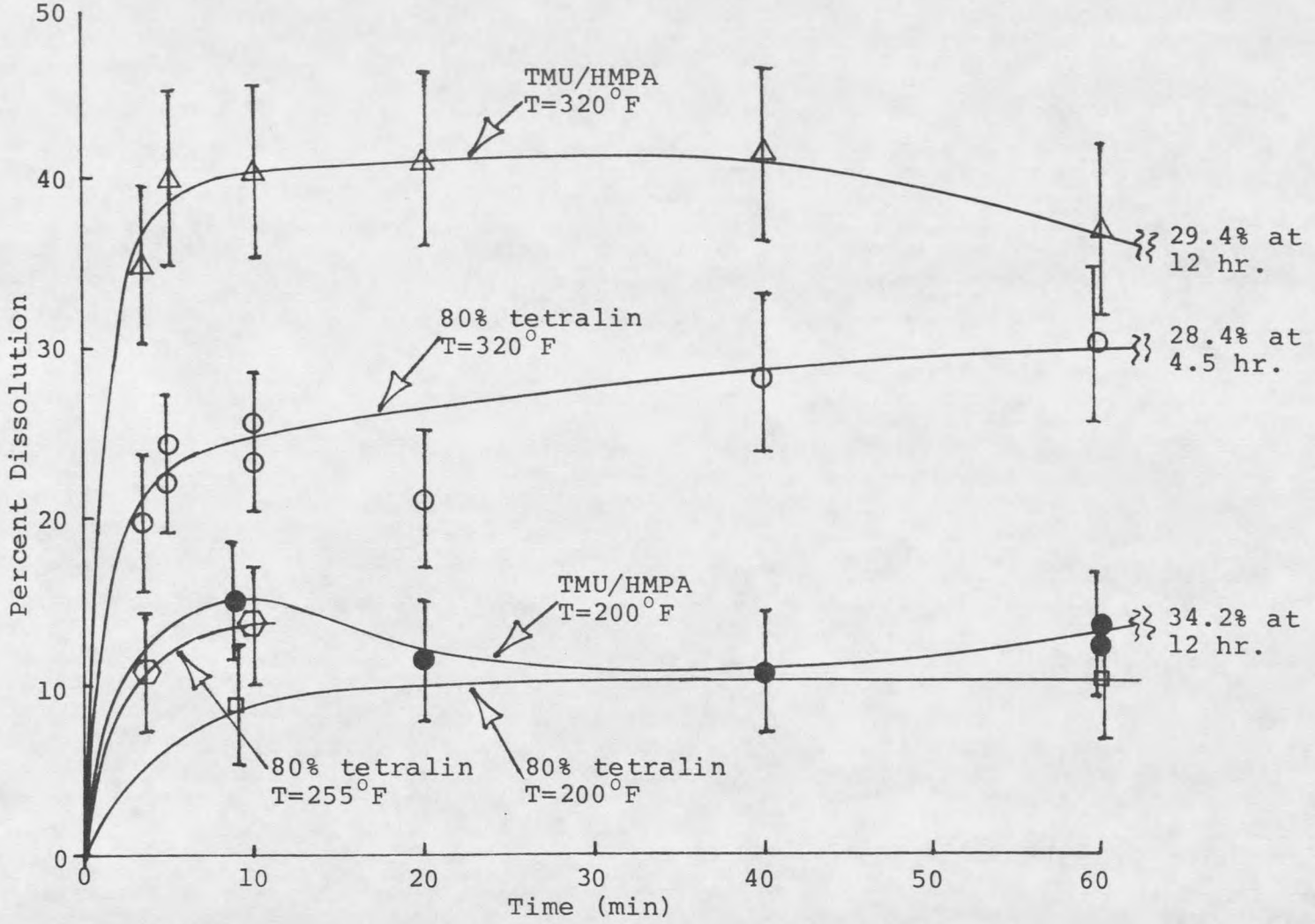


Figure 3. Dissolution vs. Time for TMU/HMPA and 80% Tetralin 20% TMU/HMPA Blend at Various Temperatures.

The very hard, brittle constitution of the residues from TMU/HMPA runs at 320°F, compared with a more friable powdery residue that results from 80% tetralin runs, also indicates that TMU/HMPA gives a much more polymerized residue than the tetralin blend. Even at short extraction time at 320°F, TMU/HMPA seems to promote a highly polymerized, or at least highly associated residue.

The dissolution limitations in these experiments are exemplified by the fact that, for both TMU/HMPA and 80% tetralin blended with TMU/HMPA, a major portion of the ultimately attainable dissolution at 320°F occurs within 5 minutes, with very slow or even retrogressive dissolution thereafter. As a rough indication of the temperature dependence of the overall dissolution rate, the ln(dissolution/time) vs. 1/T was plotted for TMU/HMPA and 80% tetralin blended with TMU/HMPA at extraction times of 5 minutes and 1 hour. This plot, presented in Figure 4, indicates that dissolution is a weak function of temperature after the first 5 minutes, which would be expected from Figure 3 also. The plot in Figure 4 is analagous to an Arrhenius activation energy plot. The results of Figure 4 are not interpreted in terms of activation energy because the form of the rate expression(s) for the dissolution reaction(s) is not known and and rate data during the initial rapid dissolution reaction was not

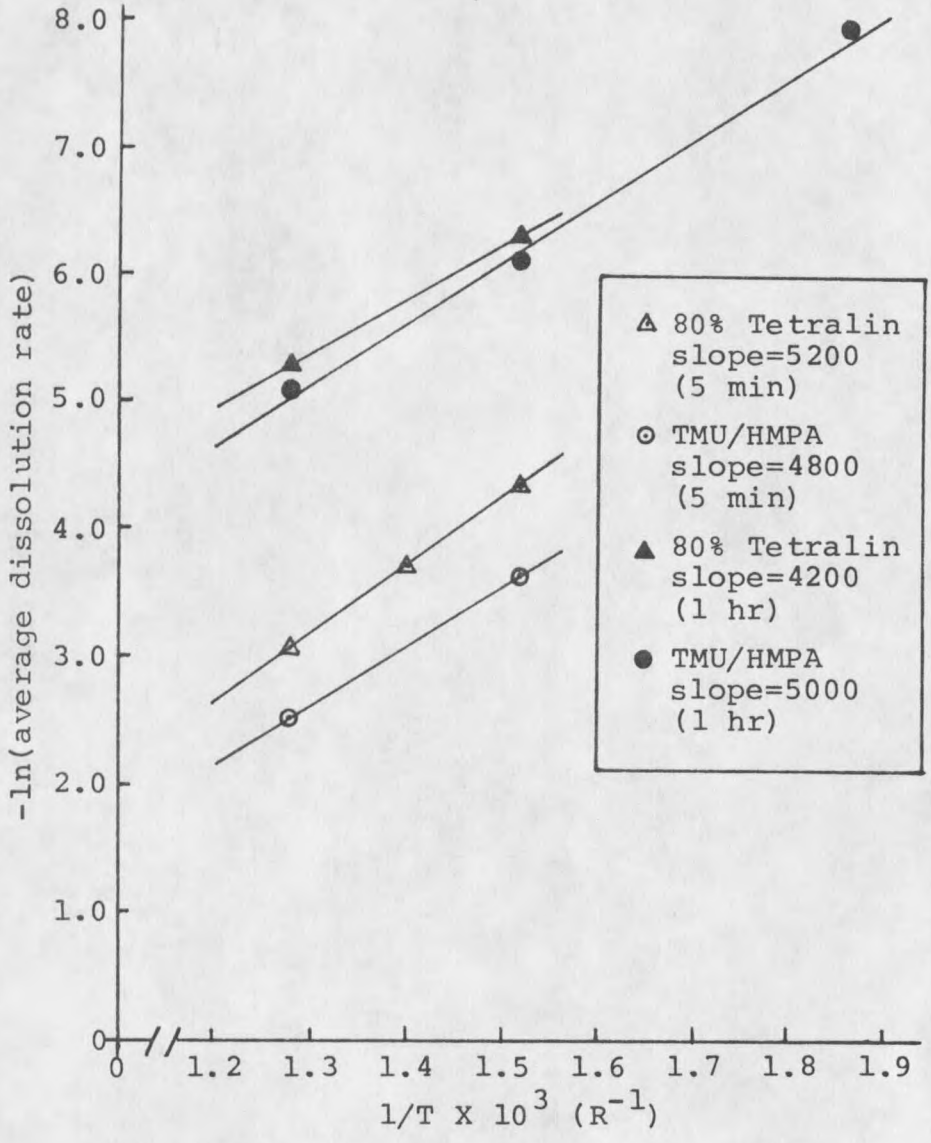


Figure 4. Temperature Dependence of Average Dissolution Rate. Dissolution rate is in g dissolved per g coal per minute.

obtainable. However activation energy for any reaction after the first 5 minutes is clearly very low.

The apparent rapid limitation on dissolution and weak temperature dependence thereafter could be accounted for in several ways: (1) the dissolution reaction proceeds quickly to a thermodynamic equilibrium situation, (2) the initially higher activation energy dissolution reactions are followed by low activation energy reactions with little increase in overall dissolution, such as radical propogation or recombination reactions, many of which are known to have activation energies less than 10 kcal/mol [40] (radical recombination or condensation is a possibility suggested by the decrease in 320°F curve at long times in Figure 3), or (3) mass transfer restrictions occur after some time, perhaps due to exhaustion of easily accessible reaction sites or by pore clogging due to swelling or product condensation.

It is most likely that a combination of these factors are at play and that the relative importance of any one is somewhat dependent on temperature, solvent blend and extent of dissolution.

Effect of Amount of Tetralin in Blends

A series of runs were made at 320°F and 200°F for 1 hour to evaluate the effect of amount of tetralin in blends with TMU/HMPA. Dissolution results for these experiments are presented in graphical form in Figure 5.

These results indicate that, initially, addition of tetralin to TMU/HMPA increases dissolution at 1 hour, and that tetralin can be present up to 70-80% without significantly decreasing the dissolving power of the blend. Tetralin retention experiments, discussed in more detail later, and high residue H/C ratios for the runs in the 50-80% tetralin range at 320°F indicate that tetralin retention in the residue may account for the lowering of the curve in that area. It is thought that accounting for tetralin retention might result in a curve similar to the dashed one in Figure 5.

The dissolution decrease that occurs with TMU/HMPA between 40 and 60 minutes should be kept in mind when interpreting Figure 5, which shows an increase in dissolution at 1 hour with increasing tetralin blends compared to TMU/HMPA. Part or all of the increase observed at 1 hour might not be observed at shorter times before the decrease occurs in TMU/HMPA dissolution.

