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# An investigation of cadmium and sulfur reactions in dimethylsulfoxide

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AN ABSTRACT OF THE THESIS OF Howard W. Hogle for the Master of  
Science in Chemistry presented July 23, 1982.

Title: An Investigation of Cadmium and Sulfur Reactions in  
Dimethylsulfoxide.

APPROVED BY MEMBERS OF THE THESIS COMMITTEE:

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Horace F. White

The study of the reaction of cadmium and sulfur in dimethylsulfoxide (DMSO) is presented. Specifically, the reaction of dissolved molecular sulfur in DMSO at temperatures greater than 90°C with freshly precipitated metallic cadmium is followed by UV-visible spectrometry, atomic absorption spectrometry, and Raman spectrometry. Evidence for the formation of a new cadmium-sulfur species and  $S_3^-$  is discussed. In a second reaction, an equilibrium sodium polysulfide solution in DMSO is titrated with a solution of cadmium ion at room

temperature and the reaction progress is followed by means of UV-visible spectrometry. A calculation of the average number of polysulfide charges reacting with each cadmium ion,  $\bar{n}_Q$ , was made using literature values of the molar absorptivities of the ions  $S_3^-$ ,  $S_8^{-2}$ , and  $S_6^{-2}$  and Beer's law. Likewise, the average number of sulfur atoms,  $\bar{n}_M$ , reacting with each cadmium ion was determined. A value of 4.8 polysulfide charges per cadmium ion was determined for  $\bar{n}_Q$  and a value of 18 sulfur atoms per cadmium ion was determined for  $\bar{n}_M$ . The significance of the possible formation of cadmium polysulfide complexes is discussed briefly in conjunction with the reaction mechanisms involved in the electrodeposition of CdS from a DMSO solution of  $CdCl_2$  and  $S_8$ .

AN INVESTIGATION OF CADMIUM AND SULFUR REACTIONS  
IN DIMETHYLSULFOXIDE

by

HOWARD W. HOGLE

A thesis submitted in partial fulfillment of the  
requirements for the degree of

MASTER OF SCIENCE  
in  
CHEMISTRY

Portland State University

1982

TO THE OFFICE OF GRADUATE STUDIES AND RESEARCH:

The members of the Committee approve the thesis of Howard W. Hogle presented July 23, 1982.



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This work is dedicated to my parents, Harold W. Hogle and Sophia M. Hogle.

## TABLE OF CONTENTS

	PAGE
ACKNOWLEDGEMENTS . . . . .	iii
LIST OF TABLES . . . . .	v
LIST OF FIGURES . . . . .	vi
 CHAPTER	
I INTRODUCTION . . . . .	1
II MATERIALS . . . . .	9
III APPARATUS . . . . .	12
IV PROCEDURE AND RESULTS . . . . .	14
Stability of molecular sulfur in dimethylsulfoxide . . . . .	14
Reaction of metallic cadmium with S <sub>8</sub> dissolved in dimethylsulfoxide . . . . .	17
Reaction of cadmium ion with polysulfides in dimethylsulfoxide . . . . .	25
V DISCUSSION . . . . .	30
REFERENCES . . . . .	54
APPENDIX A: FORMATION OF POLYSULFIDE SOLUTIONS . . . . .	57
APPENDIX B: DERIVATION OF EQUILIBRIUM EQUATION USING SAWYER'S CONSTANTS . . . . .	59

## LIST OF TABLES

TABLE	PAGE
I	Summary of Molar Absorptivities for Polysulfides . . . . . 6
II	Summary of Equilibrium Constants, $K_1$ and $K_2$ . . . . . 7
III	Summary of Experimental Results from Reaction of Dissolved Sulfur with Metallic Cadmium . . . . . 20
IV	Solubility of CdS in DMSO . . . . . 25
V	Molar Absorptivities of $S_3^-$ at Various Wavelengths . . . 36
VI	Molar Absorptivities of $S_8^{-2}$ at Various Wavelengths . . 37
VII	Summary of Molar Absorptivities for $S_3^-$ , $S_8^{-2}$ , and Hypothetical Cadmium Polysulfide Complex . . . . . 38
VIII	Relative Deviation of Experimental Polysulfide Concentrations from Theoretical Polysulfide Concentrations . . . . . 46
IX	Values of $K_2$ Calculated for DMSO Solutions of $Na_2S_8$ . . 49



## LIST OF FIGURES

FIGURE	PAGE
1. UV-visible spectra of varying concentrations of sulfur in DMSO . . . . .	15
2. Absorbance versus sulfur concentration where sulfur concentration is expressed as mmoles of S/liter . .	16
3. UV-visible spectra of a 0.075 mM S <sub>8</sub> solution as a function of temperature . . . . .	18
4. (a) Raman spectrum of 2.13 mM S <sub>8</sub> solution which was reacted with cadmium metal. (b) Raman spectrum of initial 2.13 mM S <sub>8</sub> solution . . . . .	21
5. (a) Raman spectrum of neat DMSO. (b) Raman spectrum of DMSO saturated with S <sub>8</sub> (3.23 mM S <sub>8</sub> ) . . . . .	22
6. UV-visible spectra of 0.110 mM S <sub>8</sub> solution aliquots which were passed over cadmium metal . . . . .	23
7. Elongated quartz cuvette . . . . .	27
8. Reaction of cadmium ion with polysulfides followed by UV-visible spectrometry . . . . .	29
9. Spectrophotometric curves recorded by Cauquis (21). . . . .	35

FIGURE	PAGE
10. The experimental values of $[S_3^-]$ , $[S_6^{-2}]$ , and $[S_8^{-2}]$ remaining after each addition of cadmium ion were determined from UV-visible spectra and Sawyer's constants . . . . .	39
11. Ratio of reacted polysulfide charge to cadmium ion, $\bar{n}_Q$ , versus $-\log[Q_T]$ , where $[Q_T]$ is the total charge concentration of the remaining unreacted polysulfide . . . . .	41
12. Ratio of total reacted sulfur atoms to cadmium ion, $\bar{n}_M$ , versus $-\log[M_T]$ , where $[M_T]$ is the total sulfur concentration of the remaining unreacted polysulfide . . . . .	42
13. Theoretical values for polysulfide concentrations calculated with Sawyer's equilibrium equations where sulfur atom to charge ratio equals 4.78 . . .	44
14. Expansion of Figure 13 with experimental values of $[S_3^-]$ , $[S_6^{-2}]$ , and $[S_8^{-2}]$ after each addition compared to the theoretical curves derived from Sawyer's equilibria equations . . . . .	45
15. (a) Sawyer's original plot (24). (b) An additional data point taken from Sawyer's data for an overall $[Na_2S_6]$ of $20 \times 10^{-3}$ M. (c) Modified plot . . . .	48
16. Possible ligand combinations involving only $S_3^-$ and $S_8^{-2}$ . . . . .	51

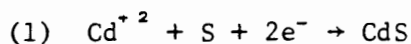
## CHAPTER I

### INTRODUCTION

Recently, research on the deposition of CdS as a photoactive semiconductor film upon conducting substrates has increased because of its applications for converting solar energy to electrical energy (1-4). In the general case of cadmium chalcogenides, the majority of the films have been formed by vapor deposition techniques (5,6). CdSe films have been formed by the direct reaction of cadmium metal with a selenium-saturated, 5 M KOH aqueous solution (7). A variety of electrochemical methods has been described; these include anodization of cadmium metal in a solution of sulfide ion to form an insoluble CdS film (8-11). Other chalcogenides, CdSe (12) and CdTe (13), have been deposited cathodically from acidified solutions containing  $\text{CdSO}_4$  and either  $\text{SeO}_2$  or  $\text{TeO}_2$ .

More recent work completed by two different groups has described the cathodic electrodeposition of sulfides and selenides from a non-aqueous solution of metallic salts and elemental sulfur or selenium (14-17). A non-aqueous solvent, such as dimethylsulfoxide (DMSO), provides a medium in which both non-polar elemental sulfur or selenium and metallic salts can be dissolved. Both groups have reported that the deposits produced photopotentials in basic aqueous sulfur-sulfide solutions, and that doping agents could be incorporated in the films during the electrochemical process.

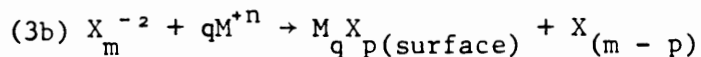
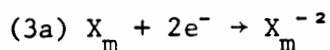
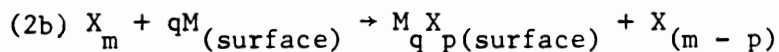
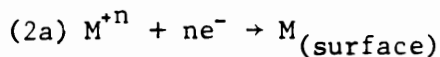
Baranski and Fawcett have successfully electrodeposited thin films of CdS and CdSe, as well as other metallic chalcogenides on substrates of Pt, Au, stainless steel, Ni, Zn, and glass covered with a conducting film of SnO<sub>2</sub>. The non-aqueous solvents used were DMSO, dimethylformamide (DMF), and ethylene glycol. Noting that the overall reaction in the case of CdS is



they have proposed a mechanism in which a freshly electrodeposited metal monolayer reacts with the dissolved sulfur (14,15). The mechanism is complicated by the fact that elemental sulfur in solution exists as the polyatomic molecule S<sub>8</sub>. X-ray diffractometer patterns revealed the material deposited had an interplanar distance of 3.34 Å which compares favorably with the value of 3.36 Å for β-CdS.

A Rutherford spectrum for α particles back-scattered from the CdS deposit gave two peaks--one for Cd and one for S. The film composition was estimated from these peaks to be uniform as a function of depth and in a sulfur/cadmium ratio of 0.9 ± 0.1 to one. An 81% coulombic efficiency, however, was observed. The remaining consumption of charge was attributed to secondary reactions involving oxygen and/or water, or to the reduction of sulfur contained in sulfur-oxygen species.

Roe, Li, and Gerischer have also reported the cathodic deposition of metal sulfides and selenides (17). The proposed reaction sequences were viewed to be either of the following pathways:



where  $X_m$  represents a sulfur or selenium molecule of unspecified molecularity, and M the metal of interest. They have reported electrodepositions of CdS, CdSe, and  $\text{Bi}_2\text{Se}_3$  on gold, graphite, titanium, and cadmium-plated copper substrates.

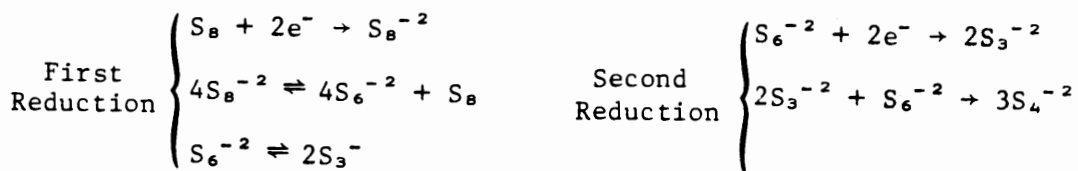
The electrodeposition process was studied by means of voltammetry. Specifically for CdS, current was measured as a function of potential at either a stationary gold electrode, or at a rotating gold ring-disc electrode. From linear potential scans and potential pulse measurements, they deduced that underpotential deposits of cadmium reacted with  $S_8$  in solution or adsorbed on the electrode surface at 25°C. At 95°C the reactions became more complicated; and at voltages greater than the underpotential of -0.4 V versus SCE, direct reduction of  $S_8$  to polysulfide competed with the electrodeposition of CdS.

