Thermochimica Acta, 154 (1989) 145–160
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

CALORIMETRIC TITRATION ANALYSIS OF A COAL-DERIVED LIQUID: DETERMINATION OF PHENOLIC, PYRIDINIC, AND CARBOXYLIC COMPOUNDS *

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(Received 13 February 1989)

ABSTRACT

The determination of the concentrations of acidic and basic compounds important in hydrogen bonding interactions is necessary to predict the thermodynamic and physical properties of coal liquids. A methanol/H_2O extraction/calorimetric titration method is presented that determines: (a) the concentrations of phenolic, pyridinic, and carboxylic compounds in coal liquid distillates important in hydrogen bonding interactions, and (b) the fractions of phenolic, pyridinic, and carboxylic compounds that are (1) unassociated, (2) self-associated, and (3) hydrogen bonded with other groups. Polar compounds are extracted into a methanol/H_2O phase, which may include HCl or NaOH, followed by titration of the aqueous extracts in the calorimeter. Concentrations of extracted compounds and enthalpy changes for protonation reactions of the compounds are calculated from the thermograms. Identification of the compounds is made from known ΔH and pK_a values. The degree of association of each class of compound is determined from the extraction pattern.

INTRODUCTION

Coal-derived liquids contain higher concentrations of polar aromatic and heterocyclic compounds than petroleum liquids. The presence of these polar compounds affects both the thermodynamic and physical properties of coal liquids. One goal of coal liquid research is to develop models for predicting the thermophysical properties of coal liquids based on easily measured properties. Such models will help define the parameters necessary to optimize the use of coal liquids as substitutes for petroleum.

Previous work on binary and ternary mixtures of model coal liquid acids and bases (*m*-cresol, quinoline, and aniline) in tetralin solvent showed both self-association reactions and complexation interactions to be important in

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* Dedicated to Professor James J. Christensen in memory of his contribution to innovation in calorimetry.

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0040-6031/89/$03.50

determining the heats of mixing of the model compounds. The relative strengths of the molecular interactions among these model compounds have been obtained from heat of mixing data [1].

The specific objective of this work was to develop techniques for the determination of: (a) the concentrations of coal liquid acids (including phenols and carboxylic acids) and coal liquid bases (including anilines, pyridines, and amines); and (b) the fractions of these polar compounds that are (1) unassociated, (2) self-associated, or (3) associated with other compounds.

The literature describes several methods used to identify and quantify coal liquid compounds. Among these are microbore liquid chromatography for determining basic nitrogen compounds [2], solvent elution chromatography followed by elemental analysis and proton NMR analysis for determining nitrogen and oxygen functional groups [3], acetylation and ^{14}C-counting for quantifying hydroxyl groups in preasphaltenes and asphaltenes [4], gas chromatography and combined gas chromatography/mass spectrometry for determining phenols [5], supercritical fluid chromatography for the determination of coal tar polyaromatic compounds [6], and anion-exchange chromatography for separating the acidic, neutral, and basic fractions of coal liquids [7]. The nature of coal liquid molecular interactions has been studied using various spectroscopic methods (^{1}H and ^{13}C NMR [8,9], near-IR [9], proton decoupled and ^{14}N NMR [10]), and calorimetric methods [11,12].

Vaughan and Swithenbank have described an enthalpometric titration technique that distinguishes between types of nitrogen bases in aqueous mixtures [13]. We have modified and applied the technique to coal-derived liquids in an attempt to rapidly determine classes and quantities of both acidic and basic compounds in coal liquid distillates. The 60% methanol/40% H_2O (v/v) solvent used by Vaughan and Swithenbank to prevent emulsions from forming in the aqueous extract [13] was also used in our extraction experiments.

The mixed solvent, which may include either HCl or NaOH, is used to extract acidic or basic compounds from the coal liquid. The aqueous extract of the coal liquid is then analyzed by acid and base titration in the calorimeter. Enthalpies of reaction and the concentrations of the various classes of extracted compounds are calculated from the thermograms. Extracted acids and bases are identified from ΔH values for proton ionization measured in the mixed methanol/H_2O solvent for model compounds and from published pK_a values for the mixed solvent [14]. Only phenols are present in the extracts without added HCl or NaOH. Phenols and carboxylic acids are present in the HCl extracts. Phenolates and carboxylates are present in the NaOH extracts. Pyridines are found in HCl extracts following NaOH extraction. No amines or anilinic nitrogen compounds have been found in any of the extracts. Coal liquid concentrations determined for extracted classes of compounds are accurate to about ±10% because of the uncertainties associated with curvature of the end points.

