Basic Properties of Coals
and Other Solids

Final Report

for Three Years

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Edward M. Arnett, Principal Investigator

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Affiliation: Department of Chemistry
Duke University
Durham, North Carolina 27706
919-660-1558

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1. Introduction

From the perspective of this project, coals may be viewed as natural heteropolymers containing acidic and basic units both as components of the polymeric structural framework and as entrapped small organic molecules and mineral matter. A significant part of the chemistry of coals involves their acid-base interactions. For example, one may cite the interactions of acidic and basic units within the coal structure itself such as hydrogen-bonding interactions of coals with external acids and bases in natural ground waters or the interactions of acidic or basic extractants in coal processing. Some previous quantitative studies have reported the interactions of coals with solutions of various kinds of acids and bases using a variety of techniques (1-18).

One of the most fundamental classifications of chemicals, and of the materials derived from them, is through their behavior as acids or bases. Although this classification goes back to the age of alchemy, it remained for the Lewis-Langmuir theory of the electronic structure of molecules to provide a rigorous interpretation of acid-base behavior in terms of the fundamental basic unit of the electron pair. Correspondingly, an acid is anything which will react specifically with an electron pair by coordination. Lewis acids have an open orbital which can coordinate directly with electron pairs. The most ubiquitous Lewis acid is the proton which when transferred from one base to another is discussed in terms of Brönsted acid-base theory. It should be clear from the above that operationally one studies the behavior of acids through their interactions with bases and correspondingly of bases through their interactions with acids. When there is a significant interaction between Brönsted acids (proton donors) and electron pair bases, but it is not strong enough for

proton transfer to occur, the interaction is described as hydrogen-bonding. This plays an important role in coal structure and its disruption by swelling upon exposure to acidic or basic solvents (4).

This project has employed solution calorimetry as a general means for comparing the heats of interaction of a variety of coals from Exxon, the Argonne Coal Bank and Southern Clean Fuels Division of Southern Electric International at Wilsonville, AL with a series of acids of widely varied strengths. The previous grant (DE-FG22-85PC80521) compared many of the same coals through their interactions with a series of bases.

It is well known that solid acids and bases are much more complex than their liquid homogeneous solutions (19-25). In a solid there is usually a distribution of sites of different acidities/basicities and a wide variation in accessibility to those sites. In solution all sites are of comparable accessibility, except for steric factors, and they are equilibrated to a uniform average strength. An important theme of the present and previous grant has been the comparison of various well-characterized solid acids and bases with solutions bearing the same acidic and basic functionalities as their solid counterparts.

Of fundamental significance to the strategy of this program was a demonstration of a close correlation between the heats of interaction of solutions of p-toluenesulfonic acid and slurries of a sulfonic acid resin with a wide series of organic bases (26) (Figure 1). Again; the present project demonstrated a similar high correlation between the heats of interaction of slurries of polyvinylpyridine and solutions of pyridine with a series of acids of different strengths (Figure 2). These two correlations were crucial for demonstrating that the acid-base properties

of solids were not inherently so hopelessly complex that they cannot be elucidated by comparison with appropriate acid-base solution models.

The previous project dissected the heats of interactions of a series of coals into components that represented Brönsted acidity, hydrogen-bonding acidity and dispersion force interactions through comparison with the simple prototype solid acids: sulfonic acid resin, silica, and graphitized carbon black respectively (26-28). The present grant has emphasized the interaction of basic components in the coal with strong Brönsted acids and boron trichloride, a very strong Lewis acid, with a brief examination of the interactions of the coals with phenols as weaker hydrogen-bonding acids.

Consistent with our comparison of solid acid and bases with homogeneous solution analogues, we have also compared several coals with liquids derived from them at Wilsonville and Exxon.

Finally, we have examined the effect of citric acid washing on several coals using the technique described by Silbernagel et al. (29). In view of the presence of various inorganic bases such as carbonates and oxides in low rank coals, it is highly important to test the effect of their removal on the overall basic properties of coals as determined through their interaction with solutions of acids.

Taken together the present project and its predecessor have met their goals of relating some well-characterized solid acids and bases to solutions of simple homogeneous analogues bearing the same functionalities by thermochemistry. The same approach has been used to characterize a variety of coals and coal-derived liquids in terms of simpler prototype solids and liquids.

2. Experimental

a. Handling of coal samples

The coal samples were mostly obtained in sealed ampules from the Argonne Coal Bank. Each ampule was broken inside a Vacuum Atmospheres dry box under an argon atmosphere. Each sample was transferred to a glass jar, screwcapped and left stored in the dry box. Small amounts of coal samples (about 150 mg) were removed from the dry box in sample vials and outgassed at 110 °C in a vacuum oven for about 16 hours prior to each ΔH_{imm} measurement in the acid solutions.

The literature provided by Argonne stresses the point that the samples of some coals are highly susceptible to atmospheric oxidation if left exposed to air (30). It also recommends that the samples should be used immediately after opening the ampules. However, since it would be wasteful to open a fresh 5 g ampule for each ΔH_{imm} measurement, which only requires 100 mg of the sample, we believe that sealing the open ampule in a screw-capped container in the dry box should be adequate protection. We have checked this question for a variety of the samples studied during the course of this project. The majority of the average values taken from 2 or 3 measurements for a typical acid/coal system, sometimes covering 2-3 weeks, showed a standard deviation of < 5%. The coals obtained from Wilsonville and Exxon Engineering company were stored in screw-capped glass jars and were kept outside the dry box. However freshly outgassed samples were used for the calorimetric experiments.

Analysis of the coals and coal-derived liquids are given in Tables I and II.

Treatment of coals and coal liquids

All the coal samples were outgassed at 110 °C in a vacuum oven for about 12-14 hours prior to the heats of adsorption measurements. For each ΔH_{imm} experiment freshly outgassed samples were used in order to obtain reproducible results. The specific surface areas of the coal samples were determined by the Brunauer-Emmett-Teller (BET) method. A Quantachrome BET surface area analyser employing nitrogen as the adsorbing gas at 77 K, was used for this purpose. The coal liquids were stored in the dry box and were used as 5-10% solutions in purified acetonitrile.

Citric Acid Washing of the Coal Samples

Following the procedure of Silbernagel, Gebhard, Flowers and Larsen (29) five to ten g of the coal were placed in a 500 ml round-bottom flask. Under dry argon blanket 250 ml of 1 M aqueous citric acid solution was added. The mixture was refluxed for 24-30 hours under dry argon. The mixture was then cooled and filtered through a weighed and dried soxhlet thimble. The thimble and coal were charged with 250 ml of deionized water. The extraction was carried out until the siphon water was determined to be neutral using pH paper. The thimble containing the coal was dried in a vacuum oven for 24 hours at 110°C, cooled, transferred to a screwcapped glass jar and then stored in an argon-filled dry box. About 60-100 mg of this coal was used in each of the heat of immersion (ΔH_{imm}) experiments. The coal was stored in the dry box throughout the course of the experiments.

The whole washing procedure was repeated and further ΔH_{imm} experiments were conducted in order to observe the reproducibility of the data from batch to batch in addition to within a batch. The ΔH_{imm} values

reported for the citric acid washed coals are an average of 2 or 3 independent measurements.

b. Calorimetry

Several calorimeters were used in these studies for the direct determination of the heats of interaction of a wide variety of acids with the different samples of coal and coal liquids by titration and immersion calorimetry.