The intent of our present research is to investigate the possible forms and combinations of sulfur and cadmium atoms which may come to exist in the electrolyte during the electrodeposition described by these two groups. The investigation has been limited to non-faradaic reactions of cadmium and sulfur species occurring in

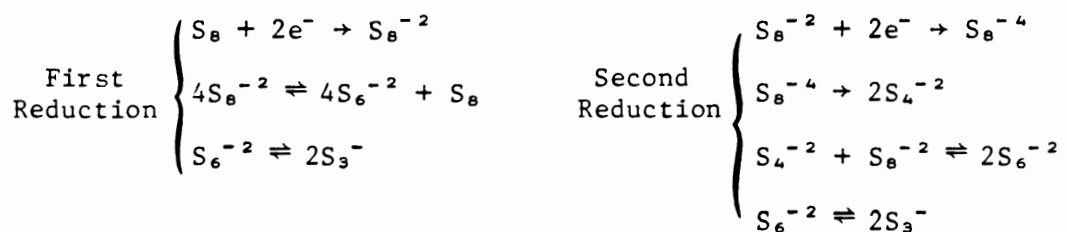
the aprotic solvent DMSO in order to separate these reactions from their electrochemical precursors. The Cd/sulfur/DMSO system was chosen because of its previous extensive study (16,17).

The identification of reduced sulfur species, or polysulfides, has a long history and the subject is still being examined. The first recorded observations of polysulfides were made by Geitner in 1864 (18). When sulfur was heated to 180°C in a sealed tube with water and traces of a base, a deep blue coloration developed and subsequently disappeared with a lowering of the temperature. In 1966 Lux and Giggenbach showed that the blue and red color carriers in polysulfide solutions migrated from cathode to anode, indicative of negatively charged particles, and not of a neutral sulfur molecular fragment (19,20).

Electrochemical methods have been used in conjunction with UV-visible spectroscopy to study polysulfides (21-28). The reduction of  $S_8$  by electrolysis in dimethylsulfoxide has been studied by two groups (21-25). Cauquis et al. studied the reduction of  $S_8$  at a platinum electrode in DMSO with 0.1 M  $Et_4NClO_4$  as an electrolyte (21,22). Reaction progress was followed by UV-visible spectrometry. Reduction occurred at two different potentials, and it was proposed that the products participated in subsequent reactions as shown below:



Sawyer et al. approached the study of polysulfides differently (23-25). Sodium polysulfides were prepared by allowing stoichiometric amounts of elemental sulfur and sodium metal to react in liquid ammonia under a dry nitrogen atmosphere; the polysulfide was isolated by evaporation of the ammonia. The UV-visible spectra of the polysulfides  $S_4^{-2}$ ,  $S_6^{-2}$ , and  $S_8^{-2}$  in DMSO were compared with the products of the two step electrochemical reduction of sulfur. The two step reduction process was concluded to be:



In 1977, F. Seel et al. reviewed the literature of polysulfides in aprotic solvents and conducted additional experiments (26). They studied UV-visible spectra obtained during the addition of  $S_8$  solutions of  $Na_2S_6$  and  $Na_2S_8$  as a function of temperature. Their conclusions included:

1. The first reduction step of  $S_8$  is primarily due to the formation of  $S_8^{-2}$ .
2. The absorption band at 618 nm is due to the radical ion  $S_3^-$ .
3. No ESR evidence of a  $S_4^-$  radical was found.
4. No UV-visible evidence of sulfur fragments  $S_2$ ,  $S_3$ , or  $S_4$  was found.

A summary of the assigned absorbance maxima for the polysulfides and the calculated molar absorptivities appears in Table I.

TABLE I  
SUMMARY OF MOLAR ABSORPTIVITIES FOR POLYSULFIDES

Ref.	Solvent	$S_8^{-2}$		$S_3^-$		$S_6^{-2}$		$S_4^{-2}$	
		$\epsilon$	$\lambda$	$\epsilon$	$\lambda$	$\epsilon$	$\lambda$	$\epsilon$	$\lambda$
24	DMSO	4000	492	4450	618	3800	475	900	420
22	DMSO	$4000 < \epsilon_B$ <6000	490	nc	618	nc	na	2000	430
26	DMF	nc	$465 < \lambda_B$ <487	4850	617	nc	460	nc	na
27	Aceto- nitrile	4400 10000	480 350	3900	613	3100 11000	450 340	nc	330
28	DMA	900 4100 7800	618 518 365	3800 400	618 518	nc	$450 < \lambda_B$ 460	nc	na

nc = not calculated.

na = not assigned.

Two equilibrium constants are frequently calculated for the dissociation of  $S_6^{-2}$  and for the global transformation of  $S_8^{-2}$  to  $S_6^{-2}$  as described below:



These values are summarized in Table II.

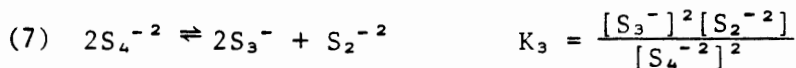
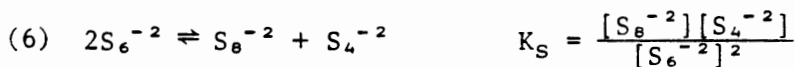


TABLE II  
SUMMARY OF EQUILIBRIUM CONSTANTS,  $K_d$  AND  $K_2$

Reference	$K_d = \frac{[S_3^-]^2}{S_6^-}$	$K_2 = \frac{[S_6][S_8]^{1/4}}{[S_8]}$	Solvent
24,25	$9 \times 10^{-3}$	$2 \times 10^{-2}$	DMSO
22	nc	$.03 < K_2 < .1$	DMSO
26	$7.9 \times 10^{-2}$	nc	DMF
27	$1.2 \times 10^{-3}$	$1.6 \times 10^{-2}$	Acetonitrile
28	$7 \times 10^{-2}$	$9 \times 10^{-4}$	DMA

nc = not calculated.

Only Sawyer et al. have attempted to calculate equilibrium constants for other possible equilibria, namely,



which are calculated to be  $4 \times 10^{-2}$  and  $4 \times 10^{-7}$  moles/liter respectively.

Extensive Raman studies have been done on alkali metal polysulfides in which Raman peaks between 400 and 500  $\text{cm}^{-1}$  have been attributed to the S-S stretching modes of  $S_8$  and of the polysulfides  $S_2^{-2}$ ,  $S_3^{-2}$ ,  $S_4^{-2}$ ,  $S_5^{-2}$  and  $S_6^{-2}$  (29-37). Raman peaks at 400, 535, and 600  $\text{cm}^{-1}$  have been attributed to the ions  $S_8^{-n}$  (37),  $S_3^{-}$  (26,34-36) and  $S_2^{-}$  (26), respectively.

Finally, the electrodeposition of CdS requires that the closed-ring structure of  $S_8$  be opened during the reaction process. Either the  $S_8$  molecule is directly reduced at the electrode to  $S_8^{-2}$ , or freshly deposited cadmium acts as a nucleophilic agent attacking the  $S_8$  ring. Several researchers have studied the nucleophilic attack of the  $S_8$  ring. Giggenbach used  $S^{2-}$  as a nucleophilic reagent to form polysulfides in DMF (20). Chivers and Drummond determined that the reducing agent in hexamethylphosphoramide (HMPA) solutions of  $S_8$  was the solvent impurity dimethylamine (34). Bartlett et al. studied the reaction of  $S_8$  with alkali cyanides and triarylphosphines (38,39). Seel et al. showed that the polysulfide  $S_4^{-2}$  may also attack the  $S_8$  ring (26).

During the present investigation, it became apparent that cadmium metal reacts spontaneously with dissolved molecular  $S_8$  to form cadmium polysulfide complexes. The free radical  $S_3^-$  was observed by means of Raman spectrometry to form during such reactions. Subsequent experiments were performed in which polysulfide solutions were titrated with a solution of  $Cd^{+2}$ . From the visible spectra of the titrated solutions, calculations were made to determine the ratio of polysulfide charge per cadmium ion and the ratio of the total sulfur per cadmium ion in the complexes as functions of the free polysulfide charge and the free total sulfur concentrations, respectively.

## CHAPTER II

### MATERIALS

#### DMSO

Analytical reagent grade dimethylsulfoxide was obtained from J. T. Baker Chemical Company and from the Crown Zellerbach Company. UV-visible spectra were obtained for both sources and were found to be optically pure from 750 to 260 nm. Water content in the DMSO was determined by Karl Fischer titration and found to be 0.50 and 0.45% by weight, respectively (40).

#### Cadmium chloride

Reagent grade cadmium chloride ( $\text{CdCl}_2 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ ) was obtained from J. T. Baker Chemical Company. The salt was ground to a fine powder with mortar and pestle to promote swift solvation in DMSO. Cadmium concentrations of DMSO titrants were determined by atomic absorption spectrometry.

#### Cadmium sulfate

Reagent grade cadmium sulfate was obtained from Allied Chemical Company and was used without further purification.

Sodium sulfide

Analytical reagent grade sodium sulfide ( $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ ) was obtained from the Mallinckrodt Chemical Works and was used without further purification.

Cadmium nitrate

Analytical grade cadmium nitrate was obtained from the Mallinckrodt Chemical Works and was used without further purification.

Sodium borohydride

Reagent grade sodium borohydride was obtained from the Eastman Kodak Company and was used without further purification.

Sulfur

99.999% pure sulfur was obtained from the Alfa Division of Ventron, Inc., and was used without further purification.

Cadmium AAS standard

A cadmium atomic absorption spectrometry standard was obtained from Anderson Laboratories, Inc. The standard contained 1000 ppm Cd in dilute HCl and was used to verify cadmium standards prepared from the solid salt  $\text{CdCl}_2\cdot 2\frac{1}{2}\text{H}_2\text{O}$ .

Sodium AAS standard

A sodium atomic absorption spectrometry standard was obtained from Harleco, Inc. The standard contained 1000 ppm Na in dilute HCl.

Nitric acid

Reagent grade nitric acid was obtained from Mallinckrodt Chemical Works and was used without further purification.

Hydrochloric acid

Reagent grade hydrochloric acid was obtained from the J. T. Baker Chemical Co. and was used without further purification.

Potassium chloride

Reagent grade potassium chloride was obtained from the J. T. Baker Chemical Co. and was used without further purification.

Sodium chloride

Reagent grade sodium chloride was obtained from Mattheson, Curtis, and Bell and was used without further purification.

Nitrogen

Nitrogen gas was obtained from Airco, Inc., and was used without further purification.

## CHAPTER III

### APPARATUS

#### UV and visible spectrometry

Ultraviolet and visible spectra were recorded on a Cary 14 spectrophotometer with 1 cm fused quartz cuvettes. A scan rate of 1.0 nm/sec was used for spectra recorded between 750 and 260 nm. Quick and careful transfer of the filtrate in experiments where a simple vacuum filtration was employed, was the only precaution taken to prevent oxygen from reacting with the products. To record spectra at elevated temperatures, the cuvette holders were fitted with water jackets through which a heated water-ethylene glycol solution was pumped with a Nescol Instruments, Inc., Exacal 110 temperature control unit. The temperature within the cuvette was monitored with a mercury thermometer.

To record spectra in experiments in which an initial polysulfide solution was employed, the sample cell was fitted with rubber septums sealed with a thin layer of vacuum grease to prevent oxygen from contaminating and reacting with the polysulfide solution. The loading of polysulfide solution was performed in a glove bag.

#### Atomic absorption spectrophotometry (AAS)

Cadmium and sodium concentrations of DMSO solutions were measured in aqueous dilutions of the original solutions using a 551

Instrumental Laboratories AA-AE spectrophotometer. Absorbances and concentrations of cadmium solutions were measured at 228.8 nm with the use of a D<sub>2</sub> background correction source. Absorbances and concentrations of sodium solutions were measured at 578.0 nm.

#### Raman spectroscopy

Raman spectra were recorded in a 90° geometry with a Jarrell-Ash 25-300 spectrometer equipped with an ITT FW 130 (S-20) photomultiplier and photon-counting electronics. A Coherent Radiation MG Ar-Kr ion laser was used for sample illumination. The exciting wavelength was 488.0 nm, the scan speed was 1.0 cm<sup>-1</sup>/sec, and the resolution was 3 cm<sup>-1</sup>.