The concentrations of the extracted compounds have been compared with analytical data provided by the Pittsburgh Energy Technology Center (PETC) for the specific coal liquid sample used in these studies [15,16]. In addition, the extraction pattern has been compared with a molecular interaction model for a coal liquid of known composition [1].

EXPERIMENTAL

Coal liquid

Aqueous extraction experiments were done on the undistillated T102-T8 Thermal Hydrocracker Product (650–950 °F boiling temperature range) from Wilsonville Run 245, provided by PETC. Composition of the undistilled sample (i.e. percent oxygen as phenolic O–H and percent nitrogen as basic N–H) was determined both by near-IR spectroscopy and elemental analysis at PETC [15]. The composition of the undistilled sample agreed with published values (also from PETC) for compositions taken from the average results of six 50 °F distillate cut fractions from the same Wilsonville Run 245, over the same temperature range i.e. 650–950 °F [16]. Both sets of PETC results were compared against experimental results collected from the extraction experiments reported here.

Method

NaOH and HCl solutions were prepared from stock solutions of NaOH (Fisher Scientific certified 50% w/w solution) and concentrated HCl (J.T. Baker Chemical Company), respectively, in a mixed solvent containing 60% methanol (Fisher reagent grade) and 40% distilled water (v/v). The $MeOH/H_2O$ solutions of NaOH and HCl were standardized against reagent grade potassium hydrogen phthalate (Fisher Scientific) and Trizma Base (Sigma Chemical Company) by titration in the calorimeter. The KHP and Trizma standards were dried at 120 °C for 2 h, stored in a desiccator prior to use, and dissolved in the $60MeOH/40H_2O$ solvent prior to titration.

Ten ml of the T102-T8 coal liquid was pipeted into a glass extraction vessel, after which 15 ml of mixed aqueous solvent (solvent only, or with added HCl or NaOH) was pipeted into the vessel and the contents stirred for 24 h. The extraction mixture was then cooled in a refrigerator at 0 °C for 10 min to simplify the separation of the mixed aqueous phase from the coal liquid phase by decanting. A 3 ml aliquot of the aqueous extract and 15 ml of methanol/H_2O solvent were next pipeted into a 25 ml calorimeter reaction vessel (Dewar). The diluted extract was titrated at 25 ° C with either NaOH or HCl titrant in a Tronac Model 450 titration calorimeter. Temperature–time data were collected for approximately 5 min in the lead period, 10 min in the reaction period, and 5 min in the trail period. Approximately 4 ml of titrant was delivered during the reaction period, with titrant concentrations chosen so that the final endpoint to titrate all the acids or bases present in the sample required between 3 and 4 ml of titrant. A Keithley model 195 digital volt meter and Commodore C64 microcomputer were used to log the calorimeter temperature data at 5 second intervals throughout the experiment. The calorimetric data were analyzed and thermograms generated on a VAX system 8600 mainframe computer, using software developed from data reduction techniques described by Hansen et al. [17].

Experiments

Extraction experiments were performed on the coal liquid sample using the 60/40 methanol/H_2O solvent both with and without added NaOH or HCl. A greater HCl concentration was also used to see if additional bases could be extracted. Repeat extractions using NaOH and HCl were performed on the same coal liquid samples to see if additional acidic or basic compounds could be extracted. In addition, extraction experiments were performed in which either (1) quinoline, (2) *m*-cresol or (3) both *m*-cresol and quinoline were added to the coal liquid prior to extraction to determine (1) the recovery of the added model compounds, and (2) the effects of the added model compounds on the extraction of the native coal liquid acids and bases. Experiments were also performed in which all the phenols were extracted with the basic mixed solvent, followed by extraction with the acidic mixed solvent to see if the yield of extracted coal liquid basic compounds could be improved. Methanol/H_2O solvent extractions without added HCl or NaOH were performed to determine what fraction of the coal liquid acids and bases could be extracted into the neutral solvent. Potentiometric titrations (to determine the pK_a values of extracted acids and bases) were not performed on the extraction samples because gummy precipitates formed during titrations of the extracts with both HCl and NaOH. The precipitate coated the pH electrode precluding the measurement of pH. It was our observation that heat effects associated with precipitation were small and although enthalpy changes observed for the reaction regions for titrations of aqueous mixed solvent extracts were slightly different than both the enthalpy changes observed for reaction regions in model compound titrations and for classes of compounds listed in the literature, the small differences in enthalpy changes did not preclude our ability to unambiguously identify the classes of extracted compounds.

