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INSTRUMENTAL METHODS OF ANALYSIS OF SULFUR COMPOUNDS IN SYNFUEL PROCESS STREAMS

Quarterly Technical Progress Report for October—December 1983

By
Joseph Jordan
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Jonathan Talbott
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January 1984

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The Pennsylvania State University
University Park, Pennsylvania

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INSTRUMENTAL METHODS OF ANALYSIS OF SULFUR COMPOUNDS IN SYNFUEL PROCESS STREAMS

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for the period
October - December 1983

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Prepared for the United States Department of Energy
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Patent Cleared by Chicago OPC on February 14, 1983

ABSTRACT

TASK 1. METHODS DEVELOPMENT FOR THE SPECIATION OF THE POLYSULFIDES The contributions of this project to the electrochemical analysis of sulfides and polysulfides are reviewed and summarized. Electrochemical reduction at the dropping mercury electrode (DME) is the method of choice for the determination of polysulfidic sulfur. Total sulfidic sulfur can conveniently be quantitated in mixtures of sulfides and polysulfides, by measuring diffusion currents engendered by the anodic depolarization of the DME in the presence of the moieties HS^- and S_x^{2-}.

TASK 2. METHODS DEVELOPMENT FOR THE SPECIATION OF DITHIONITE AND POLYTHIONATES. In a solvent consisting of 40% ethanol-60% water, electrocapillary curves substantiated the adsorption of ethanol at the dropping mercury electrode. The potentials where adsorption occurred paralleled a shift of 1 volt in the polarographic half potential of the reaction:

$$S_4O_6^{2-} + 2e = 2S_2O_3^{2-}$$

TASK 3. TOTAL ACCOUNTING OF THE "SULFUR BALANCE" IN REPRESENTATIVE SAMPLES OF SYNFUEL PROCESS STREAMS. Two H-Coal liquefaction sour water samples were analyzed representing different stages in the PETC clean-up procedures. One specimen was a sample stripped of H_2S and ammonia; the other, resulting from a different batch, was stripped and subsequently extracted with methyl isobutyl ketone. The stripped effluent contained less than 0.001 M concentrations of sulfide, polysulfide, thiosulfate, and sulfate. On the other hand, sulfate accounted for 90% of the total sulfur present in the "stripped and extracted" sample; the remainder consisted of sulfidic and polysulfidic sulfur as well as thiosulfate.

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OBJECTIVE AND SCOPE OF WORK

The general objective is to develop dependable and accurate instrumental analysis methods for the determination of sulfur moieties. These will include polysulfides, dithionite and polythionates. Calorimetric procedures (thermometric titrations, injection enthalpimetry) and electroanalytical techniques (voltammetry, coulometric analysis, etc.) will be used. The complete speciation of sulfur will be undertaken in representative synfuel process stream samples.

TASK DESCRIPTIONS

ASK 1. METHODS DEVELOPMENT FOR THE SPECIATION OF POLYSULFIDES.

Thermochemical and electrochemical methods of analysis will be developed for the determination of $S^=$, $S_2^=$, $S_3^=$, $S_4^=$, $S_5^=$, and of higher polysulfides if applicable.