## CHAPTER IV

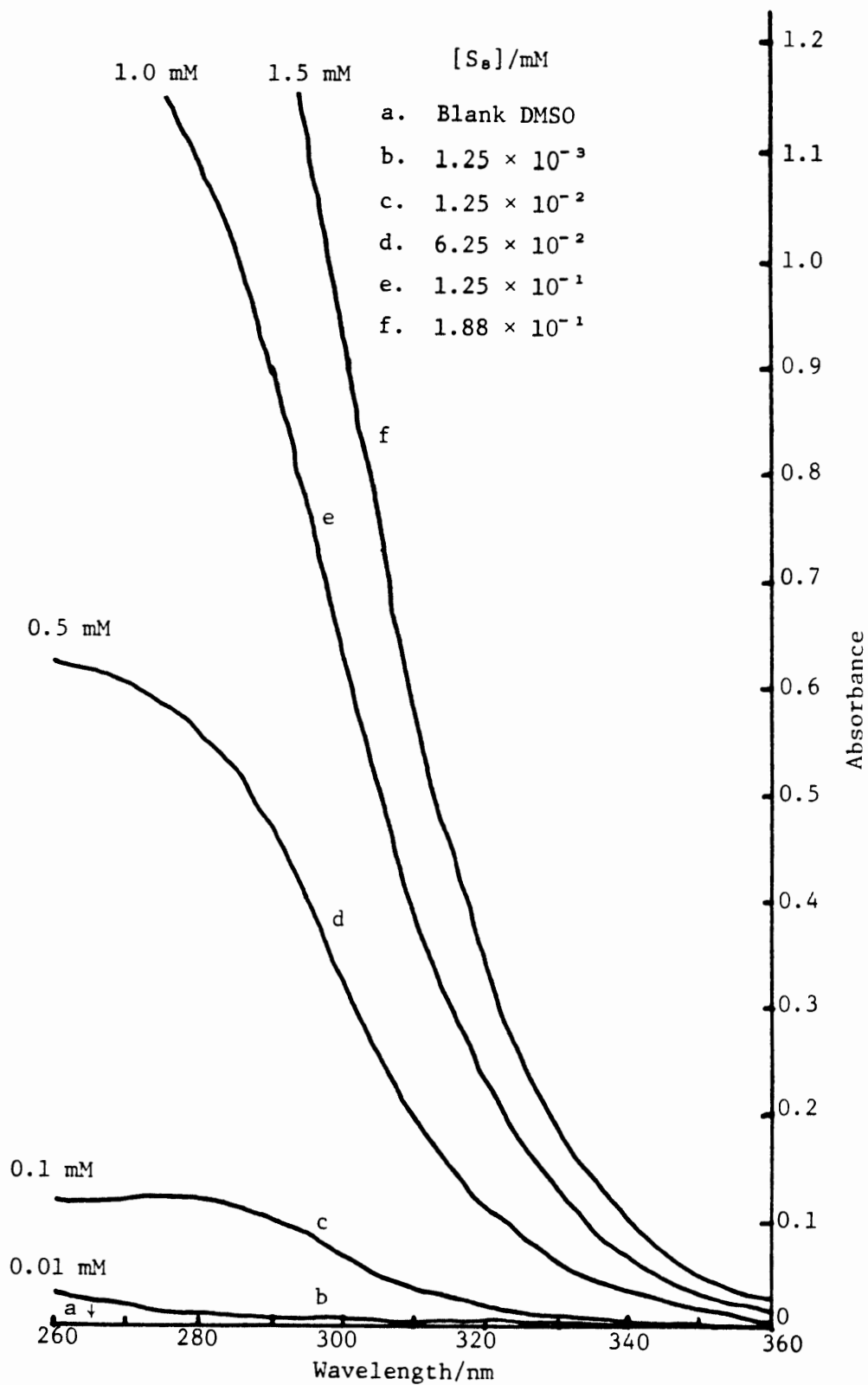
### PROCEDURE AND RESULTS

Two approaches were used to gain information about the products formed by cadmium and sulfur species in DMSO. In the first, freshly prepared cadmium metal was reacted with sulfur dissolved in DMSO. The resulting DMSO solution was examined by atomic absorption, UV-visible, and Raman spectrometry. In the second approach, sodium polysulfide solutions were prepared by the reduction of  $S_8$  with  $S^{2-}$  ion in DMSO. Microliter additions of  $Cd^{+2}$  dissolved in DMSO were made to the polysulfide solution. After each addition, the UV-visible spectrum of the solution was scanned; and from the resulting absorption bands the changes in concentrations of the polysulfides  $S_3^-$ ,  $S_6^{-2}$ , and  $S_8^{-2}$  were determined.

#### Stability of molecular sulfur in dimethylsulfoxide

Solutions of varying concentrations of  $S_8$  in DMSO were prepared and their UV-visible spectra were recorded (Figure 1). The concentration of  $S_8$  is plotted against absorbance at three different wavelengths in Figure 2. If the  $S_8$  ring fragmented in DMSO at temperatures of 90-100°C, or if an impurity in the solvent promoted the formation of polysulfides as in the case of HMPA (34), the UV-visible spectrum of the solution would be markedly altered. Spectra were





**Figure 1.** UV-visible spectra of varying concentrations of sulfur in DMSO.

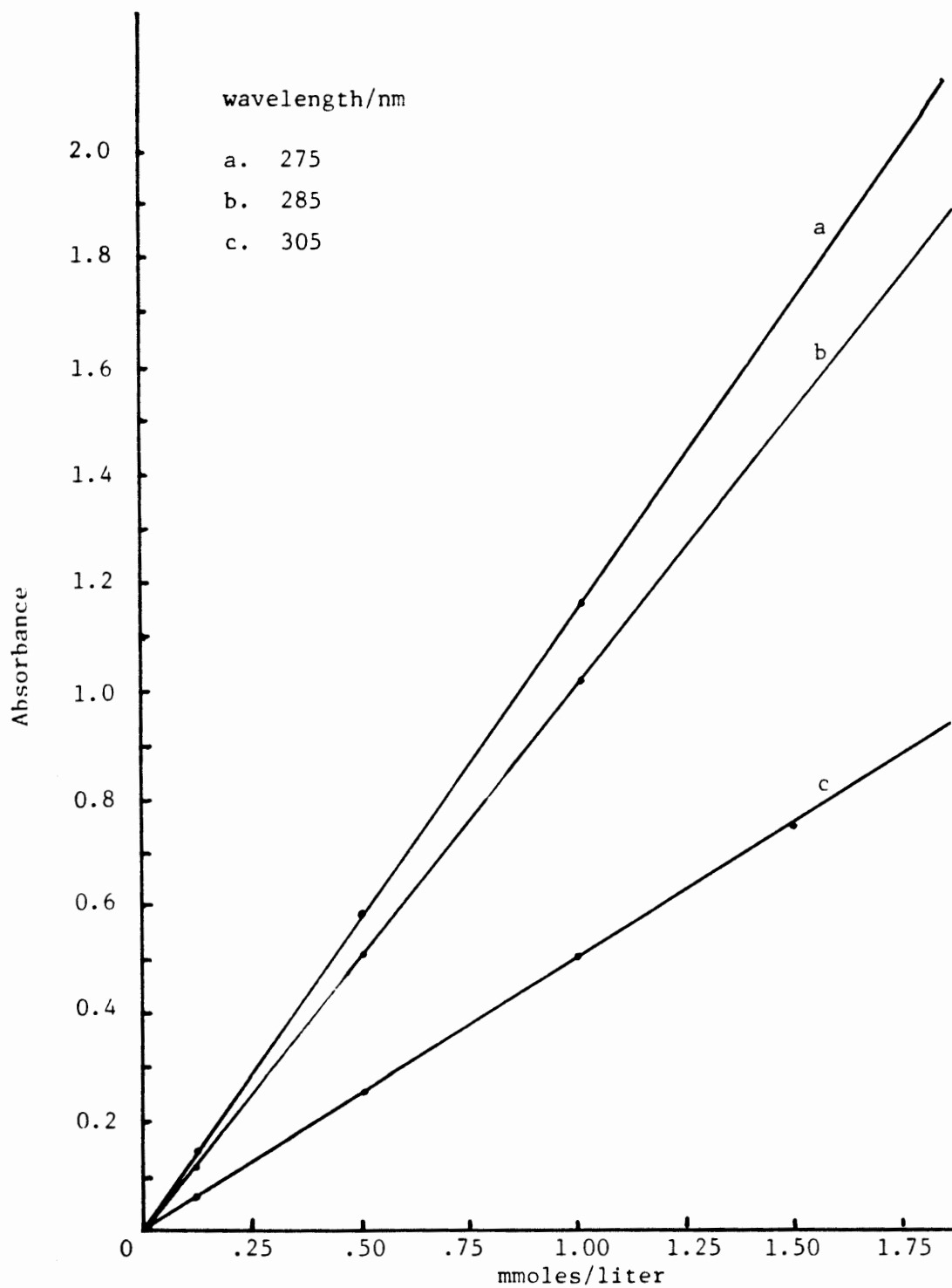
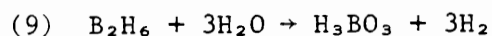
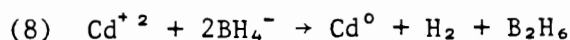


Figure 2. Absorbance versus sulfur concentration where sulfur concentration is expressed as mmoles of S/liter.

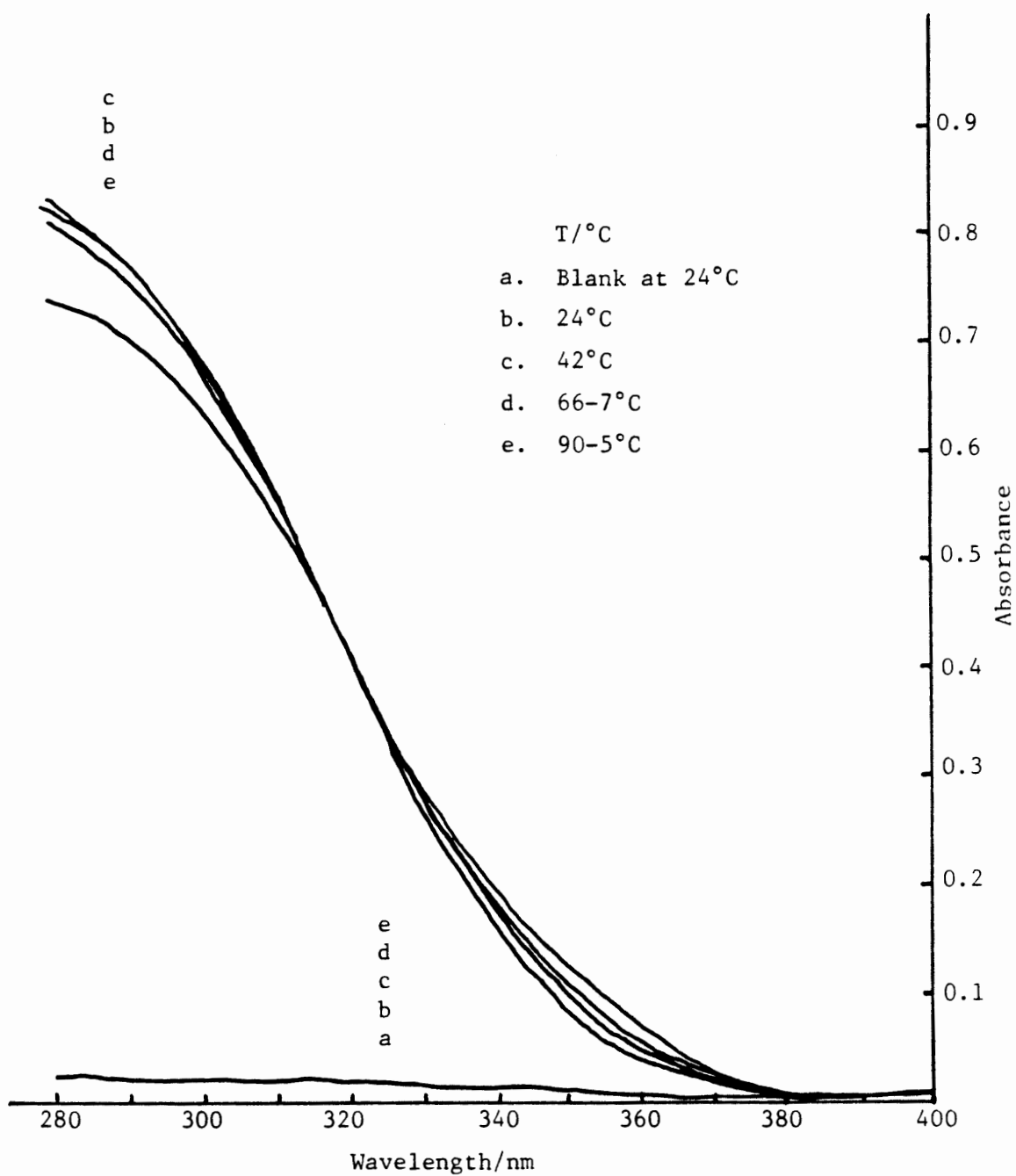
recorded for a 0.075 mM S<sub>8</sub> solution at 24, 42, 66-7, and 90-5°C. No new absorption bands appeared between 750 to 370 nm. The spectra between 380 and 260 nm are shown in Figure 3.