Titration calorimetry using the Tronac 450 calorimeter is the most desirable technique for comparing heats of interaction of strong acids or bases with solids provided that the exothermic heats of interaction are large enough and are released in a relatively short period of time (say less than two minutes). In these cases the results can be expressed in terms of kcal/mol since it is known exactly how many moles of acid or base are required to titrate the solid.

Titrametric heats of interaction are obtained, as the name implies, by titrating a solution of the acid into a stirred slurry of the basic solid or solution of the liquid base. This method measures the heat of interaction first of the most accessible and most basic sites of the solid with the acid, and then, after they are neutralized, subsequent increments of acid neutralize progressively weaker sites at progressively less accessible positions.

For cases where relatively small heats of interaction must be compared, and the total heat is given out over a long period (say one hour), heats of immersion (ΔH_{imm}) were measured with the Setaram C-80 heat flow calorimeter. It is a reliable but quite complicated instrument that was purchased under the previous DOE grant. For immersion calorimetry, in

contrast to titration calorimetry, it is more realistic to present results in cal g⁻¹ of solid base since there is no direct means of knowing how many moles of acid or base were actually involved in the interaction. The heat of immersion experiment involves the sudden release of the solid into an excess of liquid acid or its solution with an immediate neutralization of all readily accessible basic sites, both strong and weak, followed by the gradual neutralization of other sites as the liquid probes the less accessible sites on the solid. The important components that determine the shape of the heat of immersion thermogram are again the number and strength of the basic sites available at the surface, the porosity, the permeability of the solid, the extent to which it is swollen, and the degree to which the acidic and basic sites in the coal are involved in hydrogen-bonding with each other since hydrogen-bonding interactions must be broken endothermically in order to release any exothermic interaction. Figure 3 demonstrates that heats of immersion (ΔH_{imm}) may not correlate well with titration heats (ΔH_{imm}) because of the different times required for penetration and (perhaps) reaction with the solid.

c. The Setaram C-80 calorimeter

Heats of immersion were measured using this calorimeter which operates on the Tian-Calvet heat-flow principle (31). It consists of two identical and independent heat flow detectors which are surrounded by a heat conductive block whose temperature is controlled by a temperature programmer with temperature stability better than 0.1 °C. The digital output for both the thermal power and the temperature measurements provide direct data processing through a Hewlett-Packard 85 desktop computer. For a typical measurement, the inner cell containing 50-100 mg of coal sample

is installed with a cap on the mixing cell. About 1ml of mercury is placed in the cell to act as a barrier between the solid and liquid to prevent mixing prior to activating the reversing mechanism. The mixing cell is then filled with 2-3 ml of the reacting acid solution. The reference cell is prepared in an analogous manner but without the coal sample. The calorimeter is loaded with the cells and is left for 60-90 minutes to equilibrate. When the calorimeter has reached complete thermal equilibrium, the mixing is effected by actuating a mechanism which completely inverts the entire calorimetric assembly every 15 seconds. The inverting process is continued until the exotherm, as observed on the computer screen, has reached its maximum. Appropriately, the heats are expressed in terms of cal/g of coal samples. The calorimeter is calibrated by using heats of solution of potassium chloride in water at 25 °C and compared with the standard value of 4.20 kcal/mol (32).

d. The Tronac titration calorimeter

A Tronac 450 titration calorimeter was used to determine the titrametric heats of interaction of coal slurries and coal liquids. The titration run was performed by introducing an accurately known volume of the acid solution (0.60-0.70 M in acetonitrile) into a reaction vessel containing a continuously stirred coal liquid or a coal slurry (2 ml or 5 g in about 40 ml acetonitrile) of known volume, usually about 45 ml. An electrically motor-driven buret was used for this purpose which was precalibrated for its delivery rate, i.e., the amount delivered per second. Sharp thermograms showed that interactions of the acids with the coal samples did not involve processes with long term heat evolution, such as would be expected from exothermic swelling, or the attack of the acid on

the solid matrix as was observed with polyvinylpyridine polymer. The instrument was calibrated periodically by measuring the heats of reaction of aqueous sodium hydroxide and hydrochloric acid solutions using $(-13.42 \pm 0.39 \text{ kcal/mol})$ as the standard value (32).

e. The Microscal flow microcalorimeter

The Microscal is a flow microcalorimeter which can be used to measure very small heats of adsorption of liquids and gases on solids. The glass encased thermistors, which detect heat changes due to adsorption, are embedded in the granular solid under study and an imbalance of a Wheatstone bridge produces a recorded trace whose area is proportional to the heat of interaction. The solvent (or solution) delivery is controlled by two electrically driven syringe pumps (Perfusor IV) equipped with gas-tight syringes (Glenco). Accurately weighed coal samples were placed in the calorimeter cell and heats of adsorption for the substituted phenols were determined on different coal samples. 25-40 mM solutions of phenols in purified isooctane were used.

f. Adsorption of phenols on coal samples

Adsorption experiments were carried out in 100ml screw-capped glass jars. Accurately weighed (0.3-0.4 g) vacuum-dried coal samples were mixed with 10ml of the phenol solution in isooctane (purified by passing through a column of activated alumina), of known concentration and shaken vigorously for about 5-10 minutes by hand in an argon filled dry box. The slurry was then allowed to stand for about 2 hours; at the end of which the concentration of the supernatant was determined using a Diode Array UV spectrophotometer. The phenols had characteristic absorbances near 224 nm.

The amount adsorbed was calculated from the concentration of the phenol solution before and after the adsorption experiments using a Beer's law plot to interpolate concentrations.

3. Results and Discussion

a. Comparison of Polyvinylpyridine with Pyridine

In our previous study of solid acids, Dowex sulfonic acid resins were used as prototype solid Brönsted acids and silica was used as the prototype hydrogen-bonding acid for their interactions with a variety of organic bases (26). Now the situation is reversed and we have used cross-linked poly-4-vinylpyridine (PVP) as a standard solid base against which to study various types of acidic solutions. Table III compares the heats of citration (ΔH_{titr}) of PVP versus monomeric pyridine when titrated with a series of acids. Clearly (ΔH_{titr}) varies with the pK_a of the sulfonic acids as determined in aqueous solution and an excellent correlation is seen between the heats of reaction of a variety of acids with PVP and with pyridine (Figure 2). For comparison Figure 1 repeats a similar correlation plot from our previous study for the interaction of a series of bases with polysulfonic acid versus solutions of p-toluenesulfonic acid (26). (For interpretation of the differences in intercepts see that reference.)

b. Heats of interaction of the acids with silica

In our previous project silica was chosen as a prototype solid hydrogen-bonding acid and its heats of interaction with a series of bases were shown to correlate fairly well with their known heats of complexation with p-fluorophenol--a standard solution phase hydrogen-bonding acid (34). Since the silica hydroxyl groups are the hydrogen-bond donors and hydroxyl

functions are well known to be amphoteric, it is reasonable to expect that silica could also accept hydrogen-bonds from strong acids and perhaps even be protonated by them. The results presented in Table IV explore the interaction of a series of strong acids with a sample of Fisher silica whose surface properties we had examined and reported in our previous study (27). In our opinion, the results in Table IV are truly astounding since they suggest that silica is not being protonated by these strong acids, but is acting as a hydrogen-bonding acid towards them. In fact, the most exothermic heat of interaction for the whole series is for pure acetonitrile undiluted by any of the other materials.