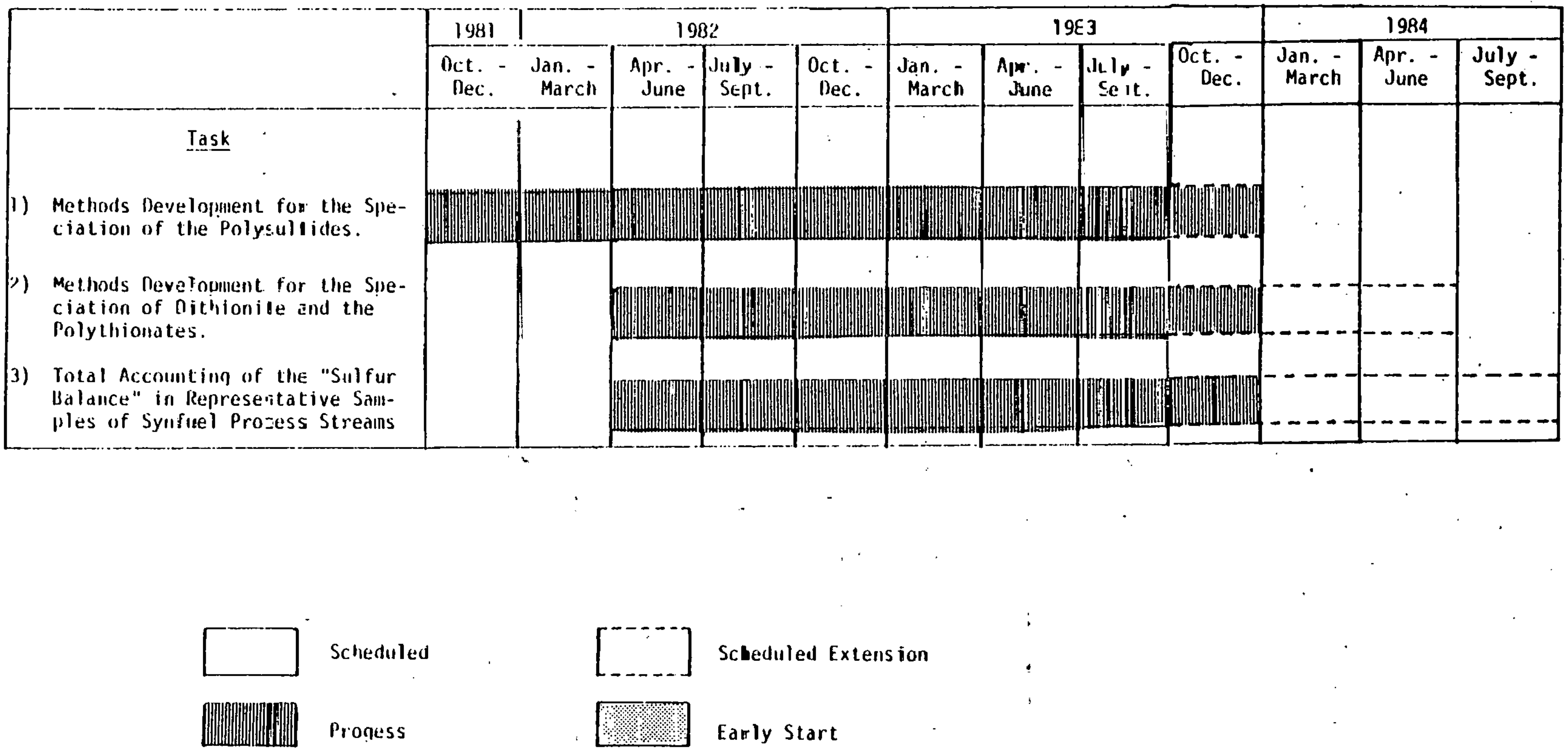
TASK 2. METHODS DEVELOPMENT FOR THE SPECIATION OF DITHIONITE AND POLYTHIONATES.

Electroanalytical and/or thermochemical methods of analysis will be developed for the determination of $S_2O_4^=$, $S_2O_6^=$, $S_3O_6^=$, $S_4O_6^=$, $S_5O_6^=$, $S_6O_6^=$, and of higher polythionates.

TASK 3. TOTAL ACCOUNTING OF THE SULFUR BALANCE IN REPRESENTATIVE SAMPLES OF SYNFUEL PROCESS STREAMS.

Diverse samples will be analyzed. The results will be intercompared critically and "fingerprint features" of sulfur distribution (between various oxidation states and conjugate Bronsted acid-base moieties, etc.) will be correlated to type of coals, methods and conditions of conversion and other significant variables.

PROGRESS REPORT CHART



SUMMARY OF PROGRESS TO DATE

This is the ninth quarterly report on work performed under Grant DE-FG22-81PC40783, initiated on September 30, 1981.

TASK 1. METHODS DEVELOPMENT FOR THE SPECIATION OF THE POLYSULFIDES. The Lewis acid p-hydroxymercuribenzoate (HMB) has been found to be a valuable reagent for the determination of polysulfides by thermometric titration. Titration of a solution containing both hydrosulfide (HS^-) and polysulfides (S^{2-}, $2<x\leq5$) has yielded two discrete endpoints. The first endpoint corresponds to hydrosulfide and the second to twice the molar-sum of hydrosulfide plus polysulfides. The average chain length of the polysulfides has been found to be dependent on pH. The trimetrically determined average chain length at pH 14 is four, corresponding to a rearrangement of both trisulfide and pentasulfide to tetrasulfide. The reactions of thiosulfate, cyanide, iodide, sulfite, ammonia and thiocyanate with HMB have been investigated and assignments made for the enthalpies and Gibbs free energy of reaction. The reagent p-HMB is characterized as an adduct of the strong, soft Lewis acid $^-OOC\phi Hg^+$ and the hard base hydroxide. On the other hand, thallium (I) is a soft Lewis acid which is selective for sulfide and polysulfide moieties as a group but lacks the specificity to distinguish between HS^- and individual polysulfides. An electrochemical technique has been developed to determine polysulfidic sulfur by polarography at the dropping mercury electrode. Electrode reactions of the type