Reaction of metallic cadmium with S<sub>8</sub> dissolved in dimethylsulfoxide

To simulate a reaction process in which hot S<sub>8</sub>/DMSO solution comes in contact with freshly deposited cadmium metal, a simple vacuum filtration experiment was employed. DMSO solutions containing S<sub>8</sub> in concentrations of 0.110, 0.323, 2.13, and 3.23 mM were prepared. The glass-fritted funnel was fitted to a filter flask with rubber adapter which in turn was connected to an aspirator. One gram cadmium samples were prepared by the reduction of aqueous cadmium ion in 10 ml of 1 M Cd(NO<sub>3</sub>)<sub>2</sub> with three times the stoichiometric amount of crystalline sodium borohydride:



The cadmium samples were collected in a glass-fritted funnel, washed with distilled water, and finally washed with three 10 ml aliquots of DMSO. The last aliquot of DMSO was set aside as a control for the measurement of residual Cd(NO<sub>3</sub>)<sub>2</sub>. Its cadmium concentration was determined by AAS. This process was repeated with another cadmium sample, but the final 10 ml aliquot of DMSO was raised to a temperature of 100°C before its contact with the cadmium metal.



**Figure 3.** UV-visible spectra of a 0.075 mM S<sub>8</sub> solution as a function of temperature.

A 10 ml aliquot of 0.110 mM S<sub>8</sub> solution at 90–100°C was passed through the funnel, collected, and stored for later measurement of its S<sub>8</sub> concentration by UV-visible spectroscopy. Since no precautions were taken to prevent O<sub>2</sub> from reacting with S<sub>8</sub>, this measurement served as a control to determine the extent of S<sub>8</sub> loss due to reaction with O<sub>2</sub>.

Four separate experiments were performed in which a short contact time between cadmium metal and sulfur solution was provided by the use of the vacuum filtration method. The initial sulfur concentrations were increased for Experiments 2 and 3 with the intent to maximize any new sulfur species which formed. In turn, each of three sulfur solutions was heated as noted in Table III, and reacted with an individual cadmium sample by pipetting sequential 10 ml aliquots of hot solution over the metal. Each aliquot was collected and stored in a separate clean glass vial.

Intermediate products, such as sulfur fragments, were then sought by examining the reacted aliquot as quickly as possible by Raman spectroscopy. Raman spectra for an initial 2.13 mM S<sub>8</sub> sulfur solution and its reacted filtrate appear in Figure 4. Raman spectra of neat DMSO and of an S<sub>8</sub>-saturated solution of DMSO appear in Figure 5.

A fourth experiment involved the reaction of a 0.110 mM S<sub>8</sub> solution with cadmium as described before. The experiment was performed at room temperature. No Raman spectra were obtained for any of these filtrates.

TABLE III  
 SUMMARY OF EXPERIMENTAL RESULTS FROM REACTION OF  
 DISSOLVED SULFUR WITH METALLIC CADMIUM\*

	Experiment 1		Experiment 2		Experiment 3		Experiment 4	
	90-100°C <sup>†</sup>		90-100°C <sup>†</sup>		110-120°C <sup>†</sup>		25°C <sup>†</sup>	
	[Cd]	[S <sub>8</sub> ]	[Cd]	[S <sub>8</sub> ]	[Cd]	[S <sub>8</sub> ]	[Cd]	[S <sub>8</sub> ]
Initial [S <sub>8</sub> ]	0	110	0	2130	0	3230	0	110
Without Cd at 100°C	0	90	---	---	---	---	---	---
DMSO blank 25°C	2	0	7	0	2	0	2	0
DMSO blank 100°C	4	0	---	---	---	---	---	---
Aliquot 1	15	50	17	700	43	750	10	30
Aliquot 2	28	50	55	710	---	---	12	48
Aliquot 3	26	54	80	760	---	---	12	50
Aliquot 4	28	54	112	760	---	---	14	50

\*Cadmium and sulfur concentrations are expressed in  $\mu\text{M}$  units and were measured at 25°C by AA and UV-visible spectrometry, respectively.

†Temperature of initial solution.

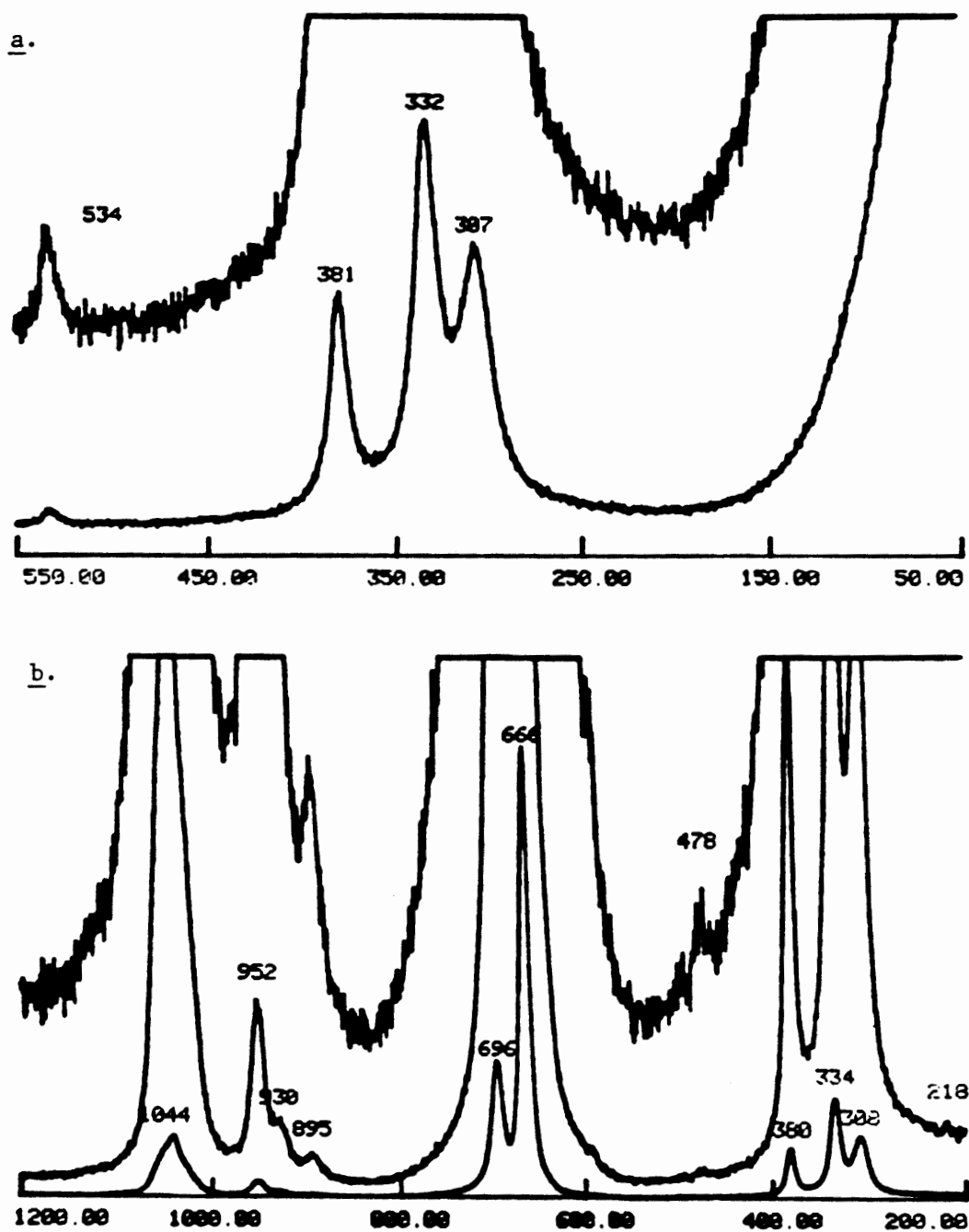


Figure 4. (a) Raman spectrum of 2.13 mM S<sub>8</sub> solution which was reacted with cadmium metal. (b) Raman spectrum of initial 2.13 mM S<sub>8</sub> solution.

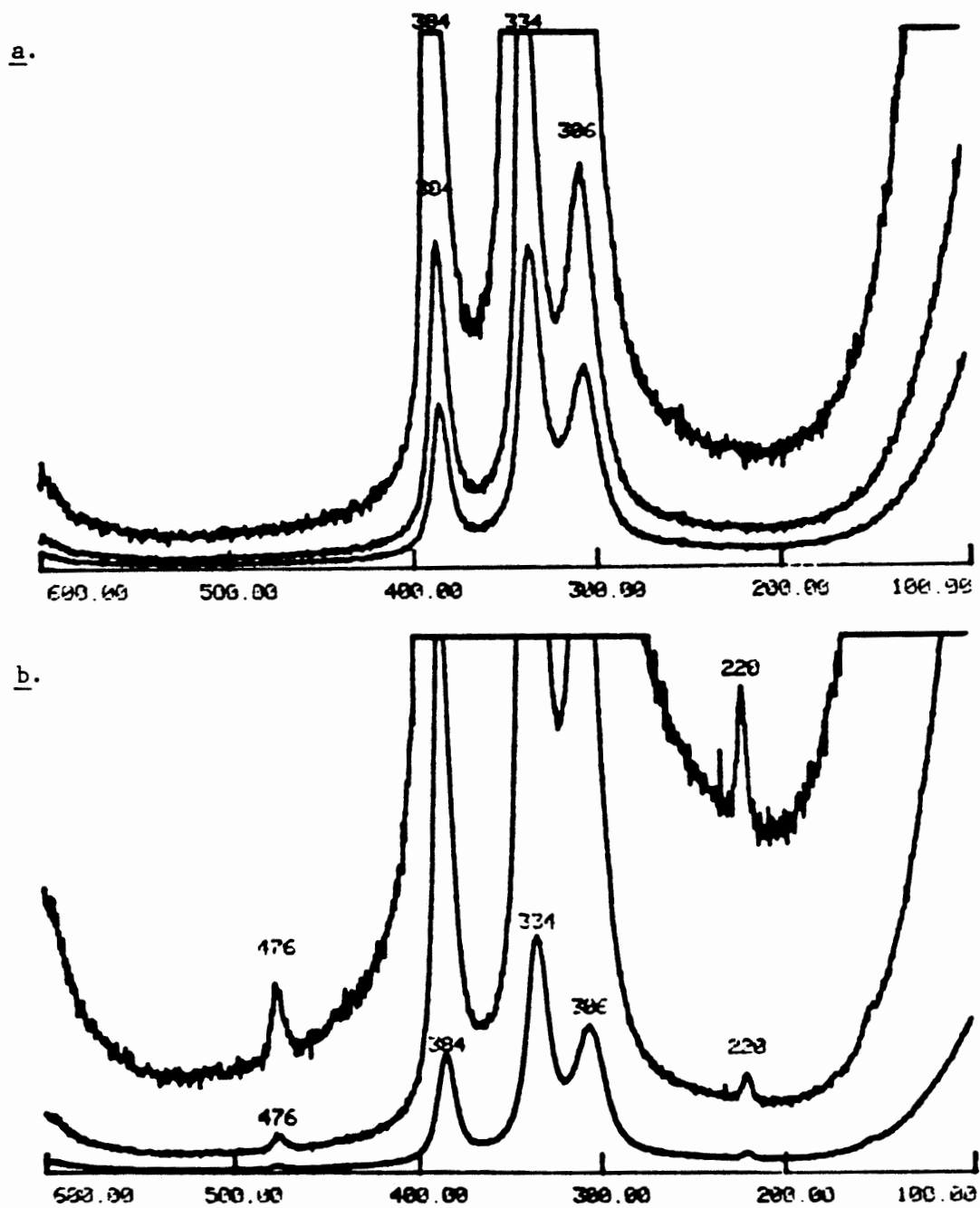


Figure 5. (a) Raman spectrum of neat DMSO. (b) Raman spectrum of DMSO saturated with S<sub>8</sub> (3.23 mM S<sub>8</sub>).