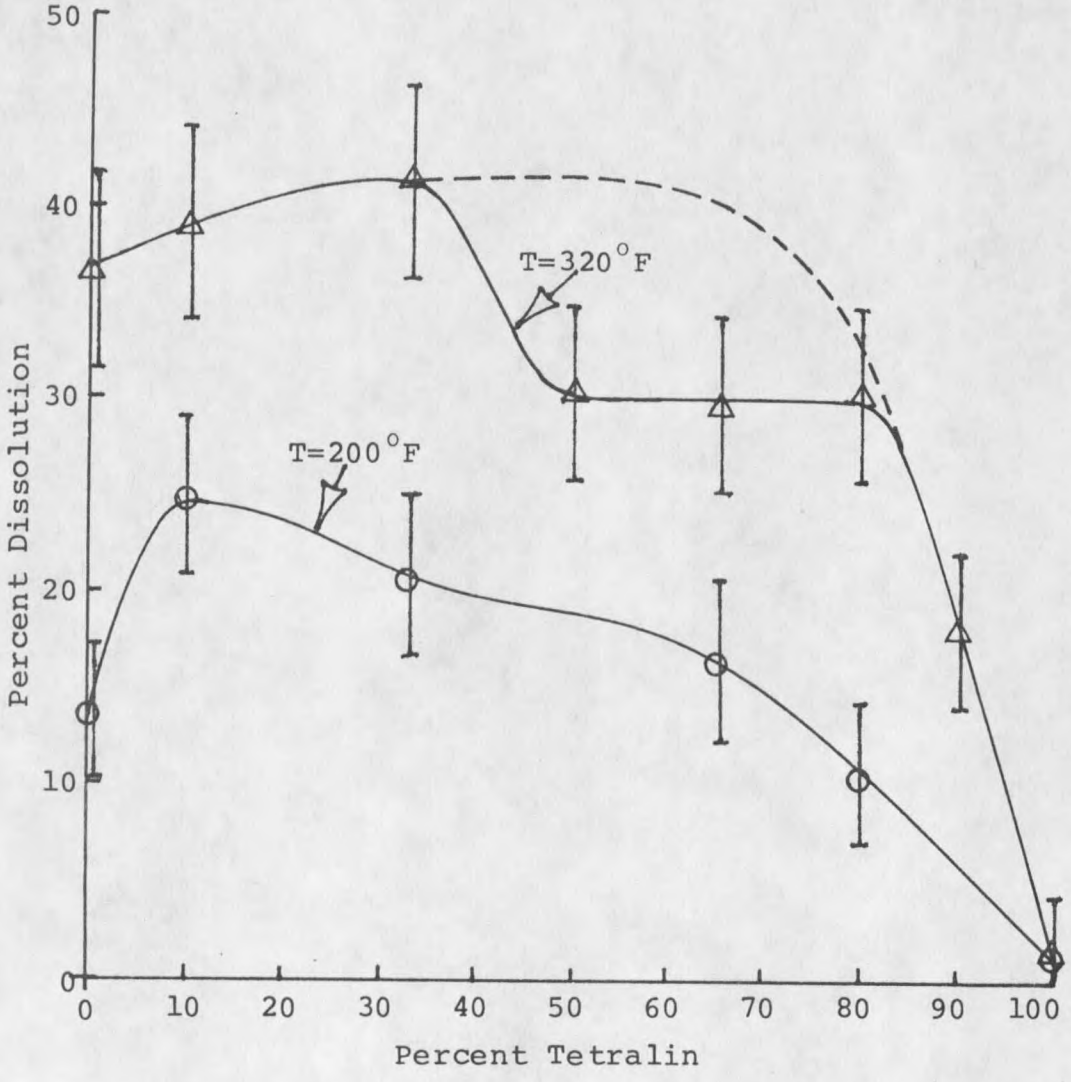


Figure 5. Effect of Tetralin on Dissolution. Balance of blend is 50/50 TMU/HMPA. Extraction time is 1 hr.

The eventual dropping of the curve at high tetralin percentage is to be expected due to the mass action effect of the relatively inert tetralin. But the increase at low percentage tetralin and the long range of effectiveness is curious. We can look at the solvent extraction process as being a series of steps: transport of solvent species into the coal, reaction to produce fragments, solvation or stabilization of fragment, and transport of product species or product-solvent complex out of the coal. In this solvolysis process, it is clear that the presence of TMU/HMPA is crucial overall, but that some steps in the process can apparently be handled by tetralin.

Tetralin is substantially unreactive with coal at these temperatures, so any active participation would have to be with coal fragments or, possibly, as a swelling agent. This and dissolution rate observations already made strongly suggest that tetralin may function to stabilize or solvate product fragments once they are generated. TMU and HMPA, being polar electron-donating solvents, would be expected to be good swelling agents for coal and good attacking agents for electron deficient groups in coal. Their ability to solvate organic materials and polymers is also notable and discussed in the Introduction of this thesis. Therefore, TMU and HMPA, though apparently able to perform all steps of the

solvolysis process themselves, appear to function most importantly as swelling agents, hence facilitating mass transport, and/or as attacking or degrading agents.

Other Solvent Blends

Several different aromatic/hydroaromatic solvents were also blended with TMU/HMPA to supplement results obtained with tetralin. Napthalene, 1-methyl napthalene, decalin, and limonene were tried in an 80% blend with TMU/HMPA at 320°F for 1 hour. Results are given in Table 9.

Table 9. Results Using Different Hydrocarbon Solvents Blended with TMU/HMPA.*

Carrier Solvent	% Diss
Napthalene	38.8
50:50 TMU/HMPA	36.7
1-Methyl Napthalene	34.7
Tetralin	30.3
Decalin	11.2
Limonene**	10.9

* Except where otherwise indicated blends are 80% of the indicated solvent and 20% TMU/HMPA, experiments run at 320°F and 1 hr.
** Run conducted by coworker I. Tsao.

There appears to be a correlation between the degree of aromatic character and the effectiveness of these hydrocarbons in blends with TMU/HMPA, though this does not necessarily mean that aromatic character is the cause of the correlation. The topic of correlation of solvent blend character with solvent effectiveness is discussed in a later section.

Several experiments were also done using TMU/HMPA blended with isopropyl alcohol, which has good hydrogen bonding and hydrogen transfer activity. The results are presented in Figure 6. The isopropyl alcohol clearly inhibits dissolving power. This could be a result of H bonding with TMU and HMPA, resulting in decreased reactivity of the TMU and HMPA. TMU and HMPA are both good H bond acceptors. It might also result from the alcohol blocking active sites on the coal. Other schemes for accounting for solvent blend action are considered in the next section.

Correlation of Solvent Blend Behavior

It has already been mentioned that the electron donor and acceptor numbers of TMU and HMPA would fall into the group of high dissolution activity for coal proposed by Marzec et al. [29]. Isopropyl alcohol, which quickly

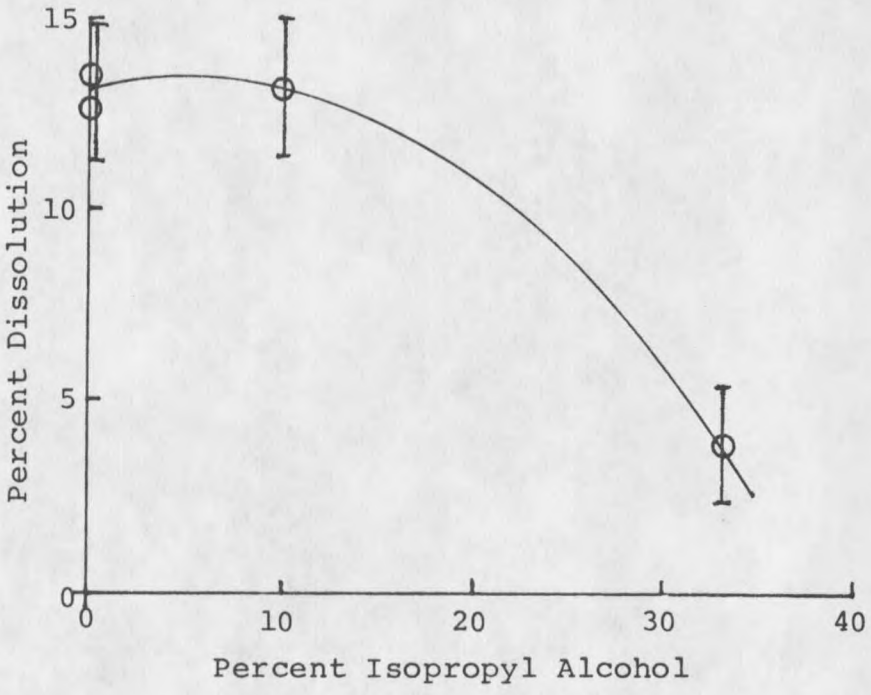


Figure 6. Effect of Blending Isopropyl Alcohol with TMU/HMPA. Balance % is 50/50 TMU/HMPA. Temp=200 ^{o}F, Time=1 hr.

decreased solvent effectiveness when blended with TMU/HMPA, falls into Marzec's group of no expected extraction on coal. The AN and DN values of napthalene, menapthalene, tetralin, decalin, and limonene aren't tabulated. But all of them should have AN values in the range of 0-15, and very low DN values, which would put them also into a group of no expected extractive ability. Of course they are ineffective by themselves, but some of them are effective when combined with TMU/HMPA. Due to lack of previous work on the effect of blending on electron donor and acceptor properties, this approach toward correlating the solvent blend behavior was not pursued further in this work.

The dissolution results for various solvent blends are presented in Table 10, along with their solubility parameter values. All of the blend solubility parameter values were determined by weighting pure component values by the appropriate volume fraction. Values of δ are based on energy of vaporization data and δ_O is determined from the δ_D, δ_P, and δ_H values, which are calculated independently. Because the calculation bases are different, the values of δ and δ_O are sometimes different. This discrepancy is especially important, as Snyder pointed out [23], for compounds which are H bond acceptors but not donors. For these types of compounds the pure

Table 10. Solubility Parameters of Solvent Blends. Blends below the dashed line were substantially less effective than unblended TMU/HMPA.*

Blend	δ ††	δ_O	δ_D	δ_P	δ_H	%Diss
80% Napthalene	10.0	9.9	9.2	1.6	3.4	38.8
TMU/HMPA (50/50)	10.4	11.0	8.6	4.1	5.5	36.7
80% Me-Napth.		10.3	9.8	1.1	2.9	34.7
80% Tetralin	9.7	9.8	9.4	1.6	2.2	30.3
TMU/HMPA (50/50)†**	10.4	11.0	8.6	4.1	5.5	13.5
10% isopropanol **	10.5	11.0	8.5	4.0	5.7	13.1
TMU †**		10.60	8.2	4.0	5.4	9.9
80% Decalin	9.1	8.9	8.8	0.8	1.1	11.2
80% Limonene †	8.6					10.9
100% Tetralin	9.5	9.75	9.6	1.0	1.4	3.3
30% isopropanol**	10.7	11.0	8.3	3.8	6.2	3.9

* Where not otherwise indicated, balance of blend is TMU/HMPA, temp. is 320°F and extraction time is 1 hr.
** Experiments at 200°F and 1 hr.
† Experiment conducted by coworker.
†† Units for δ are hildebrands $(cal/cm^3)^{\frac{1}{2}}$

liquid energy of vaporization, and hence δ, does not reflect the hydrogen bonding energy, due to lack of H bond donors in the pure liquid. This energy may be considerable, as is the case for TMU and HMPA, and is included in δ_O. TMU and HMPA are liable to behave very differently in the presence of a H bond donor than in the pure state. This was observed in the isopropanol blends where dissolution effectiveness dropped rapidly with addition of the alcohol.