$$S_x^{2-} + 2(x-1)e + xH_2O \rightarrow xHS^- + xOH^-$$

are implicated. The method is applicable to a range of concentrations between 5 x 10^{-5} and 3 x 10^{-3} M. For the determination of "sulfidic sulfur"

$$[HS^-] + \sum_{x=2}^{5} [S_x^{2-}]$$

advantage was taken of diffusion currents corresponding to the following anodic depolarization reactions of the dropping mercury electrode:

$$S_x^{2-} + Hg = HgS + (x-1)S + 2e$$

$$HS^- + Hg = HgS + H^+ + 2e$$

which overlap in a range of potentials between -0.65 and +0.2 volt versus the saturated calomel electrode.

TASK 2. METHODS DEVELOPMENT FOR THE SPECIATION OF DITHIONITE AND THE POLYTHIONATES. The literature on the electroreduction and electrooxidation of dithionite, trithionate, tetrathionate and pentathionate has been reviewed previously. Dithionate appears to be electrochemically inert. However, a wealth of information is available on electroreduction processes which are likely to yield cathodic current-voltage curves amenable for analytical utilizations. Thus trithionate is known to be electroreduced to a mixture of sulfite and thiosulfate, where as tetrathionate yields thiosulfate as its sole electroreduction product. It has been reported that pentathionate is electroreducible to a mixture of thiosulfate and elemental sulfur and dithionite yields sulfoxylate (SO^{2-}) upon electroreduction. A few electrooxidation reactions of the relevant moieties have also been reported, yielding corresponding anodic current-voltage curves. Experimentally, it has been found that trithionate, tetrathionate, pentathionate, and hexathionate indeed yielded well defined polarographic electroreduction waves at the dropping mercury electrode. A polarographic procedure has been developed for the determination of tetrathionate and pentathionate in the presence of each other. The method is based on measuring diffusion currents (at the dropping mercury electrode) at two discrete potentials where the following electrode reactions occur:

AT -0.4 VOLT VS SCE: $S_4O_6^{2-} + 2e = 2S_2O_3^{2-}$

$S_5O_6^{2-} + Hg + 2e = 2S_2O_3^{2-} + HgS(s)$

AT -0.7 VOLT VS SCE: $S_5O_6^{2-} + H^+ + 4e = 2S_2O_3^{2-} + HS$

It has been found that trithionate, tetrathionate, and pentathionate yield well-resolved differential pulse polarographic peaks at the dropping mercury electrode using a mixed solvent of 60% water/40% ethanol (v/v). Polythionate speciation is feasible without prior separation. Remarkably, the polarographic half-wave potential of the reduction of tetrathionate (to thiosulfate) is shifted by -1.1 volt when the solvent is changed from pure water to an ethanol-water mixture. Concomitantly ethanol is adsorbed at the electrode interface. However, the principal overall electroreduction stoichiometries of the polythionates are the same in the presence and in the absence of ethanol, viz.,

$$S_3O_6^{2-} + 2e = S_2O_3^{2-} + SO_3^{2-}$$

$$S_4O_6^{2-} + 2e = 2S_2O_3^{2-}$$

$$S_5O_6^{2-} + 4e + H^+ = 2S_2O_3^{2-} + HS^-$$

Furthermore, tetrathionate, pentathionate, and hexathionate were found to be electrooxidable at glassy carbon anodes, while trithionate was not. The heat of oxidation-reduction reactions of the type

$$S_xO_6^{2-} + (3x-5)Br + (4x-6)H\ O = xSO_4^{2-} + (6x-10)Br^- + (8x-12)H^+$$

and of the cyanolysis reactions

$$S_xO_6^{2-} + (x-3)CN^- + H_2O = S_2O_3^{2-} + SO_4^{2-} + (x-3)SCN^- + 2H^+$$

have been identified as promising startinig points for the development of instrumental methods for the determination of polythionates.