Cadmium and sulfur concentrations of all reacted aliquots were determined within 24 hours after reaction by AA and UV-visible spectrometry respectively. The concentration data are summarized in Table III. In Figure 6, the UV-visible spectra of the initial 0.110 mM  $S_8$  solution and of the collected filtrates are shown for Experiment 1.

Each subsequent aliquot in a given experiment with the same cadmium sample was more intensely colored than its predecessor. Extraction of this yellow-brown component with nonpolar solvents, such as carbon disulfide, toluene, and cyclohexane, was unsuccessful. Additions of methanol or acetone, however, resulted in dilution without precipitation.

In a test for the presence of sulfide or polysulfide, a few drops of dilute hydrochloric acid were placed on the reacted metal. The distinctive odor of hydrogen sulfide was immediately evident.

Many possible cadmium polysulfides of the general formula  $CdS_p$  may form when dissolved molecular sulfur comes in contact with cadmium metal. To determine if the soluble product of these experiments was the simple CdS compound, the solubility of CdS in DMSO was determined at 25 and 110°C. CdS was prepared by the reaction of  $CdSO_4$  and excess  $Na_2S \cdot 9H_2O$  in aqueous solution. The yellow precipitate was collected, thoroughly washed with distilled water, and dried at 110°C for 24 hours. Approximately 1 g of the resulting orange solid was placed in a flask with 25 ml of DMSO. The DMSO was heated to 110°C and held at this temperature for 30 minutes. A portion of the hot solution was filtered quickly through a glass-fritted funnel into a heated flask. A 1.00 ml aliquot was quickly

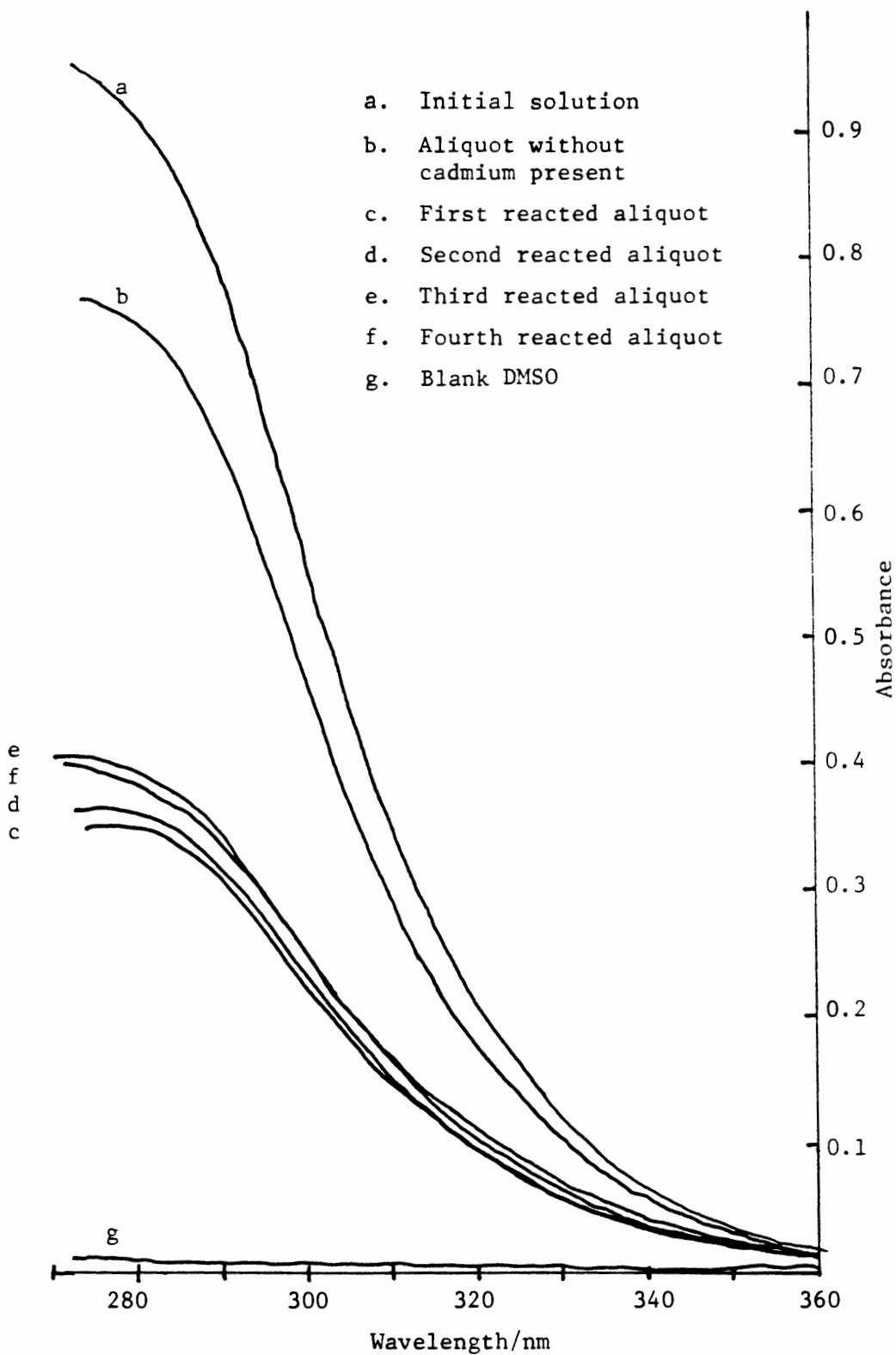


Figure 6. UV-visible spectra of 0.110 mM S<sub>8</sub> solution aliquots which were passed over cadmium metal. Initial temperature of sulfur solution was 90-100°C.

diluted to 10.00 ml in a volumetric flask. The cadmium concentration was determined by AAS. Solubility at 25°C was determined by allowing the remaining 110°C DMSO to cool to 25°C. Solid CdS was again filtered from the solution, and the cadmium concentration of the solution determined by AAS (Table IV).

TABLE IV  
SOLUBILITY OF CdS IN DMSO

Temperature	[Cd]/ $\mu$ M
25°C	32
100°C	124

#### Reaction of cadmium ion with polysulfides in dimethylsulfoxide

Initially, a polysulfide solution with an approximate molar ratio of two sodium ions for every eight sulfur atoms was prepared by the reaction of  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$  with  $\text{S}_8$  in DMSO. The various methods reported in the literature used to produce polysulfide solutions are discussed in Appendix A. The polysulfide solution was then titrated with dissolved cadmium chloride in DMSO, and the reaction of cadmium ion with polysulfides was followed by means of UV-visible spectrometry.

Great care in the preparation of the polysulfide solution was necessary to prevent the very swift reaction of oxygen with the newly-formed polysulfides. Not only atmospheric oxygen, but also dissolved

oxygen in DMSO had to be greatly reduced if not eliminated. The solubility of  $O_2$  in DMSO has been measured by several groups with good agreement. At room temperature its solubility is  $\sim 2$  mM (41-43). To ensure that oxygen contamination had been minimized, the following procedure was used.

Specifically, a 100 ml volumetric flask filled with approximately 100 ml of DMSO was heated to  $40^\circ\text{C}$  to reduce the amount of dissolved oxygen. A stream of nitrogen was then passed through the DMSO as it cooled to room temperature over a period of 30 minutes. Somewhat less than 50 ml of the DMSO was transferred to a 50 ml volumetric flask into which another stream of nitrogen was being passed through a micropipette. In order, 0.0160 g of  $S_8$  and 0.0172 g of  $Na_2S \cdot 9H_2O$  were weighed and placed in the flask. Solid material adhering to the inner neck was washed into the body of the solution as the total volume was brought to 50 ml with deoxygenated DMSO. Nitrogen was then streamed through the solution for an additional 15 minutes before the flask was capped with a glass stopper covered with a thin layer of vacuum grease. Dissolution of solid material occurred overnight.

An elongated fused quartz cuvette was used to hold the polysulfide solution in the spectrometer (Figure 7). To adjust the absorbances of the prepared solution to the absorbance range of the instrument, a dilution of approximately 2 ml DMSO to 6 ml polysulfide solution was necessary. A volume of 2.00 ml of DMSO was pipetted into the cuvette in which a stream of nitrogen was being passed. The cuvette was quickly sealed with two rubber septums and vacuum grease.