RESULTS

Solvent Extractions (without HCl or NaOH)

The calorimetric titration of the solvent extract with 0.698 M NaOH yielded a thermogram with a single reaction region which had an enthalpy change of -11.1 ± 0.3 kJ mol^{-1}. This measured heat must be for the proton ionization of the extracted compound plus the heat of formation of water. The corresponding heat of ionization would be $+23.9$ kJ mol^{-1} $(-11.1-(-37.0))$. Based on the reported values for the enthalpy changes for proton ionization of various organic acids and bases in methanol/H_2O mixtures, the class of compounds in the solvent extract which titrate with NaOH has been identified to be phenolic. There were no compounds in the solvent extract which reacted with a non-zero enthalpy change when titrated with 0.501 M HCl. Based on the PETC analysis, the concentration of phenols in the coal liquid was 0.39 M [15,16]. The concentration of the solvent extracted phenols was calculated to be 0.14 ± 0.02 M in the native coal liquid sample. Thus, approximately 36% of the total reported phenolic compounds in the T102-T8 coal liquid sample were extracted into the neutral mixed solvent. No basic compounds were extracted under these conditions.

HCl extractions

Figure 1 shows a typical thermogram for the titration of a 0.501 M HCl extract of the coal liquid sample with 0.698 M NaOH titrant. The thermogram shows two reaction regions with enthalpy changes of -36.7 ± 0.3 kJ

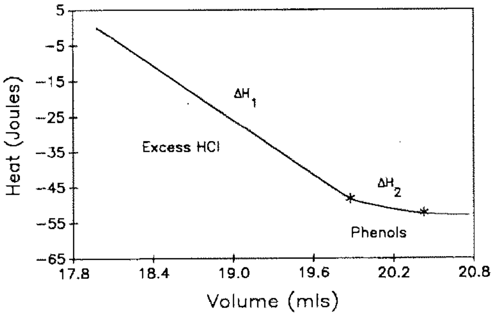

Fig. 1. Thermogram for the titration of a 2.98 ml aliquot of a 0.501 M HCl–methanol/water 60/40 (v/v) extract of coal liquid sample T102-T8. The NaOH titrant concentration was 0.698 M in the same solvent. Regions of the thermogram are for the reactions of (1) excess HCl (-36.7 ± 0.3 kJ mol^{-1}), and (2) phenolic compounds (-10.8 ± 0.3 kJ mol^{-1}). Regions in the titration curve are separated by an " * " denoting the end of one class of extracted compounds and the beginning of the next.

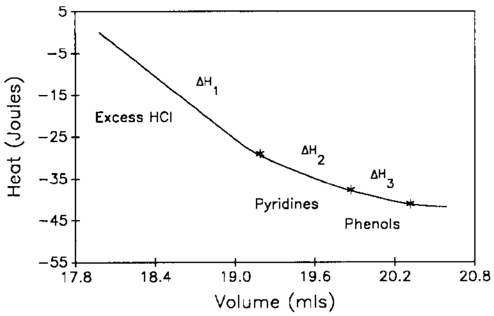

Fig. 2. Thermogram for the titration of a 2.98 ml aliquot of a 0.501 M HCl–methanol/water 60/40 (v/v) extract of coal liquid sample T102-T8 to which 0.21 M quinoline was added prior to extraction. The NaOH titrant concentration was 0.698 M in the same solvent. Regions of the thermogram are for the reactions of (1) excess HCl (-35.9 ± 0.3 kJ mol^{-1}), (2) pyridinic compounds (-18.1 ± 0.1 kJ mol^{-1}), and (3) phenolic compounds (-11.1 ± 0.1 kJ mol^{-1}). Region 2 appeared in the titration curve only when quinoline was added to the coal liquid prior to extraction.

mol^{-1} for region 1 (excess HCl), and -10.8 ± 0.3 kJ mol^{-1} for region 2 (phenols). The enthalpy changes given above are again for proton ionization and have not been corrected for heat of water formation. The compounds titrated in the two regions were identified by comparing the measured enthalpy changes for the two regions with literature data for the proton ionization of HCl and phenol in 60/40 methanol/H_2O mixtures [14], and also by measuring the heat of reaction of HCl and *m*-cresol with NaOH in the same solvent in this study. When *m*-cresol was added to the coal liquid prior to extraction, region 2 in the titration curve increased in length. When quinoline was added to the coal liquid prior to extraction, an additional region appeared in the titration curve with an enthalpy change of -18.1 ± 0.1 kJ mol^{-1} (region 2 in Fig. 2). This ΔH value is also uncorrected for the formation of water, and compares with literature data for the titration of pyridine in 60/40 methanol/H_2O mixtures [14] and with the ΔH for the titration of quinoline in 60/40 methanol/H_2O mixture measured in this study. No further extraction of coal liquid compounds was observed after two extractions with 0.501 M HCl. Also, no additional compounds were extracted using a greater HCl concentration (0.862 M).