TASK 3. TOTAL ACCOUNTING OF THE SULFUR BALANCE IN REPRESENTATIVE SAMPLES OF SYNFUEL PROCESS STREAMS. Inquiries have been sent to industrial, government, and academic organizations, soliciting appropriate specimens. Responses have been received from more than a dozen individuals, who have access to diverse samples in various locations, ranging from Washington, Oregon, and California to New York, Delaware, and the Carolinas. Specimens were stored in a nitrogen dry-box facility. Its effectiveness in minimizing sample oxidation was verified by duplicate analysis of two H-Coal® sour water samples which had been so stored for over two years. A five-step protocol has been formulated for speciating and quantitating the major and minor moieties which contribute to the total sulfur content. Analysis of polysulfides in H-Coal sour water samples yielded comparable results by electrochemical, thermochemical, and classical methods. A gasifier condensate was found to contain no sulfide, polysulfides, or thiosulfate by any method. An SRC-II aqueous effluent was found to contain some thiosulfate by both electrochemical and thermochemical methods. Analysis of aqueous H-Coal liquefaction process effluent sample by electroanalytical and thermochemical methods showed that the predominant sulfur species was HS^-. Polysulfides were present in aged specimens. In contrast, an aqueous gasification effluent sample from Grand Forks, ND, contained not only sulfidic and polysulfidic sulfur but also thiosulfate and thiocyanate. Liquefaction (SRC process) samples from the pilot plant at Wilsonville, Alabama, taken from different stages in the wastewater treatment were found to contain sulfate and thiosulfate. A liquefaction sample from PETC's Disposable Catalyst Development (DCD) unit contained a mixture of sulfide and polysulfides. Two H-Coal liquefaction effluents originating from the pilot plant at Catlettsburg, Kentucky, were treated at PETC. These wastewater samples were obtained from different stages of the PETC clean-up treatment and both contained comparatively low concentrations of sulfur which consisted predominantly of sulfate.

DESCRIPTION OF TECHNICAL PROGRESS

TASK 1. METHODS DEVELOPMENT FOR THE SPECIATION OF THE POLYSULFIDES

Work on this task has been substantively completed. This report is the final in a series of four retrospective summaries which evaluate critically the relevant accomplishments.

Methods of analysis of the polysulfides described in the literature reflect ambiguities regarding the oxidation states of sulfur in these moieties. Molecular orbital calculations[1], indicate that the two negative charges of the anions S_x^{2-} are distributed among all the sulfur atoms in any given polsylfide chain. However, S_x^{2-} moieties react chemically as if one of the sulfur atoms carried a divalent negative charge and the remainder of the chain consisted of uncharged sulfur atoms. Analysis of polysulfide mixtures is further complicated by similarities of structure and chemical reactivity among the various polysulfides, viz., S_2^{2-}, S_3^{2-}, S_4^{2-}, S_5^{2-}, etc. Other sulfur moieties, similar in chemical reactivity to the polysulfides must also be taken into account as possible interferences. Among them, sulfide S^{2-} (which hydrolizes to HS^- in aqueous solution), thiols, and thioethers are of main concern as species which are likely to be present in coal conversion wastewater streams. Additional complications are rearrangement reactions[2] of the type:

$$nS_mS^{2-} + HS^- + OH^- = mS_nS^{2-} + H_2O \qquad (1.1)$$

where: $n - m = 1$; $m = 1,2,3,4$

For example:

$$2S_4^{2-} + HS^- + OH^- = 3S_3^{2-} + H_2O \qquad (1.2)$$

As a result, polysulfide chain length and concentrations of individual polysulfide moieties may vary as a function of pH and bisulfide concentration.

A conventional nomenclature system is in use for expressing analytical findings in samples containing polysulfides and/or mixtures of sulfides, hydrosulfides, and polysulfides. The terms "polysulfidic sulfur" and "sulfidic sulfur" are defined as follows:

Polysulfidic Sulfur:

$$[S(0)] \equiv \sum_{x=2}^{5} (x-1)[S_x^{2-}] = 4[S_5^{2-}] + 3[S_4^{2-}] + 2[S_3^{2-}] + [S_2^{2-}] \qquad (1.3)$$

Sulfidic Sulfur:

$$[S(-II)] \equiv [S_5^{2-}] + [S_4^{2-}] + [S_3^{2-}] + [S_2^{2-}] + [HS^-] + [S^{2-}] \qquad (1.4)$$

The electrochemistry of the polysulfides and of sulfide was investigated[3,4] in order to develop methods for the determination of polysulfides in the presence of sulfide and other sulfur species. Current-voltage curves obtained in the presence of mixtures of various polysulfides yielded two interesting observations:

(a) Only a single polarographic wave was obtained at the dropping mercury electrode regardless of the number of polysulfides present in the sample.