It does appear that there may be some correlation between solubility parameter values and solvent effectiveness on coal. Apparently, though, both the overall parameter and the component solubility parameters have to be considered. The component solubility parameters of the blends tested are plotted on the axes of a 3-D plot in Figure 7. Figure 7 should be viewed as a juxtaposition of three 2-D plots, with a point representing each of the solvent blends shown in each of the three 2-D planes. Apparent approximate boundaries for dissolution effectiveness are also on Figure 7, with the solid symbols denoting ineffective blends and unshaded symbols used for effective blends. On the δ_H axis, the upper and lower boundaries are distinct. But on the δ_D and δ_P axes the lower boundaries are not so clear, and there is no explicit indication of the upper boundaries. From Table 10

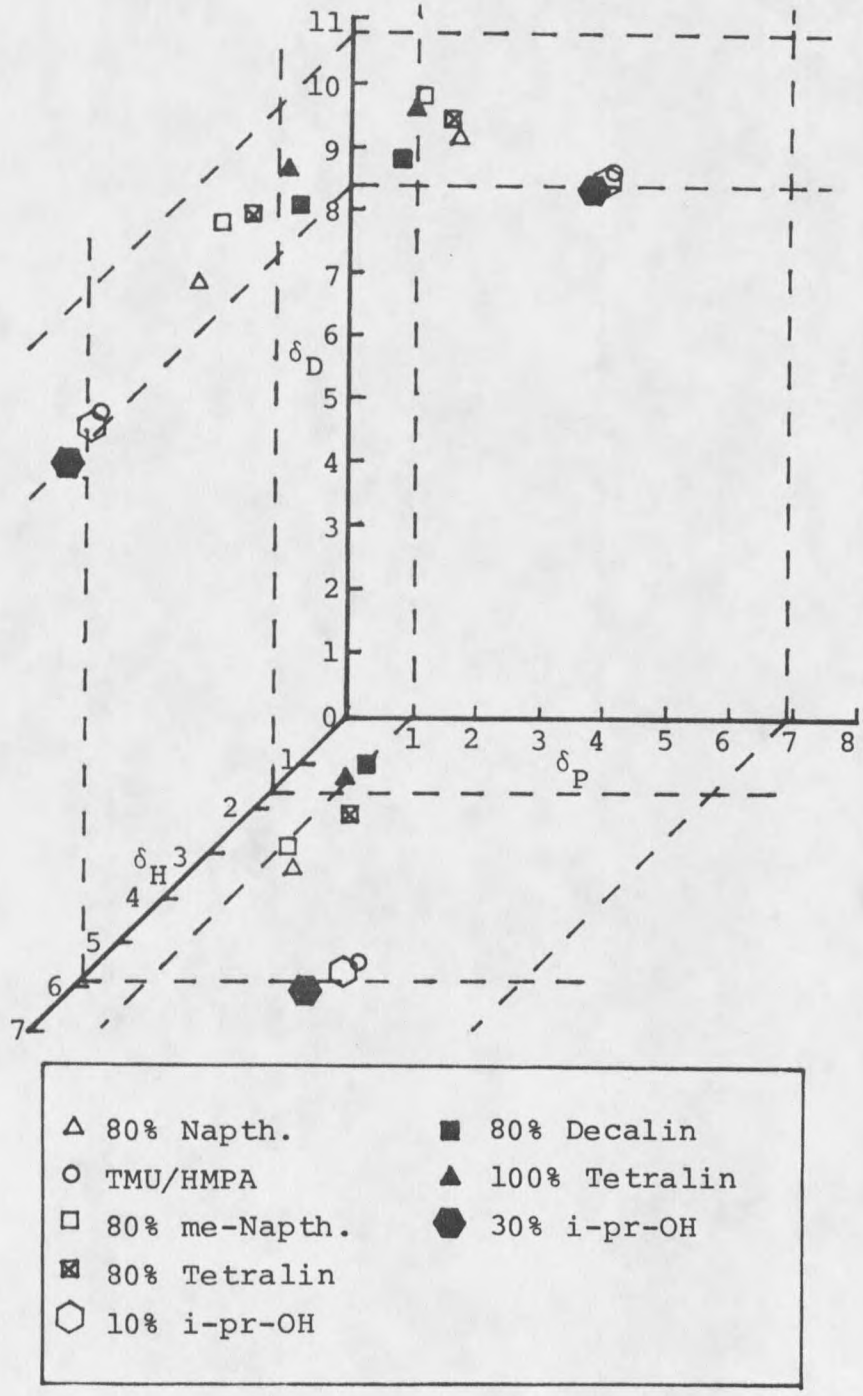
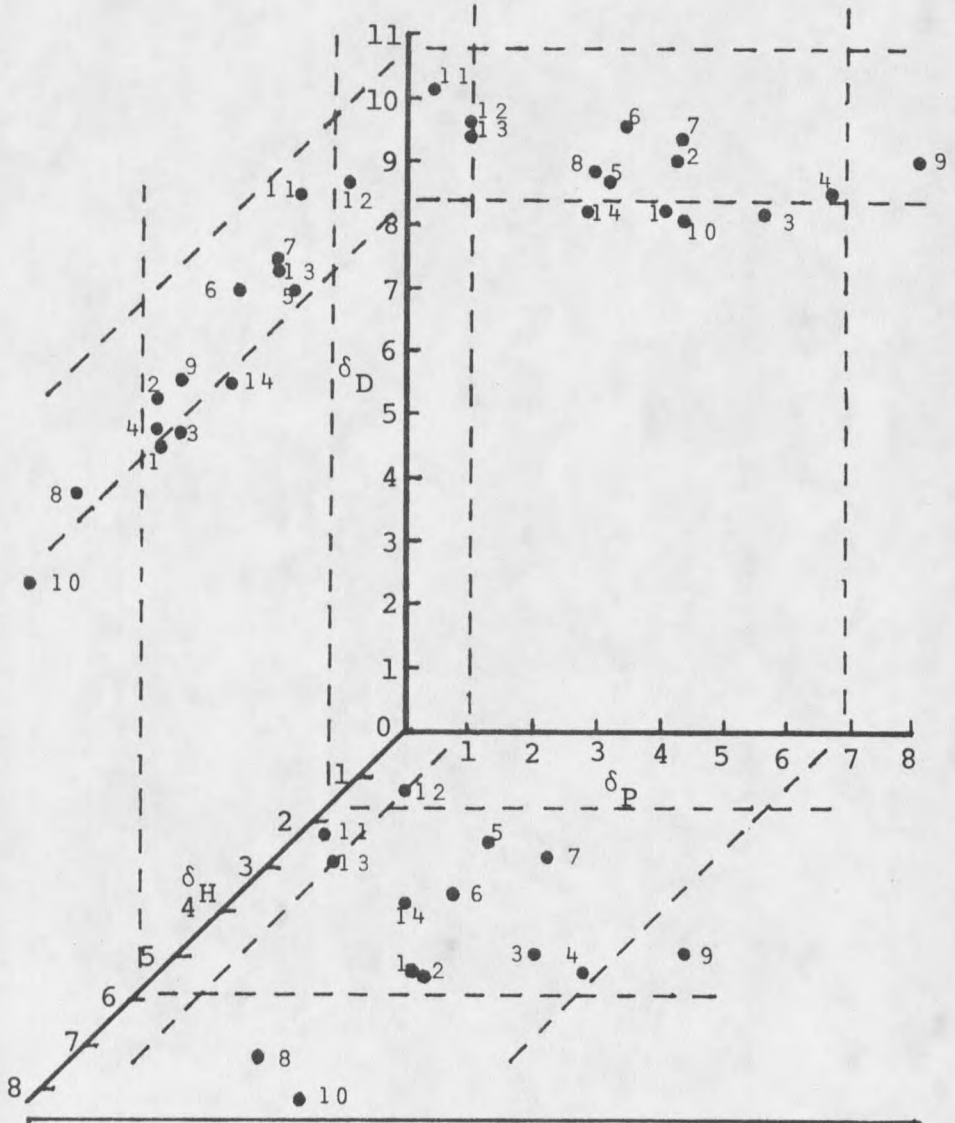


Figure 7. Component Solubility Parameter Plot for Solvent Blends.

an approximate range of effectiveness for δ_O can be abstracted as 9.8 < del0 < 11.0. The upper effective range bounds on δ_D and δ_P shown in Figure 7 were determined by applying $\delta_O^2 = \delta_D^2 + \delta_P^2 + \delta_H^2$ and the approximate minimum effective values observed for δ_D, δ_H, δ_O, and δ_P (eg. $\delta_{Dmax}^2 = \delta_{Omax}^2 - \delta_{Pmin}^2 - \delta_{Hmin}^2$).

Figure 8 shows the same type of plot as Figure 7 with the upper and lower bounds on δ_D, δ_P, and δ_H determined from the blends plotted in Figure 7. In Figure 8 the δ_D, δ_P, and δ_H components for a variety of pure solvents are shown. Several interesting observations can be made from Figure 8. Of the solvents shown, only HMPA, quinoline, pyridine, acetone and DMF (dimethylformamide) lie clearly within the effectiveness range for all three components. However the δ_O values of acetone and DMF are below the lower boundary of 9.8 indicated by the solvent blends. The δ_O values for HMPA, quinoline and pyridine are in the effective range. Quinoline and pyridine are known effective solvents for coal. TMU, DMA (dimethylacetamide), and THF (tetrahydrofuran) are all located on the lower effectiveness boundary of δ_D, suggesting that blending with a higher δ_D solvent, such as HMPA or an aromatic solvent, might be useful in improving their dissolving power for coal. DMSO (dimethylsulfoxide), EDA (ethylene



1 TMU	8 phenol
2 HMPA	9 dimethylsulfoxide
3 dimethylacetamide	10 ethylenediamine
4 dimethylformamide	11 1-me-napthalene
5 acetone	12 tetralin
6 quinoline	13 napthalene
7 pyridine	14 tetrahydrofuran

Figure 8. Component Solubility Parameter Plot for Various Solvents.

diamine), alcohols, and most hydrocarbons are contraindicated as effective by Figure 8.

The preceeding discussion has centered around distincting between "effective" and "ineffective" solvents. Figures 9-12 show that some more definite correlations can be observed between amount of dissolution and solubility parameters. The isopropyl alcohol blends are not included in Figures 9-12 because they were conducted at 200°F and can not be compared to the 320°F experiments. Figure 9 indicates a definite trend relating δ_H and dissolution. The trend with respect to δ_P, shown in Figure 10, is not so definite, though it appears there may be a sharp lower boundary on δ_P for effectiveness. Figure 11 shows no apparent correlation between δ_D and dissolution. It seems there may be an important lower bound on δ_D, above which there is no correlation. Figure 12 indicates, with the exception of the pure tetralin point, a fairly well defined correlation between dissolution and δ_O may exist. The tetralin point in Figure 12 can be explained by exclusion due to its δ_H value, which emphasizes again that both overall and component solubility parameter values have to be considered if the solubility parameter approach is to be useful.