Standard deviations for ΔH values associated with the various regions of the titration curve ranged typically from ± 0.1 to ± 0.3 kJ mol^{-1} for titrations of aliquots from the same extract and from ± 2 to ± 4 kJ mol^{-1} for titrations of aliquots from different extraction experiments. The larger variation in the ΔH values measured in different extraction experiments is attributable to differences in the aqueous phase composition resulting from evaporation effects during the extraction, as extraction time and temperature were not precisely controlled, and from differences in the transport of methanol and water into the coal liquid phase.

TABLE 1

Composition of extractable compounds in the Wilsonville T102-T8 coal liquid distillate, as determined by calorimetric titration of 0.50 M aqueous HCl extracts (in 60% methanol/40% H_2O) of the distillate sample with 0.70 M NaOH titrant (in $60MeOH/40H_2O$)

Experiment	Added (mol l^{-1})		Total found (mol l^{-1})	
	m-Cresol	Quinoline	Phenolic compounds [a]	Pyridinic compounds [b]
1	0.00	0.00	0.24 ± 0.01	0
2	0.23	0.00	0.42 ± 0.01	0
3	0.46	0.00	0.68 ± 0.02	0
4	0.00	0.21	0.28 ± 0.01	0.24 ± 0.01
5	0.00	0.47	0.35 ± 0.02	0.48 ± 0.01
6	0.20	0.21	0.41 ± 0.01	0.23 ± 0.01
7	0.42	0.42	0.88 ± 0.01	0.53 ± 0.01

[a] Enthalpy change for proton ionization plus formation of water for phenolic compounds ranged from -10 to -15 kJ mol^{-1}.

[b] Enthalpy change for proton ionization plus formation of water for pyridinic compounds ranged from -16 to -19 kJ mol^{-1}.

The concentrations of the coal liquid compounds extracted into the 60/40 methanol/H_2O solvent containing HCl are listed in Table 1. The first column lists experiment number, the second and third columns list the concentration of *m*-cresol and quinoline added to the coal liquid prior to extraction, and the fourth and fifth columns in the table list the total concentration of phenolic and pyridinic compounds extracted. The concentrations listed in Table 1 represent the concentration of extractable compound in the native coal liquid or in the coal liquid sample to which model compounds had been added and not the concentration of these compounds in the extract or diluted extract.

The concentration of phenolic compounds in the T102-T8 coal liquid sample has been reported to be 0.39 M and the concentration of basic nitrogen compounds has been reported to be 0.28 M [15,16]. The methanol/H_2O–HCl extraction of this coal liquid sample resulted in the extraction of (1) none of the native basic compounds (pyridinic, anilinic, and amino), but approximately 100% of the added quinoline, and (2) approximately 60% of native phenolic compounds and approximately 100% of the added *m*-cresol.

NaOH extractions

Figure 3 shows a typical calorimetric titration curve for the titration of a 0.698 M NaOH extract of the coal liquid sample with 0.501 M HCl titrant. Three titration regions were observed, with enthalpy changes of -37.1 ± 0.2 kJ mol^{-1} for region 1 (excess NaOH), -32.6 ± 0.4 kJ mol^{-1} for region 2 (phenols), and -10.8 ± 0.2 kJ mol for region 2 (phenols), and -10.8 ± 0.2

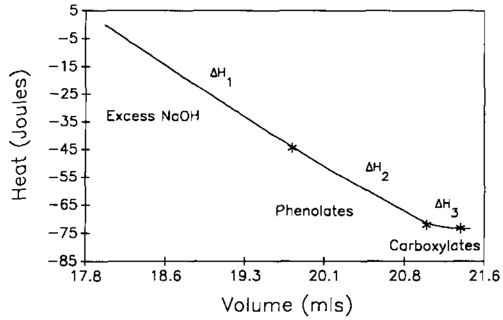

Fig. 3. Thermogram for the titration of a 2.98 ml aliquot of a 0.768 M NaOH–methanol/water 60/40 (v/v) extract of coal liquid sample T102-T8. The HCl titrant concentration was 0.663 M in the same solvent. Regions of the thermogram are for the reaction of (1) excess NaOH (−37.1 ± 0.2 kJ mol^{-1}), (2) phenolates (−32.6 ± 0.4 kJ mol^{-1}), and (3) carboxylates (−10.8 ± 0.2 kJ mol^{-1}).

kJ mol^{-1} for region 3 (carboxylic acids). These enthalpy changes are for protonation of the compounds specified in the 60/40 methanol/H_2O solvent.