Acetonitrile is well known to be a very weak acid both in the Brönsted sense and also as a hydrogen-bond donor. It is also a very weak Brönsted base since it is only partially protonated in pure sulfuric acid (41). However (and this is probably the key to the strange order in Table II), it is a fairly good hydrogen-bond acceptor (34). The principal fact that stands out from Table II is that, except for the understandably low heat of immersion of silica in hexane, all of the numbers are practically the same lying in a very short range between 16.41 cal g⁻¹ for difluoroacetic acid and 21.41 cal g⁻¹ for pure acetonitrile. Significantly, ethyl acetate, which should be similar to acetic acid as a base, but which obviously can't act as a strong protonic acid, lies in the same range as the other compounds.

Our interpretation of these results is that the principal contribution to all of these thermochemical values is that from silica serving as a hydrogen-bond donor to acetonitrile as acceptor. If this is true, the acids are simply serving as weakly basic diluents in the acetonitrile. Under these conditions they are not acting as acids at all

towards silica but as bases! These observations and discussion of them are developed in the first Annual Report and a published account (36).

c. Comparison of Coals with Polyvinylpyridine

Table V gives heats of immersion, ΔH_{imm} , of four coals and polyvinylpyridine (PVP) into acetonitrile solutions of twelve Brönsted acids and also of the very strong Lewis acid, BCl_3 . The results, obtained with the Setaram C-80 heat flow calorimeter, are given in terms of cal/g rather than kcal/mole because the total heat of reaction is released over a period of several minutes as the acid solution penetrates the solid matrix of the coal. Since all of the acids in Table V are considerably stronger than the phenols which contribute most of the hydrogen-bonding in coals, the weaker acids should be completely displaced by the stronger Brönsted acids. Presumably most of the interaction occurs with nitrogen bases to form ammonium salts; however several of protonic acids are capable of forming strong hydrogen-bonds to oxygen functions such as ethers or even hydroxyl groups. In addition, (see below) there is clear evidence for pi-pi interactions between the aromatic acids and aromatic hydrocarbon systems in the coals. Other interactions which involve only the acids in this solvent are the hydrogen-bonding dimerization between carboxylic acid molecules

that develop in non-basic solvents (37) and also the homohydrogen-bonded sulfonate anions

formed in excess sulfonic acid solution (38). Disruption of the carboxylic acid dimers makes an endothermic contribution to the heats of reaction of these acids with bases, while homohydrogen-bonding gives a significant exothermic one to sulfonic acid reactions.

The acids in Table V are arranged in terms of decreasing ΔH_{imm} of PVP in them. Most of these are so strong that their pK_a 's cannot be determined within the familiar aqueous pH scale. The listed pK_a 's have been evaluated by various complicated approaches discussed by Guthrie (39). Of more direct relevance to the present experiments than aqueous pK_a 's are the calorimetric heats of reaction with pyridine in acetonitrile (Figure 2). Pyridine and PVP are identical, within ± 1 kcal/mol, by their thermometric heats of titration (ΔH_{titr}) with these Brönsted acids and those values are a more reasonable guide than pK_a 's as a guide to acid strength for the present systems. However, even for such a "simple" system as PVP there is a rather poor correlation between titrametric heats of interaction and heats of immersion (Figure 3).

The position of trifluoromethanesulfonic acid is clearly anomalous in its ΔH_{imm} with PVP. By all accounts it is a much stronger Brönsted acid than methane- or ethanesulfonic acid (39) and is probably even strong enough to protonate the very weak base acetonitrile which is barely protonated by pure sulfuric acid (41). The titrametric heat of interaction of triflic acid with pyridine and PVP is much higher than that of methane- or ethanesulfonic acids as expected. We are unable to explain its anomalously low heat of immersion with PVP which is a warning that it should be regarded with suspicion in its interactions with the coals.

Figure 4 compares ΔH_{imm} s of Argonne Wyodak with that of PVP. A fair linear correlation is found for interactions with the aliphatic acids. The

substituted benzene sulfonic acids are much more differentiated through interaction with this and the other coals than they are with PVP and are probably affected by pi-pi interactions as well as proton transfer (see below). Figures 5, 6 and 7 compare PVP with Exxon Rawhide, Argonne Illinois #6 and Pittsburgh #8 coals. Clearly PVP is not a good, simple model for any of them and the three coals are differentiated in their behavior.

d. Comparison of Coals with Each Other

The scattered and often ambiguous plots (Figures 5-7) comparing coals with PVP imply that Brönsted acidity as a single factor is insufficient to determine the interaction of this series of acids with coals. Figure 8, which compares the ΔH_{imm} s of two subbituminous coals from different mines in the Wyoming-Dakota field, provides strong support for the use of thermochemical acid/base coal characterization. Even the point for triflic acid is correlated with the others. This plot is reminiscent of a previous report (17) which presented a good correlation between ΔH_{imm} for Wyoming Rawhide subbituminous and Texas Big Brown coals into a series of bases. These two high plains coals differ considerably in terms of their carbon and hydrogen analysis but agree well on oxygen and sulfur content. Significantly, there is no separation of aromatic from aliphatic acids in the comparison of these samples. The correlation coefficient for all 13 points is fairly good (0.95) and the slope is 1.01 showing the similarity of their responses to the complex interactions of the ΔH_{imm} experiment.

Figures 9 and 10 compare ΔH_{imm} s for the Argonne samples of Illinois #6 and Pittsburgh #8 with the Wyodak coal. Both plots separate aliphatic from aromatic acids. Since pi-pi interactions are clearly recognized non-covalent interaction in coals (2,3), it is reasonable to attribute the dispersion of points to this type of interaction with the aromatic acids although it is perhaps surprising to see it perturbing the influence of Brönsted acidity so strongly.

The definitive study by Solum, Pugmire and Grant (42) provides a detailed ^{13}C solid state NMR analysis of eight Argonne premium coals including those reported here. Illinois #6 and Pittsburgh #8 contain a considerably larger distribution of aromatic structures and clusters than do Wyodak or high plains lignites. The ΔH_{imm} results are in accord with this NMR analysis.

Although the ΔH_{imm} results for the coals can be interpreted roughly in terms of their basic and aromatic content, other complicating factors are involved since there is differentiation between the behavior of Illinois #6 and Pittsburgh #8, although their aromatic contents are quite similar. Furthermore, the order of ΔH_{imm} for the substituted sulfonic acids does not follow their acidities with any of the coals and the behavior of BCl_3 is quite erratic. Possibly, differences in structure that affect diffusion are an important factor. At this point, the results in Figures 4-11 present several intriguing and reasonable correlations but ΔH_{imm} s in strong acids appear to involve a quite complex set of interactions in addition to simple acid-base ones.

e. Comparison of Coals and Coal-Derived Liquids

Figures 12-15 provide comparisons of four coal liquids against the

coals from which they were derived as they are titrated incrementally with four strong Brönsted acids. The present status of various processes for the direct liquifaction of coals has been reviewed recently by Lumpkin (43). The process for obtaining coal liquids at Wilsonville, Alabama, utilizes a close coupled-integrated two stage liquifaction process (44). In this process a preheated (800°F) coal slurry in an appropriate organic solvent is fed, first to a thermal reactor to obtain highly volatile light liquid and then to a catalytic reactor to obtain further conversion of solid coal. The ash and unconverted coal goes to a vacuum distillation rig which separates distillate boiling over 650°F [V1072]. The combined feed of first and second stage reactor products are transferred to an atmospheric distillation column which separates out naphtha and other heavier material [V161]. The residue from this distillation combines with V1072 and is fed into another distillation column to obtain a middle distillate [V182].