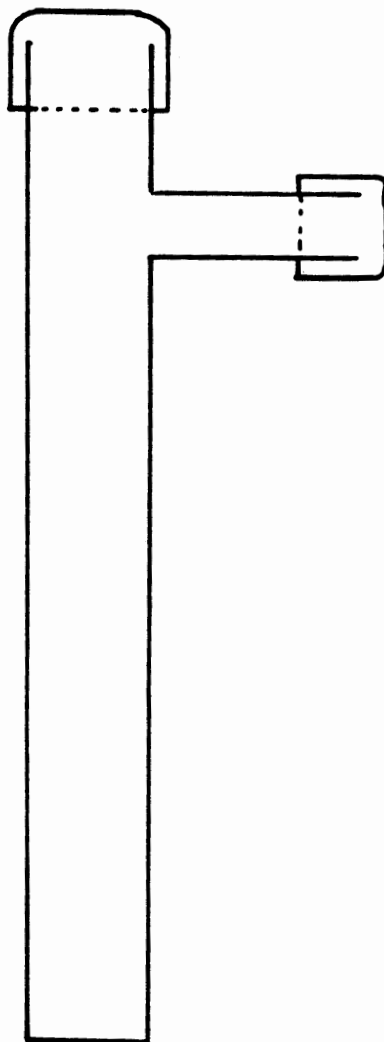


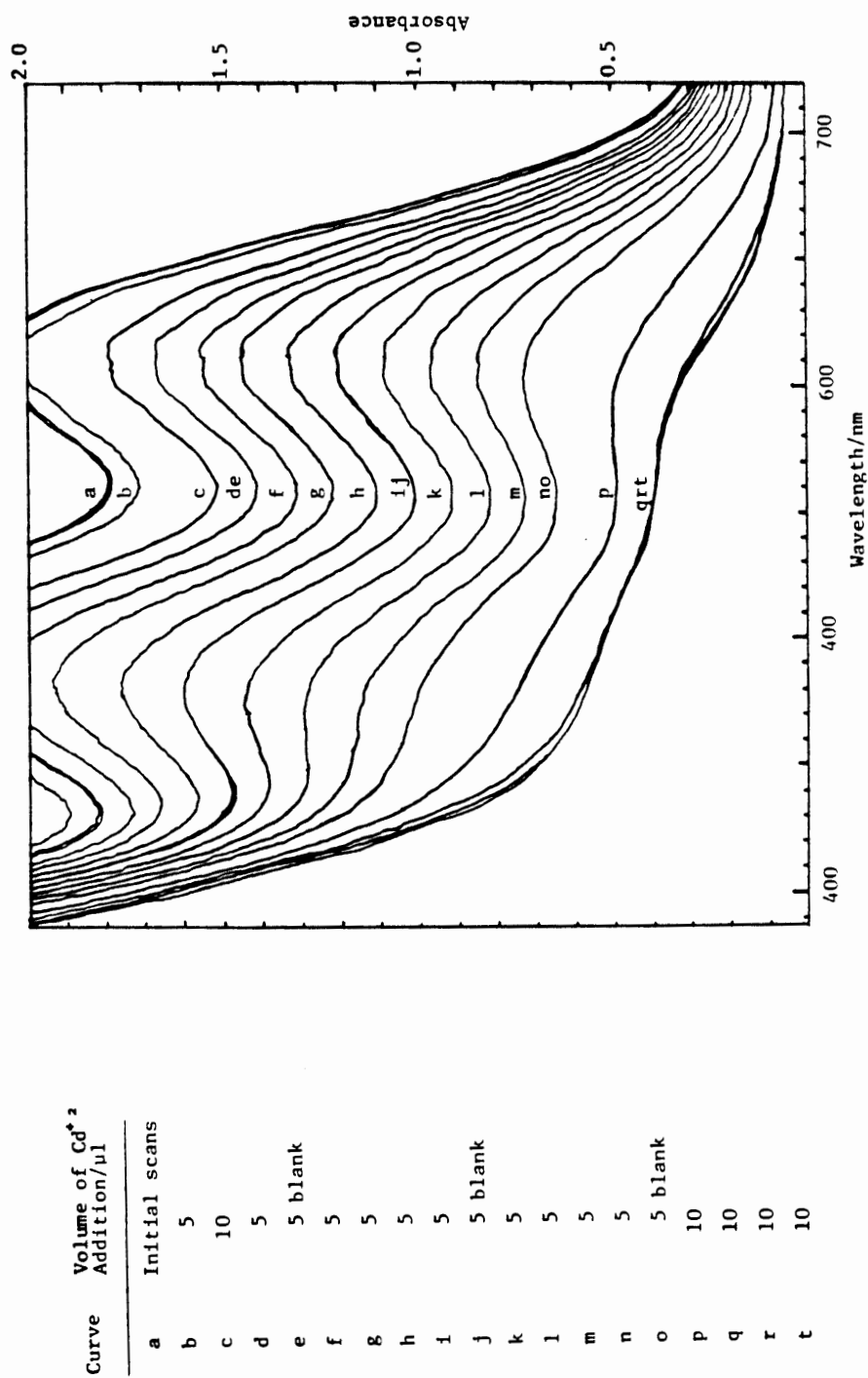
Figure 7. Elongated quartz cuvette.

The introduction of polysulfide solution to the cuvette was performed in a glove bag. To minimize the oxygen concentration within the bag, the air was evacuated and replaced with nitrogen three times. The polysulfide solution was then poured directly into the cuvette to a total predetermined value of 8.13 ml. The solution and gas in the cuvette were purged for an additional five minutes within the bag with a stream of nitrogen before being capped.

The solution was agitated by hand for 90 seconds before being placed in the spectrometer. Four consecutive scans from 720 to 390 nm revealed no significant changes with time in the absorbance pattern. Between each scan the cuvette had been agitated for 90 seconds. Since no apparent change had occurred, it was viewed that oxygen had been effectively eliminated from the cuvette.

A ~40 mM  $\text{CdCl}_2 \cdot 2\frac{1}{2}\text{H}_2\text{O}$  solution was prepared with deoxygenated DMSO and purged with nitrogen for 20 minutes. To the polysulfide solution in the cuvette, five or ten microliter additions of cadmium solution were made with a five microliter syringe. After each addition, the cuvette was agitated for 90 seconds, before the resulting solution was scanned from 720 to 390 nm. For three scans, a five microliter addition of blank deoxygenated DMSO served as a check for the presence of oxygen. The complete set of scans appears in Figure 8. With an identical polysulfide solution and similar method, five microliter additions of blank DMSO were compared to five microliter additions of 20 mM NaCl/DMSO. No significant change in absorbance occurred with the addition of chloride ion.

The concentrations of cadmium in the titrant and of sodium in the polysulfide solution were measured by AAS. The cadmium concentration was found to be 41.2 mM and the sodium concentration of the original polysulfide solution was found to be 1.77 mM.

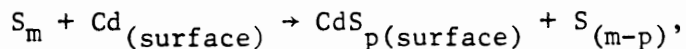


**Figure 8.** Reaction of cadmium ion with polysulfides followed by UV-visible spectrometry.  $[\text{Cd}^{+2}]$  of the titrant was measured by AAS to be 41.2 mM. Scans were made after each addition of solution.

## CHAPTER V

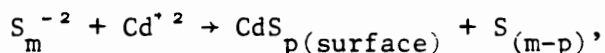
### DISCUSSION

To shed light on the nature of the reactions involved in the electrodeposition of CdS, two methods were used in the present work. The first involved an examination of an S<sub>8</sub>/DMSO solution as a function of temperature by UV-visible spectroscopy. The sulfur solution was then reacted with cadmium metal to simulate the deposition mechanism step



proposed by both Baranski and Roe (16,17). The reaction products were analyzed by Raman, AA, and UV-visible spectroscopy.

The second method involved the direct reaction of polysulfides with Cd<sup>+2</sup> in DMSO to simulate the deposition mechanism step



proposed by Roe (17). The progress of the reaction was followed by UV-visible spectroscopy.

For the deposition of CdS on metal substrates, DMSO solutions of S<sub>8</sub> are typically elevated to temperatures greater than 90°C. Below this temperature nonstoichiometric deposits were reported (16). The reactive sulfur species at T ≥ 90°C may not be S<sub>8</sub> but sulfur fragments such as S<sub>2</sub>, S<sub>3</sub>, or S<sub>4</sub>, which may form because of higher temperatures



and solvent interaction. The spectrum of  $S_8$  saturated vapor recorded below  $250^\circ\text{C}$  by Bass consists of unresolved maxima at 210, 265, and 285 nm (44). This compares very well with the absorption spectrum of  $S_8$  in nonpolar solvents at  $25^\circ\text{C}$  as well as in DMSO at  $25^\circ\text{C}$ . At  $500\text{--}650^\circ\text{C}$  and 1-10 torr, the spectrum of  $S_8$  vapor contains bands at 400 nm and at 520 nm which were attributed to  $S_3$  and  $S_4$  respectively (45). Since such high temperatures are required for the fragmentation of  $S_8$ , formation of such fragments in DMSO solution at  $\sim 100^\circ\text{C}$  is doubtful.

Polysulfides may form and become reactive species in DMSO solution at  $100^\circ\text{C}$ ; for example, in HMPA solutions of  $S_8$ , a solvent impurity reduced  $S_8$  to polysulfides (34). Polysulfides have absorbance maxima at wavelengths greater than 400 nm in aprotic solvents.

The absence of sulfur fragments such as  $S_3$  and  $S_4$ , and polysulfides in DMSO at  $T \leq 100^\circ\text{C}$  is supported by the UV-visible spectrum of an  $S_8$ /DMSO solution recorded at various temperatures (Figure 3). The solution remained optically clear from 750 to 390 nm as the temperature was increased from  $25^\circ\text{C}$  to  $90\text{--}95^\circ\text{C}$ . The absorption edge did shift to a slightly longer wavelength with a corresponding decrease in maximum absorbance which is expected with an increase in temperature. The absence of absorbances attributed to polysulfides indicates the lack of an impurity which would act as a reducing agent. The only sulfur species in solution, therefore, appears to be  $S_8$ .

When a solution of  $S_8$  in DMSO at  $T \geq 90^\circ\text{C}$  was reacted with freshly prepared cadmium metal, a simple test for the formation of polysulfides or  $S^{2-}$  was performed. With the addition of a few drops

of dilute HCl to the reacted metal, the odor of H<sub>2</sub>S was easily detected which indicates that cadmium does indeed react with dissolved S<sub>8</sub> to form CdS<sub>p</sub>, where  $p \geq 1$ . Since all polysulfides decompose in acid solutions to reform S<sup>-2</sup> and S<sub>8</sub>, the value of p remains unknown. The loss of S<sub>8</sub> in each reacted aliquot was confirmed by the measurement of the absorbance due to S<sub>8</sub> (Figure 6 and Table III).

The concentration of Cd in each reacted aliquot was determined by AAS (Table III). In the cases of aliquots with [S<sub>8</sub>]  $\geq$  2.13 mM before reaction, each succeeding aliquot of S<sub>8</sub> solution reacted with the same cadmium sample contained a higher concentration of cadmium. Since the cadmium concentration in these aliquots exceeded the cadmium concentration of a CdS-saturated DMSO solution, a cadmium-containing species other than CdS was concluded to be present. An increase in cadmium concentration corresponded to the increasing intensity of the reacted aliquot's yellow-brown color. Attempts to extract the yellow-brown component with nonpolar solvents, such as CS<sub>2</sub> and toluene, were unsuccessful. From these observations, it was concluded that the yellow-brown component is due to a CdS<sub>p</sub> species of ionic character. The possibility of the formation of S<sub>6</sub>, which is also yellow-brown, or other neutral sulfur species as reaction products was eliminated, because of their high degree of solubility in CS<sub>2</sub>.

Raman spectral evidence of reaction products containing sulfur was disappointing. For initial 0.323 mM S<sub>8</sub> aliquots, only solvent peaks were observed in the reacted solution indicating that a large percentage of the sulfur had reacted and remained with the cadmium.

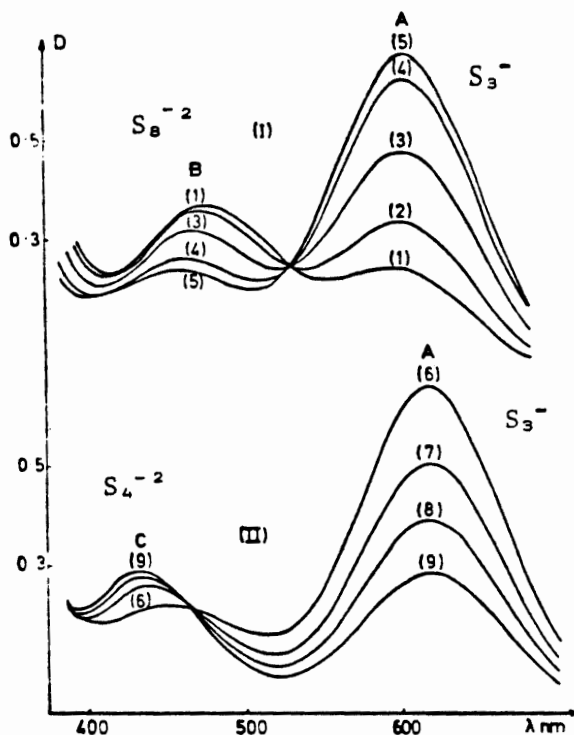
For initial 2.13 mM  $S_8$  aliquots, peaks at only  $535\text{ cm}^{-1}$  were observed for the first three aliquots, but for the fourth reacted aliquot, the original  $S_8$  peaks appeared with no peak at  $535\text{ cm}^{-1}$  (Figures 4 and 5). For initial 3.23 mM  $S_8$  aliquots, only the original  $S_8$  peaks were observed for the reacted solution. The peak at  $535\text{ cm}^{-1}$  has been assigned to the radical ion  $S_3^-$  (26,31,34). The formation of this ion is therefore a possibility during the reaction of cadmium with  $S_8$ .