When *m*-cresol was added to the coal liquid prior to extraction, corresponding increases in the length of region 2 were observed. When quinoline was added to the coal liquid prior to extraction, an additional region appeared in the titration curve with an enthalpy change of −16.8 ± 0.3 kJ mol^{-1} (for protonation), region 4 in Fig. 4. Quinoline and *m*-cresol added to the coal liquid prior to extraction continued to be found after three extractions with NaOH (quantitative recovery was observed after five extractions), although no further extraction of native coal liquid compounds was observed after three extractions.

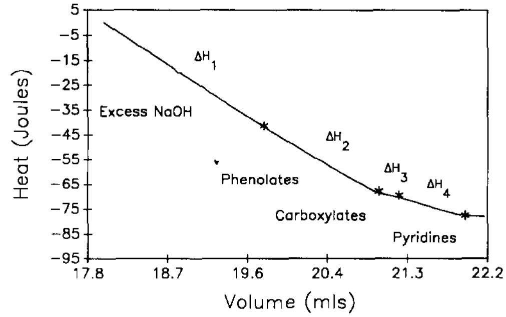

Fig. 4. Thermogram for the titration of a 2.98 ml aliquot of a 0.768 M NaOH–methanol/water 60/40 (v/v) extract of coal liquid sample T102-T8 to which 0.39 M quinoline was added. The HCl titrant concentration was 0.663 M in the same solvent. Regions of the thermogram are for the reaction of (1) excess NaOH (−37.0 ± 0.9 kJ mol^{-1}), (2) phenolates (−33.4 ± 0.6 kJ mol^{-1}), (3) carboxylates (−11 ± 2 kJ mol^{-1}), and (4) pyridinic compounds (−16.8 ± 0.3 kJ mol^{-1}). Region 4 appeared in the titration curve only when quinoline was added to the coal liquid prior to extraction.

TABLE 2

Composition of extractable compounds in the Wilsonville T102-T8 coal liquid distillate, as determined by calorimetric titration of 0.77 M aqueous NaOH extracts (in 60% methanol/40% H_2O) of the distillate sample with 0.66 M HCl titrant (in $60MeOH/40H_2O$)

Experiment	Added (mol l^{-1})		Total found (mol l^{-1})		
	m-Cresol	Quinoline	Phenolic compounds [a]	Pyridinic compounds [b]	Carboxylic acid compounds [c]
8	0.00	0.00	0.39 ± 0.01	0	0.08 ± 0.01
9	0.50	0.00	0.95 ± 0.03	0	0.08 ± 0.01
10	0.00	0.39	0.49 ± 0.02	0.36 ± 0.02	0.14 ± 0.02
11	0.00	0.82	0.39 ± 0.01	0.67 ± 0.03	0.14 ± 0.01

[a] Enthalpy change for protonation of phenolates ranged from -26 to -33 kJ mol^{-1}.

[b] Enthalpy change for protonation of pyridinic compounds ranged from -15 to -20 kJ mol^{-1}.

[c] Enthalpy change for protonation of carboxylates ranged from -8 to -11 kJ mol^{-1}.

Concentrations of compounds extracted into the 60/40 methanol/H_2O solvent containing NaOH are listed in Table 2. The first column lists experiment number, the second and third columns list the concentration of *m*-cresol and quinoline added to the coal liquid prior to extraction, and the fourth, fifth, and sixth columns list total concentrations of phenolic, pyridinic, and carboxylic acid compounds extracted from the coal liquid.

The concentration of phenolic compounds in the T102-T8 coal liquid sample has been reported to be 0.39 M, the concentration of carboxylic acids has been calculated from the phenolic concentration and total acid data, and the concentration of the basic nitrogen compounds has been reported to be 0.28 M [15,16]. The methanol/H_2O–NaOH extraction of this coal liquid sample resulted in the extraction of (1) approximately 100% of the native phenolic compounds and the added *m*-cresol, (2) approximately 100% of the carboxylic acids, and (3) none of the native basic compounds (pyridinic, anilinic, and amino), but approximately 100% of the added quinoline.

HCl/NaOH extractions

In an effort to achieve conditions whereby native basic nitrogen compounds could be extracted, a coal liquid sample which had been exhaustively extracted with NaOH to remove total phenolic compounds, was subsequently extracted with the 60/40 methanol/H_2O solvent containing 0.501 M HCl. The thermogram for titration of this extraction product with 0.682 M NaOH exhibited two reaction regions with enthalpy changes of -38.7 ± 0.6 kJ mol^{-1} (excess HCl) and -17.0 ± 0.7 kJ mol^{-1} (pyridinic compounds). The heats observed were for proton ionization plus the formation of water.

The compounds reacting in region 2 were identified as pyridines and no anilinic or amino compounds were found in the HCl extract. The concentration of extracted pyridinic compounds, 0.08 ± 0.01 M, corresponds to only 26% of the total basic nitrogen compounds reported by PETC [15,16]. No further extraction of basic compounds was observed in subsequent HCl extractions.