We have less information about the Exxon YP35 sample which was produced in the Baton Rouge liquifaction pilot plant and has a nominal boiling range of 450-650°F. Since the heats of interaction were measured incrementally by titration calorimetry it is possible to make direct comparison between the heat generated by successive additions to the acetonitrile solution of the coal-derived liquid (CDL) and to the most basic and most accessible sites of the coals. The experiment is complementary to that for measuring heats of immersion.

Important differences to be expected between the CDLs and the solid coals are the separation of the former from mineral matter which may be acidic, basic or neutral. It also seems reasonable that non-covalent interactions will be weaker in solution and that the liquids will be

effectively more basic than the solids. It is also reasonable that observed ΔH_{titr} with the parent coals are less exothermic because of relatively slow diffusion into the solid particles (45).

A common, but not general, pattern is obvious for Figures 12-15: the interaction of coal liquids with each acid is more exothermic than the interaction of the parent coal over all or most of the titration range. The profile of this difference varies from coal to coal and depends on the acid but for several of the cases is as much as 10 kcal/mol. At this point one can only speculate on the detailed reasons for the observed behavior patterns—their similarities and differences—yet it is clear that this set of organic materials, both solid and liquid are responding in a generally equivalent manner to this type of perturbation by strong Brönsted acids.

f. Comparison of Citric Acid Washed with Untreated Coals

An important question concerning the interaction of strong acids with coals is how much of the observed heat of immersion (ΔH_{imm}) is due to organic basic sites, such as nitrogen bases, and how much is due to minerals such as carbonates and basic oxides.

The mineral content of coals can be as high as 30% and can contribute not only to wasteful transportation costs but to slagging, equipment fouling and particulate formation during combustion and gasification procedures (46) Mineral impurities affect the surface potentials on coal particles (47) and these should influence some methods of coal preparation involving floatation (47, 48). Various oxides and carbonates of Si, Al, K, Ca, Mg, Na, Fe, Ti, Ba, Sr, Li, Zn and other metals contribute to the mineral content, and several methods have been used to remove or characterize coal minerals (49).

In order to approach the question of how such minerals affect the basicities of the coals we employed the citric acid wash described by Silbernagel et al. (29). Table VI shows the dramatic effect of citric acid washings on the ΔH_{imm} of Wyodak coal in the series of strong acids. Apparently, a considerable component of ΔH_{imm} s which are reported in Table V are the result of interaction with basic minerals. Silbernagel et al. were interested primarily in the effect of demineralization on the EPR properties of several Argonne premium coals and demonstrated that the effects would be considerable due to removing various inorganic paramagnetic species. In the case of our work reported here, two factors presumably are at work: First is the neutralization of basic oxides by the citric acid which presumably is too weak ($pK_1=3.13$ at 25 degC) to effectively neutralize nitrogen bases in the coal system. The second effect of citric acid would be to replace any chelating components in the coals structure towards ions such as calcium, iron, etc. Whatever the reason, citric acid wash reduces the ΔH_{imm} in the aliphatic acids and increases those in solutions of the aryl sulphonic acids. Evidence for the ion exchange process is the fact that little if any weight loss due to mineral displacement resulted from the citric acid washing. Dr. Flowers has confirmed that this (unpublished) result was also seen by Silbernagel, Gebhard, Flowers and Larsen (29).

As seen in Table VI and Figure 16 the ΔH_{imm} values for the citric acid washed Wyodak coal with alkyl sulfonic acids and trifluoroacetic acid have decreased by nearly 30% as compared to the untreated sample. The value due to trichloroacetic acid is unchanged. Its ΔH_{imm} value was also substantially less than trifluoroacetic acid even in the untreated Wyodak sample and may well be related to its restricted approach to basic moieties

in constricted pores. Surprisingly, the ΔH_{imm} s for the aryl sulfonic acids increased. One may speculate that the citric acid washing has opened up access to some aromatic areas of the coal with which the aryl sulfonic acid can interact in some manner. The value for the Lewis acid BCl_3 is unchanged within the experimental error.

In sharp contrast to the results for samples of Wyodak, the effect of citric acid washing on our sample of Illinois #6 from Wilsonville is negligible, as is readily seen from Table VI and Figure 17. The slope of the correlation is 1.02, the intercept is within a standard deviation of the o,o origin and the coefficient of correlation is 0.948.

Somewhat surprisingly, the ash content of the Illinois #6 sample is 11.5% compared to only 8% for the Wyodak coal. However the Wyodak coal (a subbituminous coal) contains more exchangeable ions such as Fe^{2+} , Ca^{2+} etc than the IL#6 and therefore the effect of citric acid washings for the removal of these ions is noteworthy.

g. Heats of Interaction of Phenols with Untreated and Citric Acid Washed Coal Samples

Tables VII and VIII record the heats of adsorption/desorption of 3,5-di-tert-butylphenol and phenol respectively on untreated and citric acid washed coal samples, obtained by flow microcalorimetry.

The limited penetration of 3,5-di-tert-butylphenol is highly noticeable on the untreated Wyodak sample, but a relatively higher value for the ΔH desorption indicates some extraction of material from the coal surface. Similar results were also observed by Fowkes, Jones, Li and Lloyd while investigating the acid/base properties of a low-ash bituminous coal (PSOC No.11) by flow microcalorimetry (16). We have also observed this

while carrying out adsorption isotherms for phenols from isooctane solutions onto coal samples.

The basic properties of the Wyodak coal sample changes drastically after it has been subjected to citric acid washing and hence the heats of adsorption are more similar to those of IL#6 untreated sample. This may be due to π - π interaction between the adsorbate and adsorbent in sites which have been opened up by the citric acid treatment.

Similar features are observed with the phenol adsorption experiments but the heat values are somewhat larger than in the case with 3,5-di-tert-butylphenol. The important feature of phenol adsorption is noteworthy; that in the first cycle of adsorption/desorption experiments, not all the phenol is desorbed from the surface indicating some penetration into the coal matrix. However, the following adsorption experiments show that the phenol is actually completely desorbed from the coal surface given sufficient time.

h. Adsorption isotherms of phenols on untreated and citric acid washed coal samples

Irving Langmuir (50, 51) suggested a theory to describe the adsorption of gases on surfaces which has found successful application to many sorption processes and it can be used to probe the sorption of weakly acidic and/or basic molecules such as phenols, pyridines and basic dyes on coal surfaces (16, 52, 53).