If the solubility parameter does apply rigorously to solvent extraction of coal, then a number of other solvent

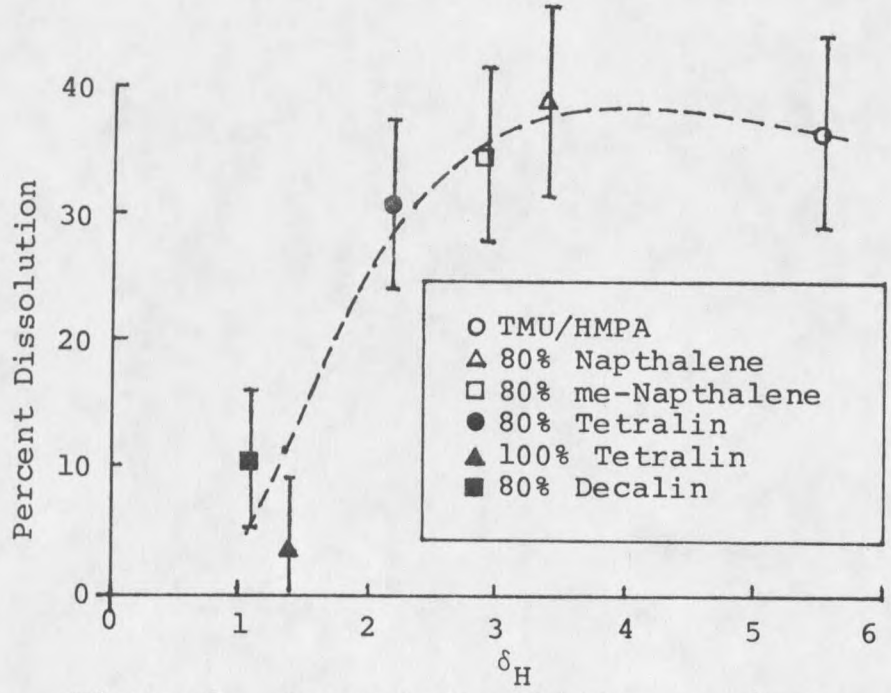


Figure 9. Percent Dissolution vs. δ_H for Solvent Blends at 320°F.

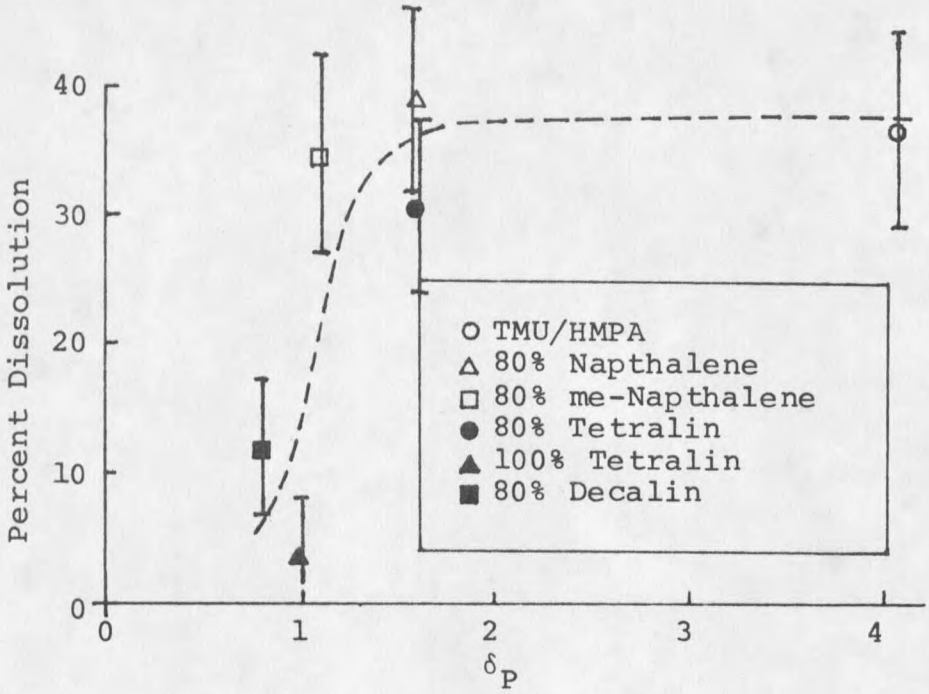


Figure 10. Percent Dissolution vs. δ_P for Solvent Blends at 320°F.

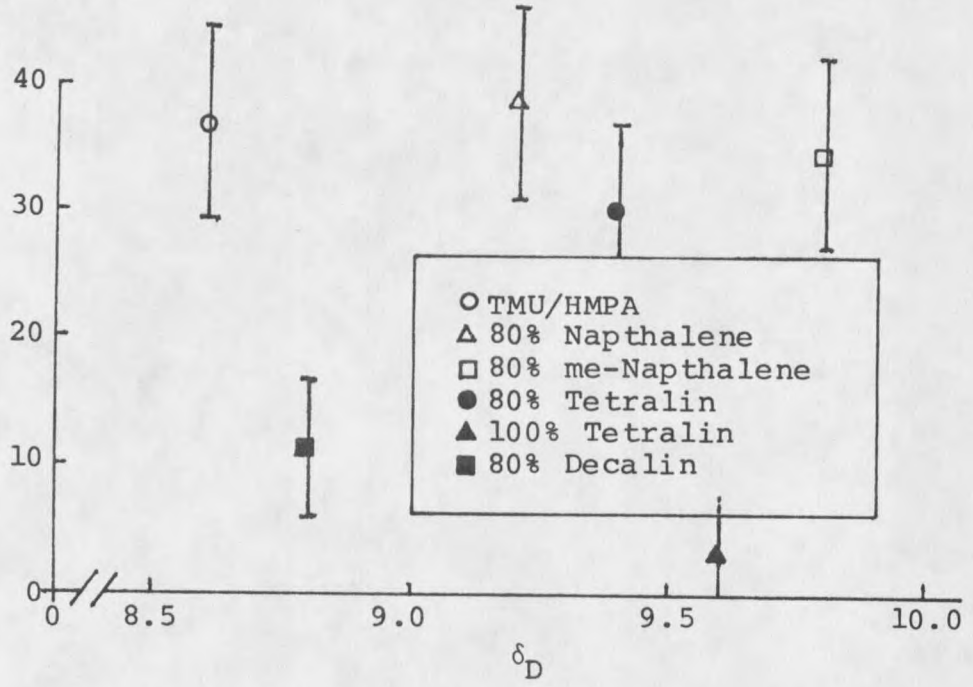


Figure 11. Percent Dissolution vs. δ_D for Solvent Blends at 320 °F.

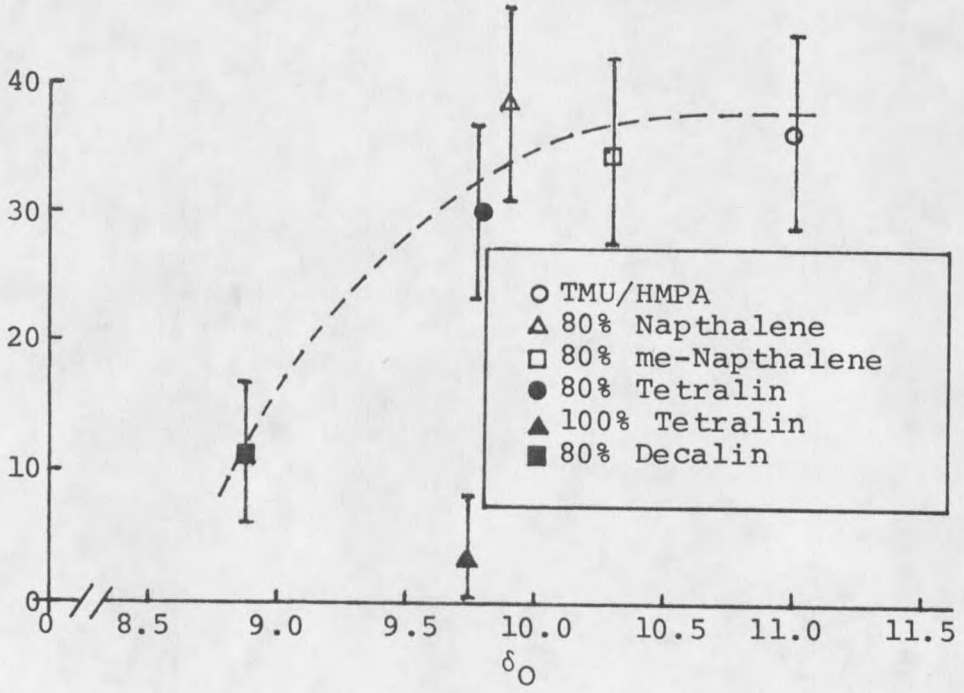


Figure 12. Percent Dissolution vs. δ_O for Solvent Blends at 320° F.

combinations with acceptable values could be proposed which should be as effective as TMU and HMPA blends. Further experimentation is needed using other solvent blends to see if the solubility parameter approach is adequate to explain the solvent action of TMU/HMPA, or if there is some other factor that makes TMU and HMPA rather unique relative to other solvents.

Snyder's polarity and selectivity parameters could also be used in a similar way to try to correlate the action of the solvent blends. However, in his scheme Snyder has intentionally thrown out dispersion interactions from his parameters because in many solvent-solute systems dispersion interactions "play little role in the selective interaction of the solvent with different solutes" [23]. Dispersions interactions might be expected to be important in coal systems, though, with coal structure being largely aromatic and aliphatic hydrocarbon. Hence the solubility parameter approach seemed more appropriate to apply, and Snyder's scheme was not considered further.

In summation, it should be remembered that the extraction of coal is probably not strictly a physical solvation process. There probably is at least weak chemical attack combined with physical and/or chemical stabilization. Therefore it is not surprising that traditional solvent behavior correlation schemes don't

appear to be entirely adequate. It could be that electron donor and acceptor properties correlate with chemical attack interactions; and solubility parameter, or some analogous scheme, correlates with the physical and/or chemical stablilization or solvation of product species.

Solvent Retention

Nitrogen contents of vacuum-dried residues resulting from extraction with TMU and HMPA made it clear that substantial retention of solvent or solvent fragments was occurring and masking true dissolution levels. Nitrogen balances were used, as described in the Experimental - Analytical Procedures section of this thesis, to calculate TMU and HMPA retention. Among the variables that might be expected to affect retention of TMU and HMPA are: extraction time, amount of dissolution, amount of other solvents in the blend, temperature, and details of the residue washing and drying procedure after extraction.