DISCUSSION

Previous work on binary and ternary mixtures of model coal liquid acids [*m*-cresol (C)] and bases [quinoline (Q), and aniline (A)] in tetralin solvent showed both self-association and complexation reactions to be important in determining the heat of mixing [1]. The model phenolic compound, *m*-cresol, was found to self-associate to form both dimers (C_2) and trimers (C_3) and to form mixed complexes with quinoline (CQ and C_2O) and aniline (CA and C_2A). The model nitrogen bases were both found to self-associate forming dimers (Q_2 and A_2). In addition, both the model acid and bases formed mixed complexes with the tetralin solvent (e.g. QT) [1].

Similar self-association and complexation reactions were expected to occur in the real coal liquid sample T102-T8. Species assumed to be present in the coal liquid sample studied were unassociated phenols (P), self-associated phenols (P_n), phenols associated with nitrogen bases (BP), unassociated nitrogen bases (B), self-associated nitrogen bases (B_n), unassociated carboxylic acids (COOH), carboxylic acids associated with nitrogen bases (COOH)B and/or phenols (COOH)P, and finally self-associated carboxylic acids $(COOH)_n$.

The concentrations of extractable compounds from the T102-T8 sample, based on PETC results from elemental analysis and near-IR work, were expected to be 0.39 M phenols, 0.15 M carboxylic acids (calculated from total acid and phenol concentrations), and 0.28 M basic nitrogen compounds, respectively [15,16]. Our results showed that we could extract 0.39 M phenolic, 0.14 M carboxylic acid, and 0.08 M pyridinic compounds from the coal liquid using acidic, neutral, or basic 60/40 methanol/H_2O solvent in a two-phase extraction procedure. The lower concentration obtained for basic nitrogen compounds, as compared to that from PETC analysis, must result from an inability to extract very hydrophobic nitrogen compounds from the coal liquid into the aqueous phase.

In the two-phase extraction procedure, we would expect to transfer polar coal liquid compounds, both acids and bases, from the coal liquid organic phase to the neutral aqueous phase, limited, to some small extent, by the solubility of the polar compounds in the methanol/H_2O mixed solvent. By acidifying the aqueous phase, we would expect to extract greater concentrations of basic compounds due to the increased solubility of their protonated

TABLE 3

Composition of extractable compounds (cumulative results from Tables 1 and 2) in the Wilsonville T102-T8 coal liquid distillate as determined by calorimetric titration of the distillate sample extracts. Column 1 lists the solutions used to extract the distillate sample. Column 2 lists the molecular species remaining in the coal liquid following extraction. Column 3 lists the molecular species identified in the aqueous extracts. Column 4 lists percentages of the total expected compounds, based on PETC analysis. Percentages were calculated from titrant volumes added during calorimetric titration

Extracting solution (in 60 MeOH/ 40 H_2O)	Species remaining in the coal liquid phase [a]	Species extracted into the aqueous phase	Percent extracted compounds [b] (%)
Neutral solvent	P, P_n, BP, B, B_n, COOH, (COOH)B, $(COOH)_n$, (COOH)P	P	36
Solvent containing HCl	P, P_n, BP, BHCl, COOH, (COOH)B $(COOH)_n$, (COOH)P	P	62
Solvent containing NaOH	B, B_n	P^- COO^-	100 100
(1) NaOH	–	–	–
(2) HCl	BHCl, B_nHCl	BHCl	26

[a] Model: P, P_n, BP, B, B_n, (COOH), $(COOH)_n$, (COOH)B, (COOH)P, where P = unassociated phenols, P_n = self-associated phenols, BP = N-base/phenol complexes, B = unassociated N-bases, B_n = self-associated N-bases, COOH = unassociated carboxylics, $(COOH)_n$ = self-associated carboxylics, (COOH)B = carboxylic/N-base complexes, and (COOH)P = carboxylic/phenol complexes.

[b] Percentages refer to the fraction of a class of extracted compound as compared to the total expected based on PETC analysis.

form. By making the extraction solvent basic, we would expect an increased extraction of coal liquid acids in their anionic form. These simple expectations were not followed exactly in our extractions due to the competing self-association and complexation reactions and due to complications resulting from hydrophobicity considerations. Table 3 lists the distribution of compounds found in both the coal liquid organic phase and the 60/40 methanol/H_2O aqueous phase following extractions with neutral mixed solvent, HCl, NaOH, and NaOH/HCl.