The fundamental assumption of the Langmuir theory is that the sorption takes place at specific sites within the adsorbent. It is further assumed that once an acidic or basic molecule occupies a site, no further adsorption may take place at that site. Theoretically, therefore a

saturation value is reached beyond which no further sorption can take place. The saturation monolayer capacity can then be represented by the expression:

$$X/X_m = K C / 1 + K C \quad (1)$$

or

$$C/X = C / X_m + 1 / X_m K \quad (2)$$

Where

C = Concentration of the adsorbate in equilibrium with the adsorbent in solution (moles/dm³)

X = Concentration of the probe adsorbed on unit mass of the adsorbent (moles/g).

X_m = Maximum concentration of the probe that can be adsorbed on unit mass of the adsorbent, so called monolayer capacity. (moles/g).

K = Langmuir equilibrium constant which is a measure of the strength of the adsorbate and adsorbent interaction.

Hence a plot of C/X vs. C theoretically should give a linear relationship which is only found with energetically homogeneous adsorbents like graphitised carbon blacks. Many real solid surfaces are heterogeneous and hence do not yield a straight line.

We have used this methodology to study the adsorption of two phenols on a few of the coal samples. An attempt has been made to estimate the number of basic sites on two IL#6 coal samples. The equilibrium adsorption isotherms of phenol on untreated IL#6, Wyodak and citric acid-washed Wyodak are shown in Figure 18, whereas those for 3,5-di-tert-butyl phenol on the untreated and citric acid washed IL#6 coal samples are shown in Figure 19.

It is interesting to note that the uptake of phenol by the Wyodak coal, at the saturation point, increases after it has been subjected to citric acid washing. In contrast the phenol uptake by the untreated IL#6 coal is by far the highest. This is probably due to the higher BET-nitrogen surface area of the IL#6 coal sample ($15.4 \text{ m}^2/\text{g}$ as compared to 5.0 ± 0.1 and $6.00 \text{ m}^2/\text{g}$ for the untreated and citric acid washed Wyodak samples respectively).

Figure 20 illustrates the linear plots of the Langmuir equation. It is evident that there are some deviation from linearity for all the coal samples. A change in the slope of the Langmuir plot implies different kinds of sorption processes (53). The Langmuir plots for all the coal samples show a reduction in the slope after an initial increase which implies an increase in the monolayer capacity of the adsorbent. As proposed by Giles (54, 55) when all the available surface sites are taken up, fresh internal surface may be created. The creation of the additional surfaces arise from the pressure of the adsorbate molecules forcing into the macro- and micro-pore structure. Therefore an increase in the monolayer capacity beyond $0.20 - 0.50 \text{ mM}$ concentration of phenol strongly suggests the penetration of phenol into the pore structure of the coals; an increase in the sorption capacity at all regions for the citric acid washed Wyodak coal suggests that the acid washing procedure opens up the pore structure and creates some extra surface for the adsorption of phenol.

Figure 21 shows the Langmuir plots for the untreated and citric acid washed IL#6 coal samples. The linearity of these plots is noteworthy. Apparently, the steric effect due to the presence of the tert-butyl groups inhibits the hindered phenol from entering into the porous structure of the coal. The monolayer capacities obtained from these plots may be used to

estimate the number of surface basic sites on the untreated and citric acid washed IL#6 coal samples.

$$X_m \text{ (untreated coal sample)} = 2.54 \times 10^{-6} \text{ moles}$$

$$X_m \text{ (treated sample)} = 1.67 \times 10^{-6} \text{ moles}$$

Using the expression:

$$A = (X_m) (a_m) (L) \quad (3)$$

where A is the BET-nitrogen area of the adsorbent, a_m , the area per molecule occupied by the adsorbate molecule and L, the Avogadro constant.

Equating the right hand side of the equation with the BET-nitrogen area of the coals one can obtain the apparent cross-sectional area for the adsorbate molecule, which may then be compared with the area (1.25 nm^2) obtained from molecular models (16). By adopting this method we have estimated that there are about 1 basic site for each 10 (nm)^2 of the coal surface which decreases to about 1 basic site per 15 (nm)^2 of the coal surface after it has been washed with the citric acid. This might represent the removal of some inorganic bases as well as nitrogen bases from the coal matrix.

This procedure for the estimation of the basic sites may be manipulated further by steric effects from tert-butyl groups of the phenol molecule. Fowkes and coworkers have also found that the surface areas calculated from the surface coverage by the tert-butylated probes are too low by a factor of 2 with coal powders having specific surface areas of $15 \text{ m}^2/\text{g}$. However in the present case the surface area calculated for the coal powder ($15.4 \text{ m}^2/\text{g}$ from nitrogen BET method) is extremely low by a factor of nearly 8. Perhaps this is due to insufficient basic surface sites to bind a tightly packed monolayer of these probe molecules.

4. Summary and Conclusions

The basic properties of a series of coals have been compared through their heats of interaction with a series of acids of widely varied strength. First it was shown that there is a close correlation between the heats of interaction of the acids with pyridine, in acetonitrile solution, and with a slurry of polyvinylpyridine (PVP) in acetonitrile. Using PVP, as a model solid base, comparisons were made to Exxon Rawhide and Wyodak, Illinois #6 and Pittsburgh #8 samples from the Argonne Coal Bank. Comparisons were also made with samples of the citric acid washed coals and with liquids derived from the coals.

Widely varied patterns resulted from the above correlations except for the fairly good agreement between the responses of Argonne Wyodak and Exxon Rawhide coals to thirteen acids. Other comparisons of the coals to PVP gave poor correlations and, interestingly, some of the coals showed a clear differentiation between their interactions with aromatic versus aliphatic acids.

Thermometric titrations of the coal-derived liquids were usually more exothermic than those with their parent coals.

Washing Wyodak coal with citric acid has a dramatic effect on its basicity indicating that inorganic bases are an important contributor to its interaction with acids. In contrast, citric acid washing has a negligible effect on Illinois #6 coal.

Preliminary experiments comparing the interaction of citric acid washed Wyodak and its parent coal with 3,5-di-*tert*-butylphenol by flow microcalorimetry were initiated but no significant results could be obtained by the termination date of the grant.

As a final conclusion it is clear that heats of interaction of coals,

coal liquids and citric acid washed coals with acids covering a broad range of strengths provide a rather sensitive means for differentiation and classification although detailed interpretation in terms of the structure of the coal and of the acid is complex.

Table IX extends our previous classification of a variety of coals in terms of their response as solid acids to a series of organic bases as relative to a series of prototype solids: Dowex sulfuric acid (a Brönsted acid), silica (a hydrogen-bonding acid) and Carbowax F (a dispersion force adsorbent). The new values from the present grant compare the coals with PVP as a model solid base to give a general profile of both the acidic and basic profile of each coal.