Figure 13 indicates that TMU/HMPA retention tends to decrease with increasing percent tetralin (decreasing percent TMU/HMPA). The data are for equal extraction time and temperature. However differences in level of dissolution and experimental variability could be accounting for some of the variability. Decreasing

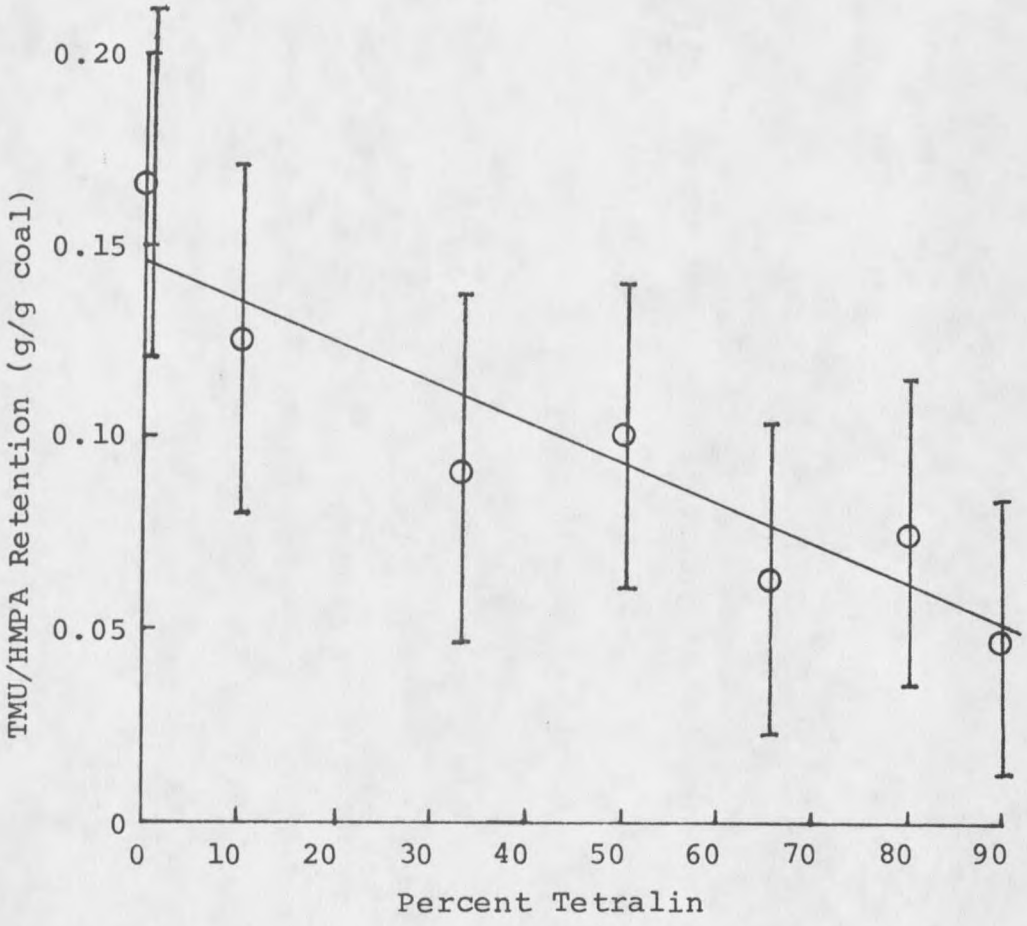


Figure 13. Effect of Tetralin on TMU/HMPA Retention. Temp=320°F, time is 1 hr.

TMU/HMPA retention with decreasing percent TMU/HMPA in the blend seems reasonable if both tetralin and TMU/HMPA are adsorbing and competing for adsorption sites. Significant tetralin retention does apparently occur and is discussed later.

Higher extraction temperature also seems to be correlated with TMU/HMPA retention, as shown in Table 11. In all but one case, TMU/HMPA retention increased with increasing temperature. Note should be made that temperature and dissolution level are highly interrelated and, though data trends can be observed, no conclusions with respect to functional relationships can be made based on these data. However it is certainly reasonable that with increasing temperature, more chemical interactions become energetically feasible for TMU/HMPA, and more retention would be expected.

The highly interrelated nature of extraction time and level of dissolution makes the separate effects of these variables on TMU/HMPA retention difficult to observe. A statistical analysis of data from ten 80% tetralin blend experiments conducted at 320°F was done, and correlations between TMU/HMPA retention and apparent dissolution, extraction time, 1/time, 1/dissolution, and exp(-time) were tested. Apparent dissolution was chosen because

total dissolution values already have solvent retention included in them.

Table 11. Temperature Effect on TMU/HMPA Retention

Experiment (solvent,time)	Sol Ret* at 200°F (Run#)	Sol Ret* at 255°F (Run#)	Sol Ret* at 320°F (Run#)
80% tet, 10 min	0.0058 (T40)	0.0569 (T37)	0.0776 (T23) 0.1335 (T31)
80% tet, 5 min		0.0553 (T36)	0.0614 (T24) 0.1134 (T32)
80% tet, 1 hr	0.0487 (T21)		0.0750 (T10)
65% tet, 1 hr	0.0717 (T22)		0.0641 (T15)
10% tet, 1 hr	0.0878 (T6)		0.1251 (T9)
33% tet, 1 hr	0.0572 (T4)		0.0911 (T8)
TMU/HMPA, 1 hr	0.0703 (#20)** 0.0619 (#27)**		0.1657 (T19)
TMU/HMPA, 5 min	0.0117 (T41)		0.2109 (T26)

* Solvent retention in g(TMU/HMPA) retained per g coal.
**Runs conducted by coworker C. Ichioka.

Alone, apparent dissolution has the strongest correlation with TMU/HMPA retention, with a coefficient of determination (R^2) of 0.35 (indicating that 35% of the variability in solvent retention values can be accounted for by regression on apparent dissolution). The variable 1/dissolution also correlates fairly well but is not significant if apparent dissolution effect is first included in the regression. A plot of the solvent

retention vs. apparent dissolution for the ten 80% tetralin experiments at 320°F is presented in Figure 14. There appears to be, and the regression analysis indicates, a slight downward slope. However the error bars in Figure 14 caution against making a definite conclusion.

Of the three time variables, none had a significant correlation alone with TMU/HMPA retention, but extraction time adds somewhat to the ability to correlate TMU/HMPA retention of a model already containing the apparent dissolution. R^2 for apparent dissolution and time together was 0.52 . The replicate experiments presented in Table 5 and discussed in the Experimental - Error and Reproducibility section of this thesis indicate that large variability in the TMU/HMPA retention values due to experimental error and inconsistency occurs. This variability is reflected in the error bars in Figure 14. If this potentially controllable experimental variability in TMU/HMPA retention values is included in a regression analysis, all remaining variability can be explained by correlation with apparent dissolution (ie. TMU/HMPA retention correlates with apparent dissolution with an R^2 value of 1.0).

It makes sense that, if dissolution is occurring as a result of TMU/HMPA attack, more dissolution would indicate more attack and, hence, probably more retention.

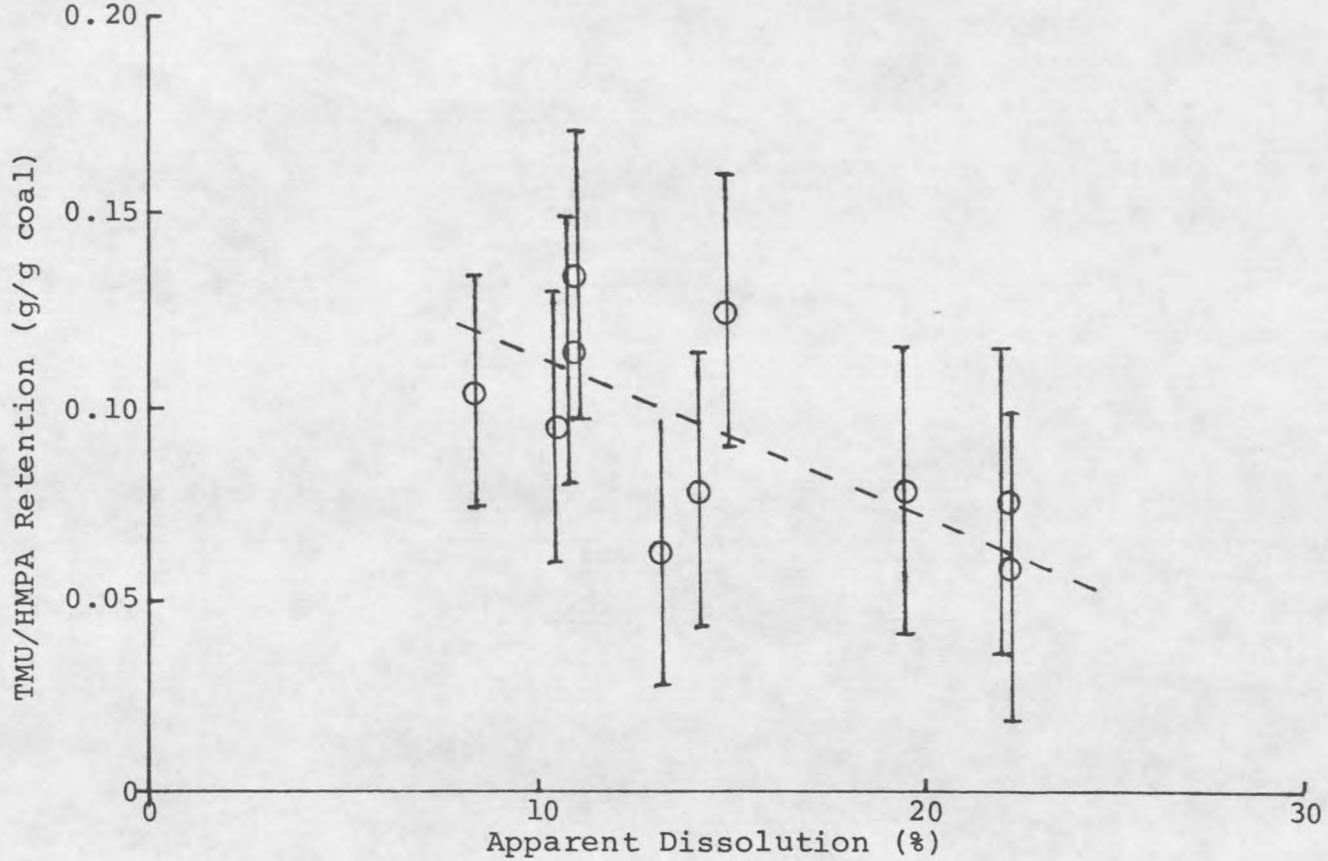


Figure 14. TMU/HMPA Retention vs. Apparent Dissolution. 80%-tetralin 20%-TMU/HMPA blend, temp=320 °F.

Time might be an important factor for very slow reactions (hence important especially at longer times), for mass transfer-limited situations, or for mass transfer, unsteady state situations, such as might occur at very short time.

Several room temperature pyridine extractions were done on coal and extraction residues. The results from these experiments, given in Table 12, allow for some interesting but contradictory observations about TMU/HMPA retention.

Table 12. Pyridine Extraction Results, Room temperature for 1 hr.

Run	Solid	Before %N	Before H/C	After %N	After H/C	App. Diss. (%)	Rel. Extract Color
PE1	Kittaning coal	1.34	0.795	2.16	0.81	-3.10*	dark
PE2	T19 Residue (TMU/HMPA run)	5.76	1.08	2.94	0.87	8.86	very light
PE3	T11 residue (pure tet run)	1.58	0.80	2.07	0.80	7.16	fairly dark
PE4	T10 residue (80% tet run)	3.42	0.90	2.76	0.85	10.39	light

* true dissolution = 2.25% calculated by subtracting pyridine retention, which was calculated as in the previous TMU/HMPA retention.