In the second approach, cadmium chloride dissolved in DMSO was reacted directly with a solution of polysulfide. The method used to prepare the polysulfide solution was similar to that of Giggenbach (20). An overall solution stoichiometry of two atoms of sodium per  $\sim 9.6$  atoms of sulfur was determined by the measurement of the solution's  $[Na^+]$  by AAS. When the ratio S:Na exceeds 4, previous researchers have shown that  $S_3^- \approx S_8^{-2} \gg S_6^{-2}$ , when total negative polysulfide charge  $\leq 5\text{ mM}$  (24-28). In the solution formed, there are theoretically major concentrations of  $S_8^{-2}$  and  $S_3^-$ , and a minor concentration of  $S_6^{-2}$ .

With each measured addition of cadmium ion a decrease in the polysulfide concentration was noted (Figure 8). During the course of the additions, the color of the solution changed from greenish blue to yellowish brown. The solution remained transparent with no trace of precipitate. Since a saturated solution of CdS in DMSO was observed to be colorless, the yellow-brown component is not the simple sulfide.

Additions of deoxygenated DMSO did not alter the spectrum of the solution; thus, the techniques employed to reduce oxygen content were successful, and the possible reaction of oxygen with polysulfide was eliminated. Additions of 10  $\mu$ l of 20 mM sodium chloride in DMSO were made to a polysulfide solution, and the resulting spectra were compared to those recorded after additions of 10  $\mu$ l of blank DMSO. There was no effect upon the spectra due to the presence of chloride ion. The sole reason for decreases in absorbance was the addition of  $\text{Cd}^{+2}$  ion. The yellow-brown component at the end of the experiment was found to be insoluble in  $\text{CS}_2$  and toluene, which indicated that the species present may be ionic in character.

Quantitative analysis of the spectra of Figure 8 was performed with the constants calculated by Sawyer and Doub since their molar absorptivities compared favorably with those of other researchers (Table II). First a working set of molar absorptivities at three wavelengths was calculated using their data as well as the spectra of Cauquis (Figure 9). These molar absorptivities were then applied to Figure 8 to calculate  $[\text{S}_3^-]$  and  $[\text{S}_8^{-2}]$  for each spectrum. Secondly, a distribution of the various polysulfides was calculated for a wide range of dilutions of a  $\text{Na}_2\text{S}_{9.6}$  stoichiometry with Sawyer's equilibrium equations. The experimental values were compared to the values predicted by Sawyer's equations. Finally some discrepancies among Sawyer's data and calculated constants were noted. Modification of the treatment of the data yielded new equilibrium constants and molar absorptivities, but their application to the present experimental work did not significantly alter the conclusions.



**Figure 9.** Spectrophotometric curves recorded by Cauquis (21). The spectra were recorded during the electrolysis of a 1.2 mM  $S_8$  solution in DMSO with a 0.1 M electrolyte of  $Et_4NClO_4$ . Optical pathway: 1 mm.  $z$  = no. of electrons consumed per sulfur molecule.

- (I) (1)  $z = 2$ ; (2)  $z = 2.2$ ; (3)  $z = 2.4$ ; (4)  $z = 2.6$ ; (5)  $z = 2.7$ .  
 (II) (6)  $z = 2.9$ ; (7)  $z = 3.3$ ; (8)  $z = 3.5$ ; (9)  $z = 3.8$ .

To use Sawyer's molar absorptivities to calculate the concentrations of various polysulfides observed in the spectra of Figure 8, molar absorptivities of  $S_3^-$  and  $S_8^{-2}$  were calculated at wavelengths other than those given by Sawyer. Cauquis presented a set of spectra in which the absorbances due to  $S_3^-$  were well defined and isolated

from those of other polysulfides. Using curves 6, 7, 8, 9 in Figure 9, the molar absorptivity of 4450 liter  $\text{cm}^{-1}$  mole $^{-1}$  at 618 nm as calculated by Sawyer, and Beer's law, the molar absorptivities for  $\text{S}_3^-$  at 690 and 700 nm were calculated and are given in Table V.

The absorbance curves for  $\text{S}_3^-$  were assumed to be symmetrical about the line drawn through the maximum at 618; therefore, the  $\epsilon_{700}^3 \approx \epsilon_{536}^3$ .

TABLE V  
MOLAR ABSORPTIVITIES OF  $\text{S}_3^-$  AT VARIOUS WAVELENGTHS

Curve	$A_{618}$	$[\text{S}_3^-]/M$	$A_{690}$	$\epsilon_{690}^3$	$A_{700(536)}$	$\epsilon_{700(536)}^3$
6	.661	$1.49 \times 10^{-3}$	.202	1360	.145	970
7	.502	$1.13 \times 10^{-3}$	.154	1360	.111	980
8	.389	$8.74 \times 10^{-4}$	.118	1350	.084	960
9	.282	$6.34 \times 10^{-4}$	.085	1340	.061	960
Ave	---	---	---	1350	---	970

The concentration of  $\text{S}_6^{-2}$  in solutions of the stoichiometry of two sodium atoms per eight sulfur atoms is small. For example, in a solution containing  $2.4 \times 10^{-3}$  moles of charge per liter, only 3.4% of the charge is due to  $\text{S}_6^{-2}$ . According to Sawyer, the absorbance maximum for  $\text{S}_6^{-2}$  is at 475 nm with a molar absorptivity of  $3.8 \times 10^3$  liter mole $^{-1}$ cm $^{-1}$ . At wavelengths greater than 492 nm the molar absorptivity is less than  $3.8 \times 10^3$  liter mole $^{-1}$ cm $^{-1}$ . The absorbance contribution due to  $\text{S}_6^{-2}$  at wavelengths greater than 492 nm for such small concentrations is very small when compared to those of  $\text{S}_8^{-2}$  or

$S_3^-$ . For these reasons, the contribution of  $S_6^{-2}$  to the absorbance at 492 nm and 536 nm was considered to be zero and the absorbance at these wavelengths was taken to be the composite absorbance of  $S_8^{-2}$ ,  $S_3^-$ , and the concentration of any cadmium-polysulfide complex present.

The value of 4000 liter  $cm^{-1}$  mole $^{-1}$  attributed to  $\epsilon_{492}^B$  by Sawyer was checked against a Cauquis spectrum (Curve 1 of Figure 9) of a solution with an overall  $Na_2S_8$  stoichiometry. The concentration of  $S_3^-$  was calculated from the absorbance at 690 nm using the average  $\epsilon_{690}^B$  of 1350 liter  $cm^{-1}$  mole $^{-1}$ . The concentration of  $S_6^{-2}$  was calculated with the use of  $9.0 \times 10^3$  moles/liter as  $K_D$  for the reaction  $S_6^{-2} \rightleftharpoons 2S_3^-$ , and the concentration of  $S_8^{-2}$  was taken as the remaining charge of the solution divided by two. The molar absorptivity of  $S_8^{-2}$  at 536 nm was calculated with the use of this same spectrum and concentrations of  $S_8^{-2}$ ,  $S_6^{-2}$ , and  $S_3^-$ , and again assuming that the absorbance at 536 was due to only  $S_3^{-2}$  and  $S_3^-$ . These calculations are summarized in Table VI.

TABLE VI  
MOLAR ABSORPTIVITIES OF  $S_8^{-2}$  AT VARIOUS WAVELENGTHS

Curve	$A_{690}$	$S_3^-$	$S_6^{-2}$	$S_8^{-2}$	$A_{492}$	Calc. $\epsilon_{492}^B$	Sawyer $\epsilon_{492}^B$	$A_{536}$	$\epsilon_{536}^B$
1	.069	5.1 $\times 10^{-4}$	2.9 $\times 10^{-5}$	9.16 $\times 10^{-4}$	.369	4000	4000	.281	2520

The residual absorbance at the end of the thirteenth cadmium addition in Figure 8 was attributed to the absorbance of a cadmium polysulfide complex. An estimate of the molar absorptivities of the complex

at 492, 536, and 690 nm was made by the use of Beer's law and the assumption that the cadmium concentration at the end of the thirteenth addition was equal to the concentration of the complex.

In Table VII the molar absorptivities used in the determination of the concentrations of polysulfides for the spectra in Figure 8 are summarized. The calculated concentrations  $[S_3^-]$ ,  $[S_6^{-2}]$ , and  $[S_8^{-2}]$  were plotted as a function of the cadmium ion concentration of the solution in the cuvette in Figure 10. The total concentration of polysulfide charge in the initial diluted solution was calculated to be  $1.76 \times 10^{-3}$  M from the absorbances in Figure 8. Significantly, the total charge concentration in the initial solution was determined by the measurement of sodium by AAS to be  $1.77 \times 10^{-3}$  M.

TABLE VII  
SUMMARY OF MOLAR ABSORPTIVITIES FOR  $S_3^-$ ,  $S_6^{-2}$ , AND  
HYPOTHETICAL CADMIUM POLYSULFIDE COMPLEX

Species	$\lambda/\text{nm}$	$\epsilon/\ell \text{ cm}^{-1} \text{ mole}^{-1}$
$S_3^-$	492	0
	536	970
	690	1350
$S_6^{-2}$	492	4000
	536	2520
	690	0
Cd-polysulfide complex	492	1370
	536	1060
	690	180



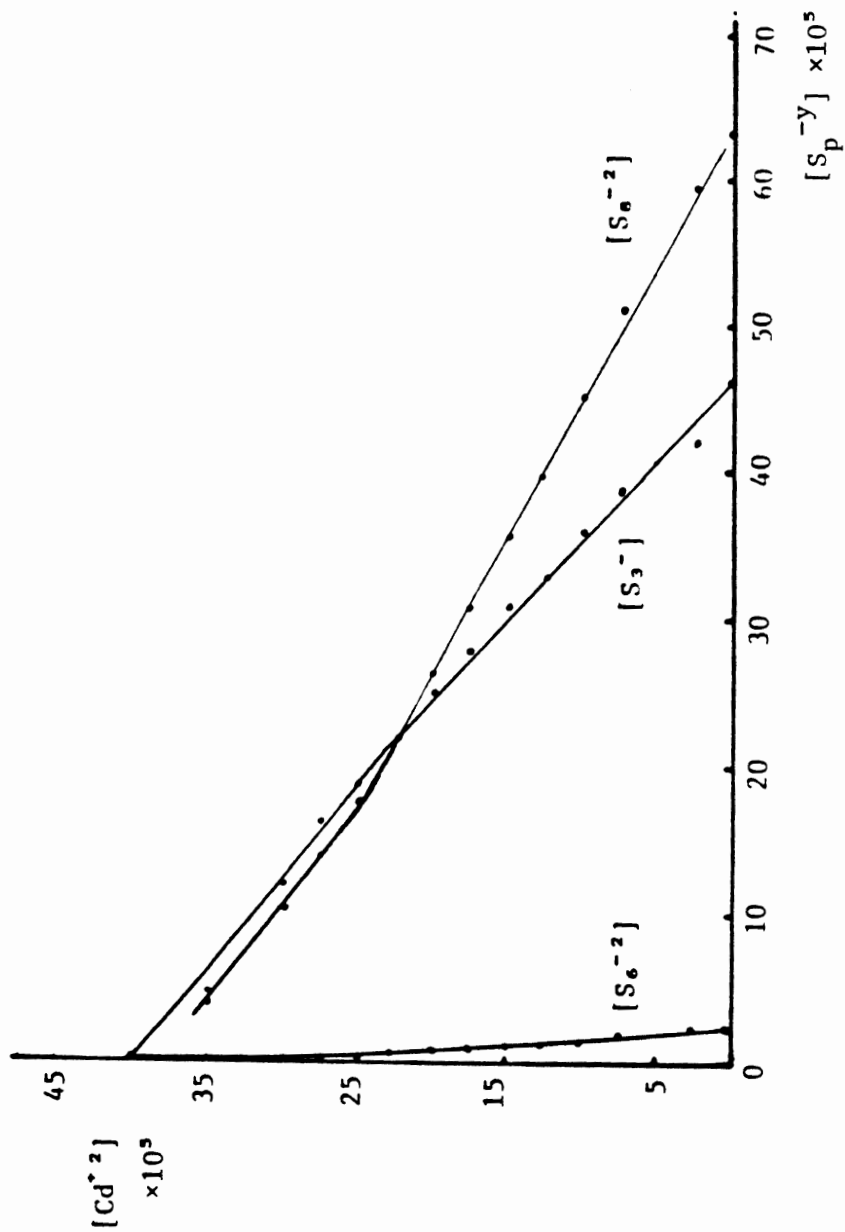


Figure 10. The experimental values of  $[S_3^-]$ ,  $[S_6^{-2}]$ , and  $[S_6^{-2}]$  remaining after each addition of cadmium ion were determined from UV-visible spectra and Sawyer's constants.