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6. Personnel

The following people were supported by this grant:

Amarnath, Kalyani	Post Doctoral Research Associate
Ahsan, Tanweer	Post Doctoral Research Associate
Richter, Marjorie	Research Technician
Olson, Eric J.	Graduate Research Assistant
Shelton, Michael	Graduate Research Assistant
Wheary, John F.	Graduate Research Assistant
Truckenbrod, Steven M.	Graduate Research Assistant
Jason Wu	Graduate Research Assistant

7. Presentations

- 1.) Invited lecture at Symposium in "Colloid Science and Solution Chemistry in Separation Science" at Boston Meeting of American Chemical Society, Thursday, April 26, 1990.
- 2.) Peer Review Assessment by Department of Energy's Office of Program Analysis, Pittsburgh, Tuesday, July 17, 1990.
- 3.) Invited lecture at Symposium on "Organic Reactions in Heterogeneous Media" at Southeast-Southwest Regional Meeting of the American Chemical Society, New Orleans, December 5-7, 1989.
- 4.) Presentation of results at the University Contractor's Review Meeting in Pittsburgh on Wednesday, June 26, 1991.
- 5.) Invited paper "Acid-Base Properties of Coals and Coal Liquids" by E.M. Arnett and T. Ahsan at Symposium on "Novel Analytical Techniques for Fossil Fuels" sponsored by the Division of Fossil Fuel Chemistry at the National ACS Meeting in New York, Tuesday, August 27, 1991.
- 6.) Presentation by Dr. Ahsan at the 65th ACS Colloid and Surface Science Symposium, University of Oklahoma, June 17, 1991, "Calorimetric Study of the Reactivity of Commercial Silica with Strong Brönsted and Lewis Acids."
- 7.) Presentation: Poster at Annual Meeting of University Coal Contractors in Pittsburgh, June 15, 1992.
- 8.) Presentation: "Calorimetric Comparisons of Solid and Homogeneous Acids and Bases," Edward M. Arnett and Tanweer Ahsan, 47th Calorimetry Conference, Snowbird, Utah, August 16-21, 1992.

8. Publications

1. E.M. Arnett and T. Ahsan, "Heats of Interaction of Strong Brönsted Acids with Silica", J. Am. Chem. Soc., 1991, **113**, 6861.
2. E.M. Arnett, T. Ahsan and K. Amarnath, "Thermochemical Comparisons of Solid and Homogeneous Acids and Bases--Pyridine and Polyvinylpyridine as Prototype Bases", J. Am. Chem. Soc., 1991, **113**, 6858.
3. Edward M. Arnett and Tanweer Ahsan "Calorimetric Comparisons of the Interactions of Seven Coals and their Derived Liquids with Thirteen Acids", Fuel (in press).

Table I. Analysis of the coal samples

% Composition						
Sample	C	H	O	S	moisture	ash
Wyodak ^a	74	5.1	19	0.5	27	8
IL#6 ^a	77	5.7	10	5.4	9	16
Pittsburgh#8 ^a	83	5.8	8	1.6	1.8	9
IL#6 ^b	70.6	4.8	8.2	3.4	5	11.5
Black Thunder ^b	68.7	5.1	18.7	0.4	25	6.1
Pittsburgh#8 ^b	69.8	4.8	5.3	4.5	03	14.5
Wyoming-Rawhide ^c	66.8	4.8	19.5	0.5	-	-

a Premium coal samples from Argonne National Laboratories.

b Nonpremium coal samples from SEI Wilsonville, Alabama.

c Nonpremium coal sample supplied by Exxon.

**Table II. Analysis of the coal liquids obtained from
Wilsonville**

Sample	% Composition					Boiling Range (F)
	C	H	N	S	O ^a	

Black Thunder subbituminous						
V182	87.5	12.6	0.40	0.04	None	500-800
Illinois#6 bituminous						
V182	88.8	10.5	0.20	0.02	0.5	500-800
Pittsburgh#8 bituminous						
V182	85.2	10.4	0.20	0.02	4.2	500-800

a By difference

Table III. Heats of interaction of some strong acids (0.25M) in acetonitrile with Poly-4-vinylpyridine and pyridine at 25 oC.

Acid	pKa	-ΔH _{titr.} (kcal/mol)		-ΔH _{imm} (cal/g)	
		PVP	Pyridine	PVP	
boron trichloride		60.65 ± 0.92	58.60 ± 4.62	-----	
trifluoromethanesulfonic		24.80 ± 0.43	23.08 ± 1.37	130.39 ± 9.45	
4-toluenesulfonic	-6.55	16.56 ± 0.46	15.24 ± 0.27	66.89 ± 1.99	
benzenesulfonic	-2.70	17.35 ± 0.34	16.61 ± 0.17	62.08 ± 0.53	
methanesulfonic	-1.92	15.49 ± 0.24	14.70 ± 0.19	147.55 ± 1.25	
ethanesulfonic	-1.68	14.65 ± 0.17	14.11 ± 0.22	148.33 ± 17.0	
4-nitrobenzenesulfonic	-4.00	11.31 ± 0.46	10.32 ± 0.23	-----	
4-chlorobenzenesulfonic		15.91 ± 0.25	14.45 ± 0.23	53.26 ± 1.37	
trichloroacetic	0.69	11.28 ± 0.12	10.52 ± 0.18	80.82 ± 1.40	
trifluoroacetic	0.54	11.20 ± 0.24	10.61 ± 0.10	85.75 ± 0.72	
dichloroacetic	1.36	7.63 ± 0.11	7.25 ± 0.05	70.56 ± 0.82	
difluoroacetic	1.30	6.75 ± 0.19	6.96 ± 0.19	74.99 ± 1.89	
cyanoacetic		3.64 ± 0.06	4.69 ± 0.08	55.86 ± 2.39	

For the source of acid dissociation constants please see the references at the footnote of table V

Table IV

Heats of Immersion (ΔH_{imm}) of Fisher Silica in some solutions ΔH_{imm} in Pure Nitrogen Bases from Previous Study
of acids and bases, 1 M in acetonitrile, at 25^o

Acids	$-\Delta H_{imm}/\text{cal. g}^{-1}$	Bases	$-\Delta H_{imm}$ cal/g silica
Hexane (neat)	3.81 $\pm$ 0.00	Cyclohexanone	18.41 $\pm$ 1.08
Ethyl acetate (neat)	15.78 $\pm$ 2.88	3,5-Dichloropyridine	18.87 $\pm$ 1.04
Difluoroacetic	16.41 $\pm$ 0.20	Acetonitrile	19.82 $\pm$ 0.52
4-chlorobenzenesulfonic	17.08 $\pm$ 0.16	2,4,6-Trimethylpyridine	21.89 $\pm$ 0.70
4-Toluenesulfonic	17.12 $\pm$ 0.26	3-Bromopyridine	22.96 $\pm$ 0.39
Benzenesulfonic	17.26 $\pm$ 0.11	4-Methylpyridine	23.02 $\pm$ 0.52
Trichloroacetic	17.53 $\pm$ 0.91	2,6-Dimethylpyridine	23.50 $\pm$ 1.04
Ethanesulfonic	17.65 $\pm$ 0.66	Diisopropylamine	24.00 $\pm$ 1.44
Cyanoacetic	17.73 $\pm$ 0.20	Triethylamine	24.44 $\pm$ 1.71
Water (neat)	18.09 $\pm$ 1.04	Pyridine	24.95 $\pm$ 0.48
Dichloroacetic	18.12 $\pm$ 0.49 (17.83 $\pm$ 0.08)*	3-Methylpyridine	25.11 $\pm$ 0.50
Trifluoroacetic	18.90 $\pm$ 1.14 (15.61 $\pm$ 0.41)*	2-Methylpyridine	26.34 $\pm$ 0.75
Methanesulfonic	20.25 $\pm$ 0.09 (17.55)*		
Water	20.41		
Chloroacetic	20.41 $\pm$ 0.28		
Acetic	19.65 $\pm$ 0.38 (16.97 $\pm$ 1.25)*		
Acetonitrile (neat)	21.41 $\pm$ 1.00		
Ethyl acetate	21.75		

* Hexane as solvent.