As expected the pyridine extractions on coal and on pure tetralin extracted residue gave the darkest extracts. Pyridine extraction of the coal resulted in an apparent weight gain and, accounting for pyridine retention, a true dissolution of 2.25%. Therefore PE3 would be expected to have less, and PE2 and PE4 much less, than 2% new material dissolved. The substantial weight losses that occured in PE2, PE3 and PE4, then, must be due to a net solvent displacement. The decrease of H/C ratio observed after pyridine extraction on Runs PE2, PE3 and PE4 also indicate displacement of higher H/C ratio material by lower H/C ratio material. The H/C results agree with the notion of pyridine displacing or washing out tetralin and TMU/HMPA (for tetralin H/C = 1.20, for TMU/HMPA H/C = 2.67, and for pyridine H/C =.985).

Rigorous mass balances are not possible without more knowledge about the nature of the extracted material and the relative amounts of retention of the various solvents. As a basis for mass balances on the pyridine extractions it was assumed that all retained TMU/HMPA in the residue before extraction (calculated as described previously) is removed during the extraction and that surplus nitrogen left in the residue after pyridine extraction is due to pyridine. Based on this assumption C, H, N and overall

mass balances were done for Runs PE2, PE3 and PE4. Results of the mass balances are given in Table 13.

More sophisticated attempts at mass balances were also made, but the problem of too many unknown elements made any results highly speculative. The data in this work are insufficient to make any final conclusions about the solvent retention, but several observations should be made. It appears that tetralin retention on the order of 8-10% may be occurring for extraction at 320°F. However H/C ratios from pure tetralin extraction residues aren't high enough relative to the parent coal to indicate that much retention, contradicting the pyridine extraction extraction results. Carbon and overall balances agree fairly well with all of the solvent retention assumptions that have been made in the various calculations. The hydrogen balances however show significant mass balance discrepencies. The hydrogen balances indicate that less net hydrogen is being removed from the residues during pyridine extractions than would be as determined by the TMU/HMPA and pyridine retention assumptions.

Based on carbon, hydrogen and nitrogen mass balance contradictions, and some anomalous H/C ratios observed for residues after extraction, it is suggested that the initial TMU/HMPA retention assumptions may be at least partially erroneous. That is, it could be that TMU/HMPA

Table 13. Mass Balance Results for Pyridine Extractions

Run	Mass Balance Results
PE2	TMU/HMPA removed = 0.2034 g/g initial material pyridine retained = 0.0944 g/g ititial material overall balance: 2% lower than measured C balance: 0.5% lower than measured H balance: 4.3% lower than measured
PE3	TMU/HMPA removed* = 0.0121 g/g initial material pyridine retained = 0.0356 g/g initial material overall balance: indicates tetralin retained + newly dissolved product = 9.5% of initial wt. assuming 2% newly dissolved product and 7.5% retained tetralin, and product %C = 78% and %H = 5.3% as determined from analyses on antisolvent separated product: C balance: 1.1% higher than measured H balance: 4.7% lower than measured
PE4	TMU/HMPA removed = 0.0947 g/g initial material Pyridine retained = 0.0732 g/g initial material Overall balance: indicates tetralin removed = 8.25% of initial wt. C balance: 0.6% lower than measured H balance: 11% lower than measured

* No TMU/HMPA should be present in the pure tetralin extracted residue, but nitrogen levels indicated that some nitrogen containing solvent must have been picked up while in the drying dessicator with other samples.

aren't retained in approximately a 50:50 ratio, or it could be that solvent fragments are being retained rather than entire solvent molecules. It is also possible that, the washing procedure not being rigidly standardized, either TMU or HMPA might be preferentially washed out, resulting in preferential retention in the residue. For TMU H/C=2.40, for HMPA H/C=3.00 and for tetralin H/C=1.20. The relative amounts of solvent retention could clearly affect the resultant residue H/C ratio.

Erratic H/C ratios were observed mainly for runs in the 0-10 minute time range. It is possible that at short time the mass transfer of product-solvent complex out of the solid may be restricted . This would result in higher amounts of product material being retained, along with solvent, for short runs than for long runs. If this was not adequately washed out, the H/C ratio would be affected, since only nitrogen containing solvent is accounted for in calculation of the final residue H/C ratios.

SUMMARY

1. Dissolution to more than 41% can be obtained using 33% tetralin blended with 67% TMU/HMPA with Kittaning coal at 320°F, compared to a maximum of 40.7% which was observed for unblended TMU/HMPA.
2. Aromatic/hydroaromatic solvents can be blended in amounts up to 80% by volume with TMU/HMPA without significantly changing dissolving power.
3. Blending tetralin with TMU/HMPA reduces the apparent dissolution rate.
4. Dissolution with TMU/HMPA and 80% tetralin blended with TMU/HMPA at 320°F is substantially complete at 5 minutes, and any subsequent reaction proceeds with low activation energy and a slow increase or even a decrease in the amount dissolved.
5. Blending TMU/HMPA with 80% tetralin helps prevent the pronounced decrease in the amount dissolved that occurs with unblended TMU/HMPA at 320°F and extraction time greater than 20 minutes. Similar behavior would presumably occur with other aromatic/hydroaromatic solvents.

6. Isopropyl alcohol blended with TMU/HMPA in amounts greater than 10% results in a dramatic decrease in the dissolving ability for coal.
7. Non-aromatic hydrocarbon solvents decalin and limonene, when blended with TMU/HMPA in the amount of 80%, resulted in a significantly lower dissolving power for coal compared to unblended TMU/HMPA.
8. The three-component solubility parameter concept shows some promise for correlating effectiveness of solvents and solvent blends on coal. When both overall and component solubilities were considered, this approach was useful in helping to correlate the dissolution effectiveness of solvent blends tested. The hydrogen bonding component appeared to be especially important.
9. Substantial retention of TMU, HMPA and tetralin, and presumably other similar solvents, occurs in the extraction residue. TMU/HMPA retention in the residue is on the order 5-20% by weight and tetralin retention of 8-10% in the residue was indicated for pure tetralin extraction at 320 F.
10. TMU/HMPA retention in the residue apparently: increases with increasing temperature, decreases with amount of aromatic/hydroaromatic solvent in the blend, and decreases with increasing dissolution and extraction time.

RECOMMENDATIONS FOR FUTURE RESEARCH

1. A rigorous mass balance study on the extraction process would be useful. This would require development of a better solvent-product separation scheme, measurement of solvent recovery efficiency to support solvent retention assumptions, elemental analyses of the product material, and more standardized residue washing and drying procedures. Retention of wash liquids might also be considered.
2. The possibility of mass transfer limitations could be investigated by experiments with different particle sizes and, possibly, the use of SEM photography to observe the effect of reaction on the outside surface.
3. More sophisticated analytical techniques, perhaps such as ESR spectroscopy, might be employed to detemine if free radical species are involved in the dissolution reaction or are present in solvated species.
4. More types of solvents blends could be tried to further evaluate the applicability of the solubility parameter concept to solvent action on coal. In particular, other solvents whose solubility parameter

values fall within the acceptable ranges indicated by these experiments might be tried.

5. Electron donor and acceptor numbers might be investigated as a scheme, or as a supplement to other schemes, to account for the action of TMU/HMPA blends on coal.

NOMENCLATURE

A.C.....ash content, weight fraction
AN.....electron acceptor number; AN , of solvent
App Diss...apparent dissolution, %
B.P.....boiling point, degrees as noted
°C.....degrees Centigrade
cal.....calories
cm.....centimeter
Diss.....dissolution, total dissolution, %
DN.....elecron donor number; DN , of solvent
°F.....degrees Fahrenheit
Filt.....filtration
g.....grams
H/C.....molar hydrogen-carbon ratio, mol/mol
ΔH.....enthalpy, kcal/mol
hr.....hours
i-pr-OH....isopropyl alcohol
kcal.....kilocalories
M.P.....melting point, degrees as noted
M.W.....molecular weight
me-.....methyl
min.....minutes
napth.....napthalene
P'.....Snyder's "polarity" or chromatographic strength parameter
R.....degrees Rankine
R^2.....statistical coefficient of determination
Res.....residue
Sol Ret....solvent Retention
Solv.....solvent
Temp.....temperature, degrees as noted
tet.....tetralin
Wt.....weight, g
x_d.....fraction of P' contributed by proton donating action, measured by interaction with dioxane
x_e.....fraction of P' contributed by proton accepting action, measured by interaction with ethanol
x_n.....fraction of P' contributed by strong dipole action, measured by interaction with nitromethane
Z.....g dissolved/g coal (ash containing basis) as determined assuming equal %N in coal and solvent-free residue

Z'.....g dissolved/g coal (ash containing basis) as determined form some assumption other than equal %N in coal and residue

δ.....Hildebrand's solubility parameter, $(cal/cm^3)^{\frac{1}{2}}$
δ_D.....dispersion component solubility parameter, $(cal/cm^3)^{\frac{1}{2}}$
δ_H.....hydrogen bonding component solubility parameter, $(cal/cm^3)^{\frac{1}{2}}$
δ_{mixt}.....solubility parameter for a mixture, $(cal/cm^3)^{\frac{1}{2}}$
δ_O.....overall solubility parameter $(cal/cm^3)^{\frac{1}{2}}$
δ_P.....polar component solubility parameter, $(cal/cm^3)^{\frac{1}{2}}$
$\delta+$.....partial positive charge density
$\delta-$.....partial negative charge density
ϕ_i.....volume fraction of component i

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APPENDICES

APPENDIX A

RAW DATA FROM EXTRACTION EXPERIMENTS

Table 14. Raw Data from Extraction Experiments.