Neutral mixed solvent extraction

As shown in Table 3, the only titratable species found in the aqueous phase after extraction of the coal liquid with neutral mixed solvent were phenolic compounds. In fact, approximately 36% of the total phenols present in the native coal liquid were extracted with the neutral mixed solvent. In the native coal liquid prior to extraction, the approximate molar ratios of phenols to bases, carboxylic acids to bases, and total acids to bases are 1.5, 0.5, and 2.0 respectively. These ratios are consistent with the formation of both 1 : 1 and 2 : 1 acid/base complexes as suggested by the model studies [1]. After extraction with the mixed solvent alone, these ratios are approximately 1.0, 0.5, and 1.5. Apparently phenols involved in P_n complexes or one of the phenols involved in formation of a P_2B complex can be extracted with solvent, leaving PB and/or P(COOH)B complexes in the solvent-extracted coal liquid. No carboxylic acid compounds or basic nitrogen compounds were extracted into the neutral solvent. The most likely explanation for the failure of either of these types of compounds to transfer to the aqueous phase is that they are either too strongly complexed or too hydrophobic to be extracted with the neutral solvent.

HCl mixed solvent extractions

When the acidic solvent was used to extract the coal liquid, again only phenols were found in the aqueous phase. As shown in Table 3, the extracted phenols accounted for approximately 62% of the total phenols in the native coal liquid. The real surprise, however, was that again no basic nitrogen compounds were found in the acidic extracts. The increase in the fraction of the phenols extracted with the acidic solvent must result from displacement of phenol from mixed complexes such as BP by one of the two reactions shown below

$$\mathrm{BP(org)} + \mathrm{H^+(aq)} + \mathrm{Cl^-(aq)} \leftrightarrow \mathrm{BHCl(org)} + \mathrm{P(aq)}$$

$$\begin{aligned}\mathrm{BP(org)} + \mathrm{H^+(aq)} &\leftrightarrow \mathrm{BH^+} + \mathrm{P} + \mathrm{RCOOH}\\ &\leftrightarrow \mathrm{BRCOOH(org)} + \mathrm{P(aq)} + \mathrm{H^+(aq)}\end{aligned}$$

In the first of these reactions, HCl is transferred into the organic phase and the protonated base is ion-paired with chloride ion. In the second of these reactions, none of the aqueous HCl is permanently transferred to the organic phase. The HCl merely plays a catalytic role by protonating the base (which releases the bound phenol), to form an intermediate at the organic/aqueous interface which then exchanges a proton for a carboxylic acid moiety. That the protonated nitrogen bases are not extracted into the aqueous base must result from these compounds being so hydrophobic that even as cations their solubility in the 60/40 methanol/H_2O mixture is too low for transfer to take place. After HCl extraction, the molar ratios of phenolic compounds to bases, carboxylic acids to bases, and total acids to bases are approximately 0.5, 0.5, and 1.0 respectively.

Results for experiments 2–7 (Table 1) show that all the added *m*-cresol (C) and quinoline (Q) were extracted from the coal liquid with the acidic mixed solvent. The complete recovery of the added model phenolic compound (*m*-cresol) indicates that phenols must be in excess in the coal liquid with respect to their formation of mixed complexes with nitrogen bases and that *m*-cresol is sufficiently soluble in the 60/40 methanol/H_2O mixture to be transferred as a neutral molecule. The complete recovery of the added model pyridinic compound (quinoline) indicates that the native pyridinic compounds are either higher in molecular weight or are more strongly associated than the added quinoline.

Greater quantities of phenolic compounds were extracted when quinoline was added to the coal liquid, suggesting that quinoline may facilitate the transfer of phenolic compounds from the coal liquid into the acidic aqueous phase. The explanation for this phenomenon is unclear, but it must result from the competitive complexation of the native phenols with the added quinoline at the expense of complexes between the native phenols and native pyridinic compounds. All of the increase in extraction of phenol with acidic solvent in comparison to neutral solvent presumably results from the extraction of phenols, originally complexed with nitrogen bases, that have become protonated during the acidic extraction (i.e. the phenols have either been displaced from these mixed complexes by a stronger acid, HCl, or the HCl has catalyzed the exchange of native phenols for native carboxylic acids).

NaOH extractions

When the basic solvent was used to extract the coal liquid, phenols and carboxylic acids were found in the aqueous phase. As shown in Table 3, the extracted phenols accounted for approximately 100% of the total phenols in the native coal liquid and the extracted carboxylic acids accounted for approximately 100% of the remaining acids.