Table V. Heats of immersion (ΔH_{imm}) of coals and Polyvinylpyridine in (0.65M) acid solutions in acetonitrile.

Acids	- ΔH_{imm} (cal/g)				
	pKa ^a	PVP	Exxon Rawhide	Wyodak	IL#6 Pittsburgh#8
Ethanesulfonic	-1.68	148.33 $\pm$ 17.0	37.35 $\pm$ 0.84	44.62 $\pm$ 1.56	22.86 $\pm$ 0.48 21.28 $\pm$ 2.13
Methanesulfonic	-1.92	147.55 $\pm$ 1.47	37.99 $\pm$ 1.46	44.79 $\pm$ 2.00	21.56 $\pm$ 0.24 21.98 $\pm$ 1.19
Triflic	-5.90	130.54 $\pm$ 9.54 ^c	59.16 $\pm$ 2.85	60.16 $\pm$ 1.61	45.08 $\pm$ 2.36 29.39 $\pm$ 1.47
Trifluoroacetic	0.54	85.75 $\pm$ 0.72	32.19 $\pm$ 0.86	35.69 $\pm$ 1.15	18.53 $\pm$ 0.48 12.62 $\pm$ 0.60
Trichloroacetic	0.69	80.82 $\pm$ 1.40	28.17 $\pm$ 0.03	23.89 $\pm$ 0.88	14.71 $\pm$ 0.72 08.07 $\pm$ 0.70
Difluoroacetic	1.30	74.99 $\pm$ 1.89	29.73 $\pm$ 0.56	31.55 $\pm$ 0.66	16.44 $\pm$ 0.45 10.03 $\pm$ 0.66
Dichloroacetic	1.36	70.56 $\pm$ 0.82	29.06 $\pm$ 0.22	26.52 $\pm$ 0.49	16.38 $\pm$ 0.38 09.90 $\pm$ 1.50
4-Toluenesulfonic	-6.55	66.89 $\pm$ 1.99	24.81 $\pm$ 1.02	24.81 $\pm$ 0.95	20.39 $\pm$ 0.41 08.92 $\pm$ 1.25
Benzenesulfonic	-2.70	62.08 $\pm$ 0.53	30.55 $\pm$ 0.94	29.30 $\pm$ 0.22	23.79 $\pm$ 1.87 18.58 $\pm$ 0.24
Chloroacetic		60.00 $\pm$ 0.82	27.25 $\pm$ 0.07	26.72 $\pm$ 0.94	16.75 $\pm$ 0.59 07.60 $\pm$ 0.66
4-Chlorobenzenesulfonic		53.26 $\pm$ 1.37	24.89 $\pm$ 0.94	24.09 $\pm$ 1.21	19.14 $\pm$ 0.98 10.82 $\pm$ 0.66
4-Nitrobenzenesulfonic	-4.00		23.24 $\pm$ 0.27	26.23 $\pm$ 1.00	20.81 $\pm$ 0.79 07.13 $\pm$ 0.71
Boron trichloride ^b			24.10 $\pm$ 1.79	26.18 $\pm$ 2.40	33.78 $\pm$ 2.23 16.94 $\pm$ 0.27

^a Acidic dissociation constants of sulfonic acids in water at 25 oC from Grumrine et al; *J.Org.Chem.* 1986,51,25,5013. and J.P.Guthrie; *Can.J.Chem.* 1978,56,2342. which describes the unusual difficulties of comparing the strengths of very strong acids. ^b Hexane as solvent.
^c See the text

Table VI. Heats of immersion of PVP, untreated and citric acid washed Argonne Wyodak and Wilsonville IL#6 coals in various strong acids at 25 °C

Acid	$\Delta H_{imm}(\text{cal/g})$ PVP	$\Delta H_{imm}(\text{cal/g})$ Untreated Wyodak	$\Delta H_{imm}(\text{cal/g})$ citric acid washed Wyodak	$\Delta H_{imm}(\text{cal/g})$ Untreated IL#6 Wilsonville	$\Delta H_{imm}(\text{cal/g})$ citric acid washed IL#6 Wilsonville
Ethanesulfonic	148.33 $\pm$ 17	44.62 $\pm$ 1.56	31.70 $\pm$ 1.69	29.73 $\pm$ 2.62	27.39 $\pm$ 2.67
Methanesulfonic	147.55 $\pm$ 1.47	44.79 $\pm$ 2.00	32.72 $\pm$ 1.15	27.49 $\pm$ 0.60	31.58 $\pm$ 1.12
Trifluoroacetic	85.75 $\pm$ 0.72	35.69 $\pm$ 1.15	24.00 $\pm$ 0.53	23.89 $\pm$ 0.21	21.57 $\pm$ 0.72
Trichloroacetic	80.82 $\pm$ 1.40	23.89 $\pm$ 0.88	24.95 $\pm$ 0.50	19.35 $\pm$ 2.99	23.31 $\pm$ 0.45
Difluoroacetic	74.99 $\pm$ 1.89	31.55 $\pm$ 0.66	22.85 $\pm$ 0.96	19.17 $\pm$ 0.40	19.57 $\pm$ 0.10
Dichloroacetic	70.56 $\pm$ 0.82	26.52 $\pm$ 0.49	22.87 $\pm$ 0.91	21.12 $\pm$ 0.30	19.18 $\pm$ 0.45
4-Toluenesulfonic	66.89 $\pm$ 1.99	24.81 $\pm$ 0.95	30.55 $\pm$ 0.68	31.43 $\pm$ 0.14	28.80 $\pm$ 0.40
Benzenesulfonic	62.08 $\pm$ 0.53	29.30 $\pm$ 0.22	34.29 $\pm$ 0.17	32.79 $\pm$ 1.65	28.19 $\pm$ 1.27
Chloroacetic	60.00 $\pm$ 0.82	26.72 $\pm$ 0.94	22.38 $\pm$ 0.64	19.40 $\pm$ 0.03	15.02 $\pm$ 0.52
4-Chlorobenzenesulfonic	53.26 $\pm$ 1.37	24.09 $\pm$ 1.21	31.60 $\pm$ 0.45	27.03 $\pm$ 2.37	28.83 $\pm$ 0.43
4-Nitrobenzenesulfonic		26.23 $\pm$ 1.00	30.09 $\pm$ 0.51	27.60 $\pm$ 0.54	22.20 $\pm$ 1.56
Boron trichloride		26.18 $\pm$ 2.40	26.44 $\pm$ 0.90	42.29 $\pm$ 0.82	44.46 $\pm$ 0.44
Triflic	130.54 $\pm$ 9.54	60.16 $\pm$ 1.61	52.25 $\pm$ 0.75	50.28 $\pm$ 3.22	50.50 $\pm$ 0.01

Table VII. Heats of adsorption of 3,5-di-tert-butylphenol on different coal samples by Flow microcalometry.