Run #	Coal Wt (g)	Res Wt (g)	Temp† (Var) (F)	Solvent	Diss Time (min)	Residue %N	Residue %C	Residue %H	Filt Time (min)
T1	4.0275	3.9683	200 (3)	100% Tet	60	1.37	74.41	4.95	5-10
T2	3.8892	3.6309	200 (10)	Tet/HMPA 50/50	60	2.12	72.27	5.01	45
T3	4.0177	3.8810	200 (12)	Tet/TMU 50/50	60	1.89	74.73	5.14	20
T4	3.9248	3.4093	200 (10)	33% Tet	60	2.79	71.04	5.12	-
T5	3.9177	3.8464	200 (2)	33% i-pr-OH	60	1.71	76.34	5.20	10
T6	3.9351	3.3900	200 (10)	10% Tet	60	3.60	70.30	5.41	15-20
T7	4.0284	3.7705	200 (8)	10% i-pr-OH	60	2.64	73.86	5.30	15
T8	3.9234	2.7994	320 (4)	33% Tet	60	4.18	67.19	5.30	10

Table 14--Continued

Run #	Coal Wt (g)	Res Wt (g)	Temp† (Var) (F)	Solvent	Diss Time (min)	Residue %N	Residue %C	Residue %H	Filt Time (min)
T9	3.8958	3.0021	320 (8)	10% Tet	60	4.96	66.68	5.62	15-20
T10	3.8704	3.0933	320 (6)	80% Tet	60	3.42	71.23	5.40	-
T11	4.0083	3.9339	320 (4)	100% Tet	60	1.58	77.24	5.18	10
T12	4.0811	2.8002	320 (2)	80% Napth	60	2.61	67.62	4.98	10-15
T13	3.9945	3.5187	320 (10)	90% Tet	60	2.53	73.85	5.37	5
T14	4.0188	3.0063	320 (12)	80% 1-Me-Napth	60	3.22	69.53	5.36	10
T15	4.0158	3.1785	320 (10)	64% Tet	60	3.13	69.81	5.27	5-10
T16	3.9864	3.2864	320 (2)	50% Tet	60	4.06	68.14	5.54	5-10

Table 14--Continued

Run #	Coal Wt (g)	Res Wt (g)	Temp† (Var) (F)	Solvent	Diss Time (min)	Residue %N	Residue %C	Residue %H	Filt Time (min)
T17	4.0076	3.6232	320 (6)	80% Tet	20	3.65	71.21	5.61	-
T18	4.0392	3.3200	320 (5)	80% Tet	40	3.44	71.13	5.36	3
T19	4.0393	3.3595	320 (12)	TMU/HMPA	60	5.76	64.87	5.85	5
T20	3.9827	3.1766	320 (13)	80% Tet	120	2.98	68.63	5.02	5
T21	4.0007	3.8076	200 (8)	80% Tet	60	2.46	71.97	5.16	10
T22	3.9821	3.6652	200 (12)	65% Tet	60	3.06	71.14	5.26	5-10
T23	3.9911	3.5074	320 (8)	80% Tet	10	3.24	63.91	5.02	2-3
T24	3.9757	3.5277	320 (4)	80% Tet	5	2.81	68.20	5.09	2-3

Table 14--Continued

Run #	Coal Wt (g)	Res Wt (g)	Temp† (Var) (F)	Solvent	Diss Time (min)	Residue %N	Residue %C	Residue %H	Filt Time (min)
T26	4.0266	3.4046	320 (6)	TMU/HMPA	6	6.94	64.39	6.30	5
T28	4.1211	3.9432	320 (0)	80% Dec	60	2.73	74.59	5.42	-
T30	4.0763	3.5231	320 (30)	80% Tet	270	4.58	69.11	5.70	-
T31	4.0595	3.6526	320 (4)	80% Tet	10	4.67	70.20	5.83	4
T32	3.9005	3.5090	320 (8)	80% Tet	5	4.17	72.10	5.76	3.5
T33	3.9842	3.2409	320 (8)	TMU/HMPA	20	6.50	66.28	6.20	4.5
T34	3.9809	4.1285	65 (-)	100% Tet	60	1.77	77.85	5.25	15
T35	3.9873	3.6851	320 (2)	80% Tet	3	3.84	72.20	5.75	2.5

Table 14--Continued

Run #	Coal Wt (g)	Res Wt (g)	Temp† (Var) (F)	Solvent	Diss Time (min)	Residue %N	%C	%H	Filt Time (min)
T36	3.9772	3.8016	255 (5)	80% Tet	4	2.64	75.32	5.46	4
T37	4.0004	3.7294	255 (12)	80% Tet	11	2.71	75.00	5.4?	4
T38	4.0491	3.5256	320 (3)	TMU/HMPA	3	6.25	67.23	6.23	3.5
T40	3.9771	3.6840	200 (2)	80% Tet	9	1.48	77.22	5.16	18
T41	4.0312	3.5244	200 (3)	TMU/HMPA	9	1.64	75.76	5.07	15
12*	4.0015	3.8350	200 (2)	TMU/HMPA	60	2.96	70.18	5.18	
13*	3.9919	3.8735	200 (5)	TMU/HMPA	40	2.86	68.89	5.05	
14*	4.0082	3.9560	200 (2)	TMU/HMPA	20	2.25	71.29	4.93	

Table 14--Continued

Run #	Coal Wt (g)	Res Wt (g)	Temp† (Var) (F)	Solvent	Diss Time (min)	Residue %N	Residue %C	Residue %H	Filt Time (min)
15*	3.9848	3.2334	200 (6)	TMU/HMPA	720	4.67	66.00	5.39	
19*	2.9538	2.8289	200 (3)	TMU/HMPA	20	2.78	74.43	5.26	
20*	3.0139	2.5219	320 (5)	TMU/HMPA	20	5.12	63.19	5.43	
27*	4.0077	3.7679	200 (6)	TMU/HMPA	60	2.79	72.15	5.36	
28*	3.9869	3.4422	320 (5)	TMU/HMPA	720	4.68	60.82	5.00	
29*	3.9979	3.9461	200 (5)	TMU/HMPA	2880	5.90	67.40	5.93	
33*	3.9970	3.7521	82 (1)	TMU/HMPA	2880	1.58	76.33	5.44	
34*	3.9959	3.2505	200 (5)	TMU/HMPA	720	3.17	73.66	5.67	

Table 14--Continued

Run #	Coal Wt (g)	Res Wt (g)	Temp† (Var) (F)	Solvent	Diss Time (min)	Residue %N	Residue %C	Residue %H	Filt Time (min)
36*	3.9881	3.2797	320 (3)	TMU/HMPA	40	6.11	62.03	5.62	3
37*	3.9784	3.2407	320 (2)	TMU/HMPA	10	5.70	64.53	5.62	3
102**	3.9676	3.7471	320	80% limonene	60	2.39	77.81	5.40	

† Value in parentheses is maximum variation from desired temp observed.
* Experiment conducted by Christina Ichioka.
** Experiment conducted by coworker I Hsing Tsao.

APPENDIX B

RAW RESULTS FROM EXTRACTION EXPERIMENTS

Table 15. Raw Results from Extraction Experiments.

Run #	Solvent	Temp (F)	Diss Time (min)	Total Diss* (%)	Solvent Retention* (g/g coal)	Solvent Free Residue*			
						%N	%C	%H	H/C
T1	100% Tet	200	60	1.90	-	1.31	74.49	4.94	.79
T2	Tet/HMPA (50/50)	200	60	11.04	0.0342	1.31	73.49	4.82	.78
T3	Tet/TMU (50/50)	200	60	6.43	0.0246	1.31	75.32	5.00	.79
T4	33% Tet	200	60	20.70	0.0572	1.31	72.82	4.76	.78
T5	33% i-pr-OH	200	60	3.92	0.0175	1.31	76.89	5.11	.79
T6	10% Tet	200	60	24.84	0.0878	1.31	73.08	4.86	.79
T7	10% i-pr-OH	200	60	13.10	0.0554	1.31	75.62	4.99	.79
T8	33%Tet	320	60	41.45	0.0911	1.31	70.32	4.57	.77
T9	10% Tet	320	60	38.92	0.1251	1.31	70.73	4.72	.80

Table 15--Continued

Run #	Solvent	Temp (F)	Diss Time (min)	Total Diss* (%)	Solvent Retention* (g/g coal)	Solvent Free Residue* %N	%C	%H	H/C
T10	80% Tet	320	60	30.27	0.0750	1.31	73.86	4.90	.79
T11	100% Tet	320	60	3.33	-	1.31	77.62	5.12	.79
T12	80% Napth	320	60	38.81	0.0397	1.31	68.96	4.66	.80
T13	90% Tet	320	60	18.32	0.0478	1.31	75.46	5.09	.80
T14	80% 1-Me-Napth	320	60	34.63	0.0636	1.31	71.73	4.90	.81
T15	64% Tet	320	60	29.92	0.0641	1.31	71.92	4.83	.80
T16	50% Tet	320	60	30.35	0.1009	1.31	71.25	4.88	.82
T17	80% Tet	320	20	20.86	0.0941	1.31	74.16	5.07	.81
T18	80% Tet	320	40	28.09	0.0779	1.31	73.78	4.85	.78
T19	TMU/HMPA	320	60	36.55	0.1646	1.31	69.57	4.76	.82
T20	80% Tet	320	120	28.72	0.0593	1.31	70.46	4.60	.78
T21	80% Tet	200	60	10.64	0.0487	1.31	73.38	4.88	.79

Table 15--Continued

Run #	Solvent	Temp (F)	Diss Time (min)	Total Diss* (%)	Solvent Retention* (g/g coal)	Solvent Free Residue*			
						%N	%C	%H	H/C
T22	65% Tet	200	60	16.60	0.0717	1.31	73.28	4.84	.79
T23	80% Tet	320	10	23.08	0.0776	1.25	65.66	4.51	.82
T24	80% Tet	320	5	20.21	0.0614	1.25	69.86	4.70	.80
T26	TMU/HMPA	320	6	39.85	0.2109	1.34	70.56	4.98	.84
T28	80% Dec	320	60	11.17	0.0592	1.34	76.49	5.10	.79
T30	80% Tet	320	270	28.41	0.1247	1.34	73.04	4.93	.80
T31	80% Tet	320	10	25.49	0.1335	1.34	74.45	5.06	.80
T32	80% Tet	320	5	23.32	0.1134	1.34	75.89	5.11	.80
T33	TMU/HMPA	320	20	40.74	0.1870	1.34	72.31	4.98	.82
T34	100% Tet	65	60	-.98	-	1.34	77.90	5.22	.80

Table 15--Continued

Run #	Solvent	Temp (F)	Diss Time (min)	Total Diss* (%)	Solvent Retention* (g/g coal)	Solvent Free Residue* %N	%C	%H	H/C
T35	80% Tet	320	3	19.49	0.1029	1.34	75.51	5.19	.82
T36	80% Tet	255	4	10.85	0.0553	1.34	77.13	5.17	.80
T37	80% Tet	255	11	13.59	0.0569	1.34	76.90	5.10	.79
T38	TMU/HMPA	320	3	34.87	0.1904	1.34	73.23	5.10	.83
T40	80% Tet	200	9	8.67	0.0058	1.34	77.42	5.15	.79
T41	TMU/HMPA	200	9	14.99	0.0117	1.34	76.17	5.00	.78
12 †	TMU/HMPA	200	60	12.57	0.0703	1.31	72.10	4.78	0.79
13 †	TMU/HMPA	200	40	10.85	0.0669	1.31	70.59	4.66	0.79
14 †	TMU/HMPA	200	20	6.10	0.0413	1.31	72.40	4.70	0.77
15 †	TMU/HMPA	200	720	34.23	0.1212	1.31	69.52	4.53	0.78
19 †	TMU/HMPA	200	20	11.59	0.0626	1.31	76.42	4.91	0.77

Table 15--Continued

Run #	Solvent	Temp (F)	Diss Time (min)	Total Diss* (%)	Solvent Retention* (g/g coal)	Solvent Free Residue* %N	%C	%H	H/C
20†	TMU/HMPA	320	20	33.71	0.1418	1.31	66.71	4.44	0.79
27†	TMU/HMPA	200	60	13.45	0.0619	1.31	74.00	5.01	0.81
28†	TMU/HMPA	320	720	29.40	0.1294	1.31	63.44	4.07	0.76
29†	TMU/HMPA	200	2880	23.70	0.2015	1.31	72.90	4.82	0.79
33†	TMU/HMPA	82	2880	7.96	0.0113	1.31	76.70	5.38	0.84
34†	TMU/HMPA	200	720	27.86	0.0673	1.31	76.16	5.26	0.82
36†	TMU/HMPA	320	40	41.21	0.1773	1.25	66.49	4.34	0.78
37†	TMU/HMPA	320	10	40.20	0.1608	1.25	69.13	4.48	0.77
102††	80% limonene	320	60	10.88	0.0442	1.34	79.38	5.16	0.77

* Calculated assuming equal N percentage in coal and solvent free residue.
† Experiment conducted by coworker C. Ichioka.
††Experiment conducted by coworker I. Tsao.