(b) That wave had the character of a composite wave, i.e., it exhibited both anodic and cathodic limiting current regions.

The cathodic diffusion current of the composite wave was proportional to the polysulfidic sulfur concentration (defined in Equation 1.3) irrespective of the chain length of the polysulfides. Analysis of the reduction products and coulometric experiments implicated the following type of electrode reactions:

$$S_x^{2-} + 2(x-1)e + xH_2O = xHS^- + xOH^- \qquad (1.5)$$

For example:

$$S_5^{2-} + 8e + 5H_2O = 5HS^- + 5OH^- \qquad (1.6)$$

Controlled potential coulometry of reaction intermediates and cyclic voltammetry revealed that the reaction sequence 1.7-1.8 accounted for the overall reaction 1.5.

$$S_x^{2-} + (x-1)Hg + H_2O = (x-1)HgS + OH^- + HS^- \qquad (1.7)$$

$$(x-1)HgS + 2(x-1)e + (x-1)H_2O = (x-1)HS^- + (x-1)Hg + (x-1)OH^- \qquad (1.8)$$

This is a so-called CE mechanism consisting of a chemical reaction (Reaction 1.7) followed by an electron transfer process (Reaction 1.8) which involves the product of the preceding reaction.

For example:

$$S_5^{2-} + 4Hg + H_2O = 4HgS + HS^- + OH^- \qquad (1.9)$$

$$\underline{4HgS + 8e + 4H_2O = 4HS^- + 4OH^-} \qquad (1.10)$$

$$S_5^{2-} + 8e + 5H_2O = 5HS^- + 5OH^- \qquad (1.9 + 1.10)$$

When a glassy carbon indicator electrode was used in lieu of the dropping mercury electrode no measurable current corresponding to Reaction 1.5 was observed.

On the other hand, the anodic portion of the composite wave was proportional to the total concentration of the polysulfides:

$$\sum_{x=2}^{5} [S_x^{2-}] = [S_5^{2-}] + [S_4^{2-}] + [S_3^{2-}] + [S_2^{2-}] \qquad (1.11)$$

These results were accounted for by electrode reactions of the type:

$$S_x^{2-} + xHg = xHgS + 2e \qquad (1.12)$$

For example:

$$S_5^{2-} + 5Hg = 5HgS + 2e \qquad (1.13)$$

Reactions 1.12 and 1.13 are so-called "anodic depolarization" processes, involving the electrooxidation of mercury. Similar reactions are known to occur in the presence of other depolarizers, such as sulfide, thiosulfate, sulfite, thiocyanate, cyanide, and chloride. Sulfide is the only moiety which anodically depolarizes mercury at the same potential as the polysulfides. An extensive study was undertaken to investigate the anodic depolarization of mixtures of polysulfides and sulfides. It was observed that the anodic current was proportional to the sum of the concentrations of sulfides and polysulfides. Thus, the measurement of the anodic current provided a means to determine the total sulfidic sulfur (defined in Equation 1.4) content of samples.

Electrochemical methods are the techniques of choice for the determination of polysulfides and hydrosulfide due to their ability to discriminate between sulfidic and polysulfidic sulfur. The relative proportion of these is not affected by Rearrangement Reaction 1.1. The determinations were found to be remarkably free of interferences by other moieties normally encountered in coal conversion process streams.

TASK 2. METHODS DEVELOPMENT FOR THE SPECIATION OF DITHIONITE AND THE POLYTHIONATES

In previous work[5,6] the polarography of the polythionates was investigated in a mixed solvent (ethanol-water) system. The results of the investigation were compared with findings obtained in aqueous solutions in the absence of ethanol. Two distinct effects of ethanol were evident:

(a) The half-wave potential of $S_4O_6^{2-}$ undergoes a very large negative shift.

(b) In lieu of the two well-defined waves observed in aqueous solution, $S_5O_6^{2-}$ yields only a single well-defined wave (plus two ill-defined small prewaves).