Coal samples		ΔH Adsorption (cal/g)	ΔH Desorption (cal/g)
<hr/>			
Wyodak untreated	(1)	0.037	0.055
Argonne sample	(2)	0.030	0.055
	(3)	0.030	0.054
Wyodak			
Citric acid washed	(1)	0.838	0.378
Argonne sample	(2)	0.880	0.425
IL#6 untreated			
	(1)	1.22	0.797
Wilsonville sample	(2)	0.818	0.823
	(3)	0.739	0.730

* The numbers in parentheses signify the sequence of experiments done on the same sample without removing the sample from the calorimeter.

Table VIII. Heats of adsorption of phenol on different coal samples by Flow microcalorimetry.

Coal samples		ΔH Adsorption (cal/g)	ΔH Desorption (cal/g)
<hr/>			
Wyodak untreated	(1)	1.529	0.826
Argonne sample	(2)	0.849	0.544
Wyodak			
Citric acid washed	(1)	3.56	2.93
Argonne sample	(2)	2.98	3.17
	(1)	3.48	2.80
	(2)	2.92	2.93
IL#6 untreated	(1)	3.31	1.98
Wilsonville sample	(2)	2.64	1.81

* The numbers in parentheses signify the sequence of experiments done on the same sample without removing the sample from the calorimeter.

Table IX. Regression of Premium Coal Immersion Values Against Those for Dowex, Silica, Carbopack and Polyvinylpyridine.

10 bases: Pyridine, Dimethyl sulfoxide, 4-methylpyridine, Toluene, Cyclohexane, n-hexylamine, 2,6-dimethylpyridine, n-butylamine, 2,4,6-trimethylpyridine, propylene carbonate.

7 acids: Methanesulfonic, Ethanesulfonic, Chloroacetic, Dichloroacetic, Trichloroacetic, Difluoroacetic, Trifluoroacetic.

$$\Delta H_{\text{Wyodak}} = -10.33 - 0.75 \Delta H_{\text{Dowex}} + 4.44 \Delta H_{\text{Silica}} - 7.22 \Delta H_{\text{Carbopack F}} + 0.11 \Delta H_{\text{PVP}}$$

$$r = 0.962; r_{\text{Dowex}} = 0.546; r_{\text{Silica}} = 0.886; r_{\text{Carbopack F}} = 0.468; r_{\text{PVP}} = 0.97 \text{ (aliphatic acids only).}$$

$$\Delta H_{\text{ILL\#6}} = 61.81 - 0.31 \Delta H_{\text{Dowex}} + 3.62 \Delta H_{\text{Silica}} + 1.13 \Delta H_{\text{Carbopack F}} + 0.07 \Delta H_{\text{PVP}}$$

$$r = 0.947; r_{\text{Dowex}} = 0.662; r_{\text{Silica}} = 0.942; r_{\text{Carbopack F}} = 0.078; r_{\text{PVP}} = 0.91 \text{ (aliphatic acids only).}$$

$$\Delta H_{\text{Pitts\#8}} = 29.87 - 0.37 \Delta H_{\text{Dowex}} + 2.82 \Delta H_{\text{Silica}} - 1.20 \Delta H_{\text{Carbopack F}} + 0.16 \Delta H_{\text{PVP}}$$

$$r = 0.946; r_{\text{Dowex}} = 0.618; r_{\text{Silica}} = 0.934; r_{\text{Carbopack F}} = 0.235; r_{\text{PVP}} = 0.98 \text{ (aliphatic acids only).}$$

$$\Delta H_{\text{N.Dakota}} = -52.70 - 0.905 \Delta H_{\text{Dowex}} + 3.48 \Delta H_{\text{Silica}} - 9.56 \Delta H_{\text{Carbopack F}} + 0.20 \Delta H_{\text{PVP}}$$

$$r = 0.893; r_{\text{Dowex}} = 0.375; r_{\text{Silica}} = 0.715; r_{\text{Carbopack F}} = 0.596; r_{\text{PVP}} = 0.98 \text{ (aliphatic acids only).}$$

$$\Delta H_{\text{Pocah.\#3}} = -5.084 - 0.085 \Delta H_{\text{Dowex}} + 0.202 \Delta H_{\text{Silica}} - 0.519 \Delta H_{\text{Carbopack F}}$$

$$r = 0.658; r_{\text{Dowex}} = 0.156; r_{\text{Silica}} = 0.466; r_{\text{Carbopack F}} = 0.453$$

Fig. 1 Plot of ΔH_{Dowex} vs. ΔH_{PTSA} with some strong bases at 25 °C

Fig.2 Plot of ΔH_{PVP} vs. ΔH_{PYR} with some strong acids at 25 °C

Fig. 3 Plot of ΔH_{imm} vs. ΔH_{titr} for PVP in various acids at 25 °C. 1.Ethanesulfonic acid; 2.Methanesulfonic acid; 3.Trifluoroacetic acid; 4.Trichloroacetic acid; 5. Difluoroacetic acid; 6.Dichloroacetic acid; 7.Cyanoacetic acid; 8.4-Toluenesulfonic acid; 9.Benzenesulfonic acid; 10.4-Chlorobenzenesulfonic acid.

Fig. 5 Comparison of ΔH_{imm} of Exxon Rawhide and PVP in strong acids

Fig. 6 Comparison of ΔH_{imm} of Argonne IL#6 and PVP in strong acids

Fig 7 Comparison of ΔH_{imm} of Argonne Pitts#8 and PVP in strong acids

Fig. 8 Comparison of ΔH_{imm} of Argonne Wyodak and Exxon Rawhide coals in strong acids

Fig. 9 Comparison of ΔH_{imm} of Argonne Wyodak and Argonne IL#6 coals in strong acids

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Fig 11 Comparison of ΔH_{imm} of Argonne Pitts#8 and IL#6 coals in strong acids

Fig.12 $\Delta H_{\text{titr.}}$ profile for coal liquid(V182) and coal slurry(IL#6) both from Wilsonville with some strong acids in acetonitrile.

**Fig13 $\Delta H_{\text{titr.}}$ profile for coal liquid(V182) and coal slurry(Blk.Thunder),¹
both from Wilsonville, with some strong acids in acetonitrile**

METHANESULFONIC ACID

TRIFLIC ACID

TRIFLUOROACETIC ACID

Fig 14 $\Delta H_{\text{titr.}}$ profile for coal liquid(V182) and coal slurry(Pitts#8), both from Wilsonville, with some strong acids in acetonitrile

Fig 15 $\Delta H_{\text{titr.}}$ profile for coal liquid(ExxonYP35) and coal slurry(Exxon Rawhide) with some strong acids in acetonitrile

Fig.16 Comparison of ΔH_{imm} of untreated and citric acid washed Argonne Wyodak coal samples in acids

Fig.17 Comparison of ΔH_{imm} of untreated and citric acid washed Wilsonville IL#6 coal samples in acids

Fig.18 Adsorption isotherms of phenol from isooctane solution on different coal samples

Fig. 19 Adsorption isotherm of 3,5-di-tert-butyl phenol from isooctane solution on IL#6 coal

Fig. 20 Langmuir plots for the adsorption of phenol on different coal samples

Fig. 21 Langmuir plots for the adsorption of 3,5-di-tert-butyl phenol on IL#6 coal samples

END

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