Considering the fact that no basic nitrogen compounds were extracted in the acidic mixed solvent, it should come as no surprise that no nitrogen bases were extracted using the basic mixed solvent. The increase in the fractions of phenols and carboxylic acids extracted with the basic solvent is an obvious result of the greater solubility of the phenolate and carboxylate anions over the neutral molecules

$$\mathrm{POH} + \mathrm{OH}^- \leftrightarrow \mathrm{P}^- + \mathrm{H_2O}$$

$$\mathrm{RCOOH} + \mathrm{OH}^- \leftrightarrow \mathrm{RCOO}^- + \mathrm{H_2O}$$

The concentration of extracted carboxylic acids ranged from a low of 0.08 M (53%) to a high of 0.14 M (95%) in the NaOH extractions. The range in concentration for extracted carboxylic acids is due to experimental conditions that resulted in short reaction regions for the titration of carboxylic acids and to curvature in these same reaction regions that made location of endpoints (especially the endpoints between the pyridinic and carboxylic acid regions) somewhat difficult. For these reasons the concentrations determined for the carboxylic acids and the pyridinic compounds have larger errors than the concentration determined for the total of these two classes of compounds or for any of the other extractable compounds.

Following the base extraction, the coal liquid contained 100% of the native nitrogen bases, as much as 20% of any added quinoline, 0% of native phenols or added cresol, and 0% of native carboxylic acids. Obviously, the nitrogen bases remaining in the coal liquid can no longer be hydrogen bonded to phenols or carboxylic acids but may still be self-associated.

NaOH / HCl extractions

When the basic solvent was first used to exhaustively extract the coal liquid, complete removal of phenols and carboxylic acids from the coal liquid was accomplished. As shown in Table 3, subsequent extraction with acidic mixed solvent resulted in extraction of approximately 26% of total basic nitrogen compounds from the coal liquid. It should be remembered that no basic nitrogen compounds were extracted in experiments employing only the acidic mixed solvent. The limited extraction of basic nitrogen compounds even after the removal of all coal liquid acids must be due to the hydrophobicity of these compounds. The observation that no nitrogen compounds are extracted if phenolic and carboxylic acid compounds are not first completely removed using NaOH, indicates that the presence of these compounds must block the extraction of the nitrogen compounds presumably because the nitrogen compounds must be completely associated with coal liquid acids. The observance that 74% of the total nitrogen bases are not extracted with HCl, even after completely removing both the phenolic and carboxylic acid compounds with NaOH, indicates that these remaining nitrogen compounds are either higher in molecular weight (extensively self-associated) than quinoline (or the extracted nitrogen compounds) or are too hydrophobic to be extracted.

As was observed in the HCl extractions, both the added *m*-cresol and quinoline were extracted in the NaOH extractions (experiments 8–11). The native basic nitrogen compounds in the coal liquid behave quite differently than the added quinoline. The native basic nitrogen compounds are probably polcyclic with more than two fused rings, accounting for their apparent hydrophobicity in comparison to quinoline. This conclusion is consistent with the average coal liquid molecular weight for T102-T8 reported by PETC from both vapor pressure osmometry and freezing point depression measurements (274–297 g mol^{-1}) [15,16]. This molecular weight would be consistent with, for example, polycyclic acidic and basic compounds containing four rings.

CONCLUSIONS

The extraction pattern for coal liquid acidic and basic compounds shown in Table 3 is consistent with a molecular interaction model for coal liquids which indicates that the polar compounds are extensively involved in complexation reactions. One new fact borne out by these experiments is that the hydrophobicity of the basic nitrogen compounds in this mid-boiling coal liquid is not well modelled by quinoline, at least with respect to solubility in the 60/40 methanol/H_2O mixed solvent. The solvent extraction calorimetric titration procedures described here will undoubtedly yield additional information about molecular interactions in coal liquids as they are applied to other coal liquid samples and to narrow boiling-point distillate fractions of coal liquids.

The calorimetric titration curves for the coal liquid extracts typically show 4 or 5 differently sloped regions with, as a general rule, relatively sharp endpoints. However, rounding of endpoints occurs whenever species with similar pK_a values are titrated in the calorimeter. This occurred, for example, when extracts containing pyridines and carboxylic acids were studied. Enthalpy changes associated with the different reaction regions of the titration curves permit an identification of various classes of acidic and basic compounds found in coal liquids and that can be extracted into the mixed solvent.

The extraction/calorimetric titration method developed here has allowed us to probe and begin to describe a very complex coal liquid, despite the fact that the particular coal liquid sample studied (T102-T8) was a high boiling sample containing high molecular weight compounds. This coal liquid sample was particularly difficult to study due to high concentrations of polycyclic fused ring compounds which were strongly associated and/or strongly hydrophobic. The methods described here should be applicable to the rapid characterization of other systems of similar complexity.

ACKNOWLEDGEMENT

The authors wish to express appreciation to the Department of Energy for providing support for this project under grant number DE-FG22-85PC80535, and to the Pittsburgh Energy Technology Center for providing the coal liquid samples necessary for the research.

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