However, the overall electrode reactions were nevertheless found to be the same in both media, viz.,

$$S_3O_6^{2-} + 2e = S_2O_3^{2-} + SO_3^{2-} \tag{2.1}$$

$$S_4O_6^{2-} + 2e = 2S_2O_3^{2-} \tag{2.2}$$

$$S_5O_6^{2-} + 4e + 2H_2O = 2S_2O_3^{2-} + H_2S + 2OH^- \tag{2.3}$$

During this quarterly period, work was undertaken to explain the experimental observations. Electrocapillary measurements were performed in order to ascertain whether adsorption of ethanol at the dropping mercury electrode was implicated. Electrocapillary curves were obtained by measuring drop time (which is proportional to surface tension[7]) as a function of potential. Figures 2.1 and 2.2 illustrate a comparison between electrocapillary curves in the absence and presence of ethanol. It is apparent that ethanol shifted the electrocapillary maximum and "flattened" the electrocapillary curve in the range of potentials between 0.0 and -1.0 volt versus SCE. This indicates that under the experimental conditions, ethanol was absorbed at the mercury interface beginning at zero volt and gradually desorbed at -1.0 volt. These potentials parallel the observed shift of half-wave potential of tetrathionate when changing solvents from pure water to water and ethanol. Correlations of this type have been accounted for in the literature[8,9] by electric double layer effects