APPENDIX C

SAMPLE CALCULATIONS OF DISSOLUTION AND SOLVENT RETENTION

SAMPLE CALCULATIONS

The calculations used to determine the total dissolution, solvent retention, and "solvent free" residue properties, based on apparent weight loss, nitrogen content of the residue, and the solvent retention assumptions described in the Experimental section, are described below. Potential error in calculated total dissolution and solvent retention values due to error in the assumption of equal percent nitrogen in coal and solvent free residue is also discussed.

The description below parallels the sequence of calculations in the computer program used. A copy of the program is included for reference after the discussion. A nitrogen balance on the coal and residue, assuming the same percent nitrogen in coal and solvent free residue (hence also in the dissolved product), gives the following:

initial N in coal	-	N in dissolved product	=	N in solvent containing residue	-	N in residue due to solvent

or

$$\frac{(\text{Coal Wt})(\text{Coal \%N})}{100} - \frac{Z \times (\text{Coal Wt})(\text{Coal \%N})}{100} =$$

$$\frac{(\text{Res Wt})(\text{Res \%N})}{100} - \frac{[\text{Res Wt} - (1-Z)(\text{Coal Wt})](\text{Solv \%N})}{100}$$

where Z = g truly dissolved per g coal

Solving for Z gives:

$$Z = \frac{(\text{Coal Wt})(\text{Solv \%N}-\text{Coal \%N}) - (\text{Res Wt})(\text{Solv \%N}-\text{Res \%N})}{(\text{Coal Wt})(\text{Solv \%N} - \text{Prod \%N})}$$

If Product %N = Coal %N then:

$$Z = 1.0 - \frac{\text{Res Wt}}{\text{Coal Wt}} \times \frac{\text{Solv \%N} - \text{Res \%N}}{\text{Solv \%N} - \text{Coal \%N}}$$

From Z, the total % dissolved, put on an ash free basis is:

$$\%\ \text{Diss} = \frac{Z}{(1.0-\text{Ash Con})}$$

where Ash Con = Wt fraction ash in the coal

The solvent retention then is the difference between solvent containing and solvent free residue weights. Put on a per gram of initial coal basis this is:

$$\text{Ads Sol} = \frac{\text{Res Wt} - (1-Z)(\text{Coal Wt})}{\text{Coal Wt}} = \text{g solvent retained per g coal}$$

The C, N, and H in the solvent free residue were then calculated by subtracting the weight of each element due to retained solvent from the weight in the solvent containing residue. Dividing by the total solvent free residue weight then gives the percent of each in the solvent free residue.

Dry Res %N = Coal %N by assumption

$$\text{Dry Res \%C} = \frac{(\text{Res \%C})(\text{Res Wt}) - (\text{Ads Sol})(\text{Coal Wt})(\text{Solv \%C})}{(1-Z)(\text{Coal Wt})}$$

$$\text{Dry Res \%H} = \frac{(\text{Res \%H})(\text{Res Wt}) - (\text{Ads Sol})(\text{Coal Wt})(\text{Solv \%H})}{(1-Z)(\text{Coal Wt})}$$

Molar H/C is given by:

$$\text{H/C} = \frac{(\text{Dry Res \%H})(12.01115)}{(\text{Dry Res \%C})(1.00797)}$$

The solvent C, H and N percentages were calculated by assuming the retained solvents to be in the same volume ratio as they were in the blend. The pure solvent percentages were then appropriately weighted.

The potential effect of error in the assumption of equal N in coal and solvent-free residue on the dissolution and TMU/HMPA retention results can be determined by considering the complete expression for Z;

$$Z = \frac{(\text{coal Wt})(\text{Solv \%N-Coal \%N}) - (\text{Res Wt})(\text{Solv \%N-Res \%N})}{(\text{Coal Wt})(\text{Solv \%N-Prod \%N})}$$

If Z' = value determined without assuming Prod %N=Coal %N

and Z = value determined assuming Prod %N=Coal%N

$$\text{then } Z' = Z \frac{\text{Solv \%N - Coal \%N}}{\text{Solv \%N - Prod \%N}}$$

Example calculations of potential error:

1. If Prod %N = 2.0(Coal %N)
   Coal %N = 1.3
   Solv %N = 23.79 (50/50 TMU/HMPA)

   then: Z' = 1.06(Z) or true dissolution would be 6% higher than as determined by assuming equal %n in coal and product.

   Absolute error in TMU/HMPA retention, Ads Sol, would be Z'- Z = 0.06(Z)
   For Z = 0.20, error in Ads Sol = 0.012 g/g coal
   For Z = 0.40, error in Ads Sol = .0240 g/g coal

2. If Prod %N = 0.5(Coal %N)
   Coal %N = 1.3
   Solv %N = 23.79

   then: Z' = 0.97(Z) or true dissolution would be less than determined by assuming equal %N in coal and product

   Absolute error in Ads Sol would be 0.03(Z) g/g coal
   For Z = 0.20 error in Ads Sol = 0.006 g/g coal
   For Z = 0.40 error in Ads Sol = 0.012 g/g coal

Table 16. Fortran Program for Calculation of Total Dissolution, Solvent Retention and Solvent Free Residue Properties.

```
C  COALPN = COAL % NITROGEN
C  ASHCON = COAL ASH CONTENT (WT FRACTION)
C  SOLPN,SOLPC,SOLPH,SOLPO = SOLVENT % NITROGEN,CARBON,
C    HYDROGEN, AND OXYGEN
C  NRUN = RUN NUMBER
C  COALWT,RESWT = COAL, RESIDUE WEIGHT (G)
C  RESPN,RESPC,RESPH = RESIDUE % NITROGEN, CARBON,
C     HYDROGEN
C  DISS = TOTAL DISSOLUTION % (ASH FREE BASIS)
C  X = G DISSOLVED/G COAL
C  ADSSOL = SOLVENT RETENTION (G/G COAL)
C  PNDRY,PCDRY,PHDRY,HCDRY = % NITROGEN,CARBON,HYDROGEN,
     AND HYDROGEN/CARBON RATIO FOR SOLVENT FREE RESIDUE
C  POADS = PERCENT OXYGEN IN RESIDUE DUE TO SOLVENT
     RETENTION

4        K=2
1        WRITE(108,200)
         INPUT COALPN,ASHCON
         IF(K.EQ.1) GO TO 2
3        WRITE(108,300)
         INPUT SOLPN,SOLPC,SOLPH,SOLPO
2        WRITE(108,700)
         INPUT NRUN
         WRITE(108,100)
         INPUT COALWT,RESWT
         WRITE(108,400)
         INPUT RESPN,RESPC,RESPH
         X=1.-(RESWT/COALWT)*(SOLPN-RESPN)/(SOLPN-COALPN)
         CWTRES=RESPC*RESWT/100.
         HWTRES=RESPH*RESWT/100.
         ADSSOL=(RESWT-COALWT*(1.-X))/COALWT
         IF(ADSSOL.LE.0.) ADSSOL=0.
         DISS=X/(1.-ASHCON)
         IF(DISS.LE.0.) DISS=0.
         TWTDRY=COALWT*(1.-X)
         CWTDRY=CWTRES-ADSSOL*COALWT*SOLPC/100.
         HWTDRY=HWTRES-ADSSOL*COALWT*SOLPH/100.
         PNDRY=COALPN
         PCDRY=(CWTDRY/TWTDRY)*100.
         PHDRY=(HWTDRY/TWTDRY)*100.
         HCDRY=(PHDRY/1.00797)/(PCDRY/12.01115)
         POADS=ADSSOL*COALWT*SOLPO/RESWT
         OUTPUT NRUN,PNDRY,PCDRY,PHDRY,DISS,ADSSOL,HCDRY,POADS
         WRITE(108,500)
         INPUT L
         WRITE(108,600)
         INPUT K
         IF(L.EQ.1.AND.K.EQ.1) GO TO 2
         IF(L.EQ.1.AND.K.NE.1) GO TO 3
         IF(L.NE.1.AND.K.EQ.1) GO TO 1
         GO TO 4
100      FORMAT(X,'INPUT COAL WT (G),RESIDUE WT (G)')
200      FORMAT(X,'INPUT COAL PERCENT N,ASHCONTENT')
300      FORMAT(X,'INPUT SOLVENT PERCENT N,C,H,O')
400      FORMAT(X,'INPUT RESIDUE PERCENT N,C,H')
500      FORMAT(X,'ANOTHER RUN WITH SAME COAL?',/
       1 X,'1=YES   2=NO')
600      FORMAT(X,'SAME SOLVENT?')
700      FORMAT(X,'INPUT NRUN')
         END
```

APPENDIX D

TMU SOLUBILITIES

Table 17. Solubilities of Various Substances in TMU at 22°C. (g per 100 g of TMU) *

Aliphatic and cycloaliphatic compounds			
cyclohexane	c.m.	Acetamide	44.7
Methanol	c.m.	dimethylformamide	c.m.
Ethanol	c.m.	N-Methylpyrrolidone	c.m.
Ethyl acetate	c.m.	Urea	2.5
Acetone	c.m.	Chloroform	c.m.
Acetic acid	c.m.	Thiourea	7.2
Aromatic compounds			
Benzene, toluene, xylenes	c.m.	2,4-Dinitrotoluene	s.
Napthalene	s.	Benzoic acid	67
Phenanthrene	50	2-Aminobenzoic acid	85
Anthracene	3.8	1,2-Diaminobenzene	46
Phenol	c.m.	2-Aminophenol	40
Hydroquinone	40	Benzoquinone	60
Nitrobenzene	c.m.		
Heterocyclic compounds			
Tetrahydrofuran	c.m.	Pyridine	c.m.
Dioxane	c.m.	Benzimadazole	50

Macromolecular Substances		
High-pressure polyethylene	(75°C)	0.11
Polypropylene	(75°C)	0.14
Poly(vinyl chloride)	(22°C)	Swells and dissolves
Poly(vinylidene dicyanide)	(22°C).	sol.
Poly(acrylonitrile)	(175°C)	-
Viscose	(100°C)	-
Cellulose 2,5-acetate	(22°C)	sol.
Cellulose triacetate	(22°C)	sol.
Polymethacrylate	(22°C)	swells and dissolves
Polyester (Terylene)	(125°C)	5-10
Polycarbonate (BAYER)	(22°C)	swells and dissolves
Polyurethane(BAYER)	(175°C)	swells and dissolves
Bakelite	(175°C)	-
Polystyrene	(22°C)	ca.30

* Data obtained from A. Luttringhaus and H.W. Dirksen, Angew. Chem., Int. Ed. Engl., vol.3, no.4, p.264, (1964).