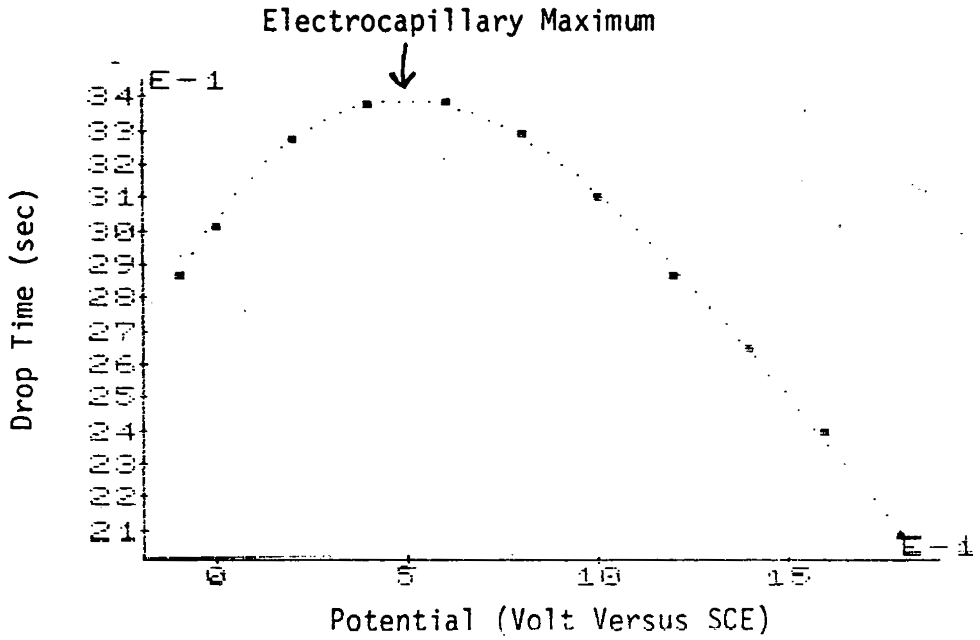


Figure 2.1. Electrocapillary Curve in the Absence of Ethanol

Solvent: Pure water
Supporting Electrolyte: 0.12 M phosphate buffer, pH 6.5

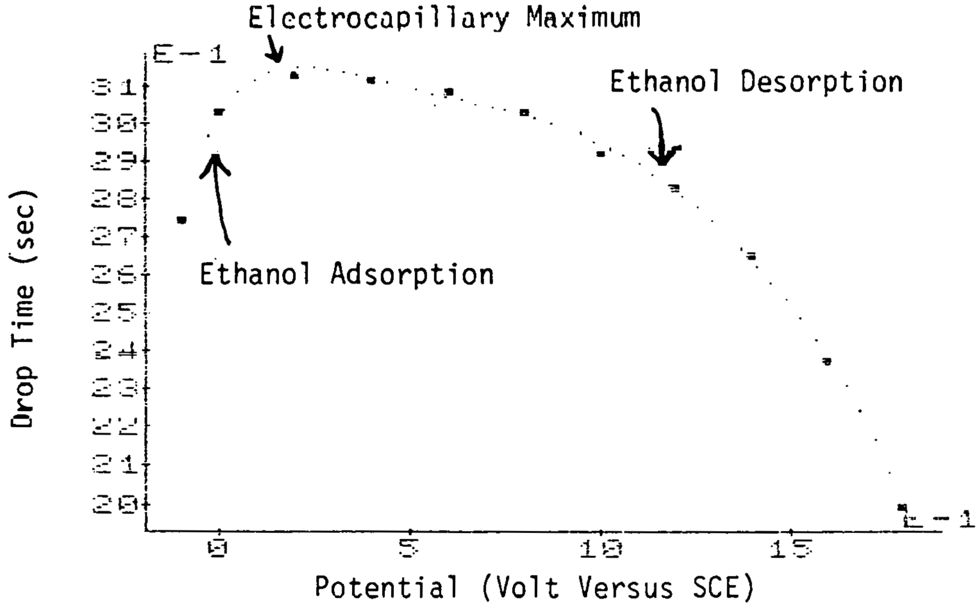


Figure 2.2. Electrocapillary Curve in the Presence of Ethanol

Solvent: 60% (v/v) water, 40% ethanol
Supporting Electrolyte: 0.12 M phosphate buffer, pH 6.5

engendered by adsorption at electrode interfaces. The magnitude of the effect observed in the present study is remarkable and warrants further investigation. Appropriate work is in progress.

TASK 3. TOTAL ACCOUNTING OF THE SULFUR BALANCE IN REPRESENTATIVE SAMPLES OF SYNFUEL PROCESS STREAMS

Two sour water samples resulting from the H-Coal process[10] were received in August, 1983. These samples, by-products of the direct liquefaction of Kentucky #9 coal at the Catlettsburg, Kentucky, pilot plant, were treated at the Pittsburgh Energy Technology Center (PETC). One sample, designated as "stripped" (L-6), resulted from the following generalized procedure[11]: the sour water was heated to 90°C in a still equipped with a nitrogen bleed to remove hydrogen sulfide and ammonia until the ammonia concentration was reduced to less than 500 mg/L. The other sample, termed "stripped and extracted" (L-7), was similarly stripped and then subjected to countercurrent extraction using methyl isobutyl ketone to remove phenol[11]. Subsequently, the water was heated to 40°C in a second still using a nitrogen bleed to drive off residual ketone. Upon arrival in our laboratories, the samples were stored in a nitrogen glove box. A description of these samples and their treatment history is presented in Table 3.1. Following a prescribed protocol[3] the total sulfur, redox potential, and pH were determined, as reported in Table 3.2. Sulfur speciation results appear in Table 3.3.

ANALYSIS OF THE STRIPPED H-COAL LIQUEFACTION SAMPLE (L-6), using electroanalytical and thermometric techniques showed that sulfide, polysulfide, thiosulfate, and sulfate were all found to be below the detection limits of the respective methods (Table 3.3). A sulfur balance from Table 3.3 could not account for the total sulfur obtained by classical methods (Table 3.2, Column 4). The low total sulfur concentration, the pH of 6.2 and the redox potential of +0.671 volts (versus NHE) were expected though, as will be discussed in the conclusions section of this report. Sulfate should be the predominant species in this specimen as the high positive potential is indicative of a highly oxidized sample[12].

ANALYSIS OF THE STRIPPED AND EXTRACTED H-COAL LIQUEFACTION SAMPLE (L-7) yielded interesting results. Speciation revealed the presence of sulfide, polysulfides, thiosulfate, and sulfate (Table 3.3). The predominant sulfur moiety was found to be sulfate, which is consistent with the high positive redox potential, +0.353 volt (versus NHE), and the pH, 6.9 (Table 3.2)[12]. The anomalous pH and redox potential will be discussed in more detail in the conclusions section of this report. The sulfidic sulfur concentration was found to be 0.8 mM thermometrically, and 0.71 mM electrochemically. These are in good agreement. The polysulfidic sulfur obtained by the different methods disagrees. Anomalous appearance of curvature at the thermometric titration endpoints (which may indicate the presence of interferents) casts doubt on the thermochemical results[13]. Additionally the value for the total sulfur, 13.6 mM (Table 3.2), agrees with the sum of the individual moiety concentrations, 13.4 mM, estimated from Table 3.3.

Table 3.1

Description of Samples of Synfuel Process Streams

Identification	L-6	L-7
Supplier	D. Drummond DOE, PETC P.O. Box 10940 Pittsburgh, PA 15236	D. Drummond DOE, PETC P.O. Box 10940 Pittsburgh, PA 15236
Description	Aqueous effluent of H-Coal process; Catlettsburg, KY, plant; Kentucky #9 coal processed Nov. 1982. Stripped at PETC.	Aqueous effluent of H-Coal process; Catlettsburg, KY, processed Nov. 1982. Stripped and extracted at PETC.
Storage before arrival at Penn State	Sealed in polyethylene bottle.	Sealed in polyethylene bottle.

Table 3.2

Characterization of Aqueous Coal Conversion Process Stream Specimens

(1) Identification[a]	(2) pH	(3) Redox Potential[b]	(4) Total Sulfur[c]
L-6	6.2	+0.67	0.0017 ± 0.0001
L-7	6.9	+0.35	0.0136 ± 0.0001

(a) See Table 3.1

(b) Volt versus normal hydrogen electrode

(c) Moles sulfur per liter, weighed as $BaSO_4$

Table 3.3

Summary of Results of Determination of Sulfur Moieties in Synfuel Process Stream Samples[a]

Concentrations (millimole·ℓ^{-1})	Sample L-6		Sample L-7	
	Method		Method	
	Thermochemical	Electrochemical	Thermochemical	Electrochemical
Sulfidic S(-II)	<0.08[b]	<0.04[b]	0.8	0.71
Polysulfidic S(0)	<0.08[b]	<0.04[b]	0.6	0.07
Thiosulfate	<0.1[b]	<0.01[b]	---	0.24
Sulfite	---	<0.01[b]	---	---
Sulfate	<0.2[b]	---	11.8	---

(a) See Table 3.1 for identification
(b) Detection limit

CONCLUSIONS

TASK 1. METHODS DEVELOPMENT FOR THE SPECIATION OF THE POLYSULFIDES. Polarography provides a preferred approach for the analysis of mixtures of polysulfides, sulfides, and hydrosulfides. Polysulfidic and sulfidic sulfur can be determined from a single composite wave, regardless of the chain length of the various polysulfides present in the sample.

TASK 2. METHODS DEVELOPMENT FOR THE SPECIATION OF DITHIONITE AND POLYTHIONATES. Electric double layer effects may account for a cathodic overvoltage of 1 volt in the electroreduction of tetrathionate (to thiosulfate) at the dropping mercury electrode.

TASK 3. TOTAL ACCOUNT OF THE "SULFUR BALANCE" IN REPRESENTATIVE SAMPLES OF SYNFUEL PROCESS STREAMS. Several conclusions can be drawn by comparison of the results of samples L-6 and L-7 in the present document with the data obtained for a previous "untreated" aqueous effluent (L-2) of the H-Coal process from Catlettsburg, Kentucky[5]. L-2, L-6, and L-7 were processed on the same date (November 1982) at the Catlettsburg pilot plant. L-6 and L-7 were subsequently treated by PETC cleanup procedures but L-2 was not. L-2 contained 0.154 Molar sulfur as hydrogen sulfide. The pH and redox potential of L-2 were 9.3 and -0.31 volt (versus NHE) respectively.

TO BEGIN WITH, the recently analyzed effluents, L-6 and L-7, were stripped at PETC (see Description of Technical Progress, Task 3) to remove most of the hydrogen sulfide and ammonia. This explains why L-6 and L-7 contained milli-Molar sulfur concentrations (Table 3.3) instead of a 0.15 Molar sulfur concentration as in L-2.

SECONDLY, since ammonia is removed by the PETC stripping process, it is expected that the pH of the treated specimens (L-6 and L-7) would be much lower than that of the untreated sample (L-2). This was indeed observed experimentally; the pH of L-6 and L-7 were 6.2 and 6.9, respectively, while the pH of L-2 was 9.3.

THIRDLY, the redox potential of L-2 (-0.31 volt) is indicative of a reducing environment, while the redox potentials of the PETC treated effluents, L-6 and L-7, (+0.67 volt and +0.35 volt, respectively) were characteristic of an oxidizing environment. Based on the pH and redox potentials, a lower oxidation state of sulfur would be expected to prevail in L-2 while a high sulfur oxidation state would predominate in L-6 and L-7. This too was experimentally confirmed: hydrogen sulfide was the only sulfur moiety detected in L-2 while sulfate was the predominant sulfur species in L-7. The prevalance of sulfate in L-7 indicates that this effluent has been exposed to oxygen for a fairly long time, because thiosulfate (an intermediate in the oxidation of hydrogen sulfide to sulfate) is slow to oxidize.

FOURTHLY, since ammonia was removed during the PETC stripping process and phenols (weak Bronsted acids which are another major liquefaction byproduct) remained, it would be expected that the pH of the effluent obtained directly after the stripping process be slightly acidic. This was indeed the actual finding: the pH of L-6 was 6.2. L-7 was additionally treated to remove the phenol byproducts; its pH would be expected to be slightly higher than that of L-6. Again, this was experimentally observed.

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