From the calculated concentrations of the three polysulfides, the volume of solution in the cuvette, and the moles of cadmium ion added, the total polysulfide charge reacting with each cadmium ion was determined at the end of each addition. The ratio of charge to cadmium ion,  $\bar{n}_Q$ , is plotted against  $-\log[Q_T]$  in Figure 11, where  $Q_T$  is the total remaining charge associated with unreacted polysulfide and

$$(10) \quad \bar{n}_Q = \frac{\text{Total moles charge contained in reacted polysulfide}}{\text{Total moles of added cadmium ion}}$$

Similarly,  $\bar{n}_M$ , the ratio of total sulfur atoms reacting with each cadmium ion was calculated after each addition. In Figure 12,  $\bar{n}_M$  is plotted against  $-\log[M_T]$ , where  $M_T$  is the total remaining sulfur as unreacted polysulfide and

$$(11) \quad \bar{n}_M = \frac{\text{Total moles of sulfur contained in reacted polysulfide}}{\text{Total moles of added cadmium ion}}$$

The average value of  $\bar{n}_Q$  was found to be 4.8 charges/cadmium ion, while the average value of  $\bar{n}_M$  was found to be 18 sulfur atoms/cadmium ion. During the first few additions of cadmium,  $\bar{n}_Q$  and  $\bar{n}_M$  increased gradually to a maximum value which then remained relatively constant after further additions. These first low values of  $\bar{n}_Q$  and  $\bar{n}_M$  suggested that another ligand was present without a visible absorbance band. This "invisible" ligand, perhaps hydroxide, may have successfully competed for cadmium ion. With its depletion the true values of  $\bar{n}_Q$  and  $\bar{n}_M$  then appeared.

The additions of cadmium to polysulfide solution can be thought of as a gradual dilution process in which polysulfide is removed from

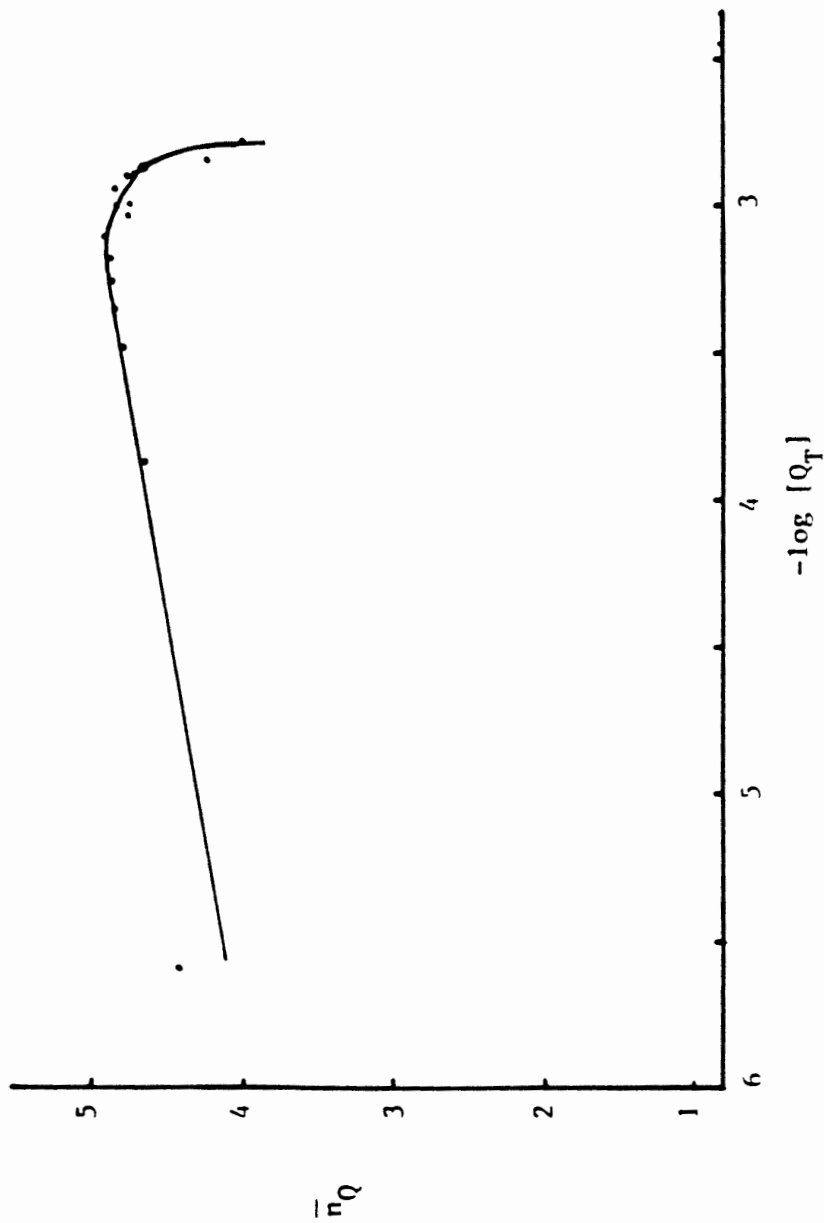


Figure 11. Ratio of reacted polysulfide charge to cadmium ion,  $\bar{n}_Q$ , versus  $-\log [Q_T]$ , where  $[Q_T]$  is the total charge concentration of the remaining unreacted polysulfide.

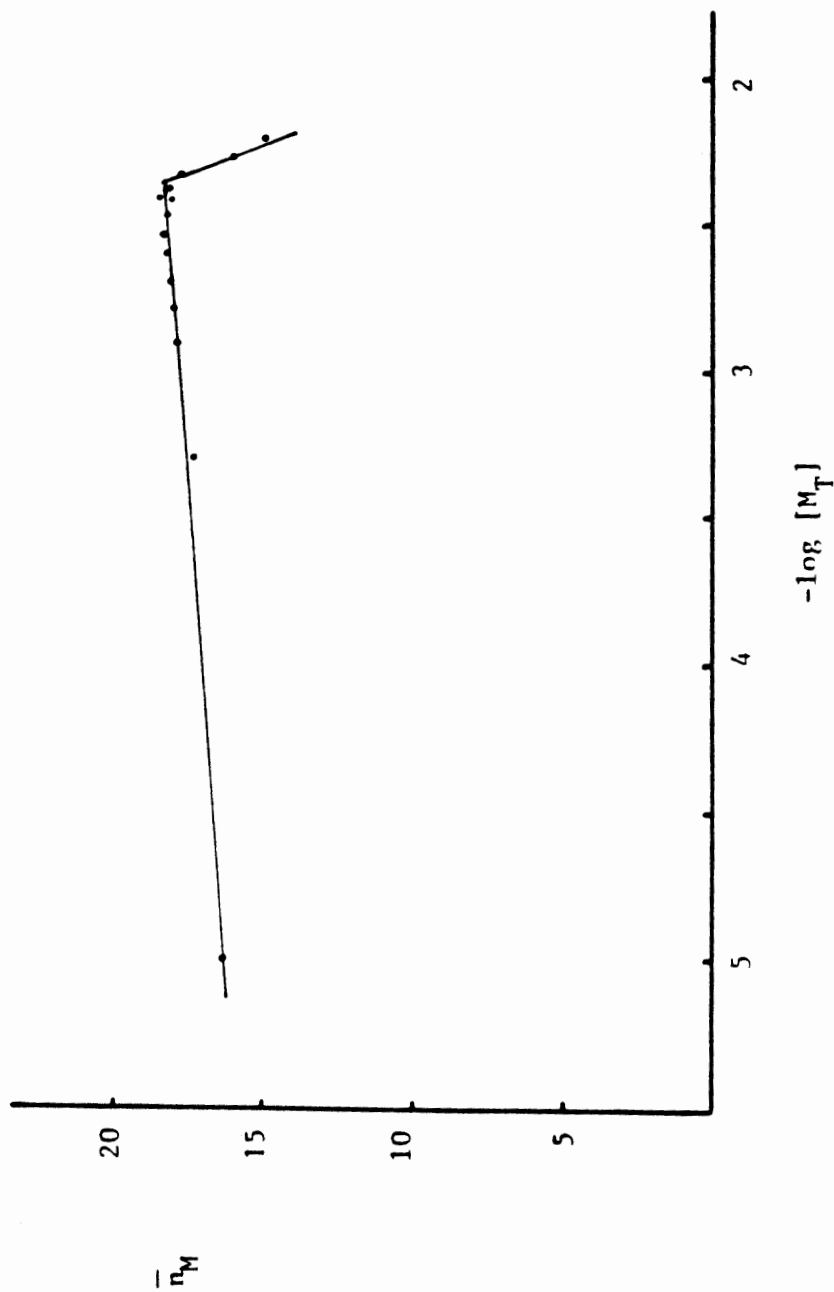


Figure 12. Ratio of total reacted sulfur atoms to cadmium ion,  $\bar{n}_M$ , versus  $-\log[M_T]$ , where  $[M_T]$  is the total sulfur concentration of the remaining unreacted polysulfide.

solution by reaction with cadmium ion. The theoretical concentrations of each of the three polysulfides present was determined as a function of the total polysulfide charge concentration,  $Q_T$ , when  $4.78 Q_T = M_T$ . This was done by means of the four equations

$$(12) \quad K_2 = \frac{[S_6^{-2}]^4 [S_8]}{[S_8^{-2}]^4} = 8 \times 10^{-8} \text{ moles/liter}$$

$$(13) \quad K_d = \frac{[S_3]^{-2}}{[S_6^{-2}]} = 9.0 \times 10^{-3} \text{ moles/liter}$$

$$(14) \quad [S_3^{-}] + 2[S_6^{-2}] + 2[S_8^{-2}] = Q_T$$

$$(15) \quad 3[S_3^{-}] + 6[S_6^{-2}] + 8[S_8^{-2}] + 8[S_8] = M_T$$

The solution of this set of equations for  $[S_3^{-}]$ , and subsequently  $[S_6^{-2}]$  and  $[S_8^{-2}]$  is discussed in Appendix B.

The theoretical concentrations are graphed in Figure 13 as a function of the log of the total polysulfide charge in solution. In Figure 14, plots of the experimental values of  $[S_8^{-2}]$ ,  $[S_3^{-}]$ , and  $[S_6^{-2}]$  are superimposed on an expansion of Figure 13. The similarity of the plots, the fact that  $[S_3^{-}]$  eventually exceeded  $[S_8^{-2}]$  upon dilution in both plots, and the fact that the deviation between theoretical and experimental concentrations remained relatively constant (Table VIII) suggested that equilibrium was quickly achieved after each addition of cadmium ion. This was further supported by the fact that each spectrum in Figure 8 remained constant after the addition was made for at least 15 minutes.

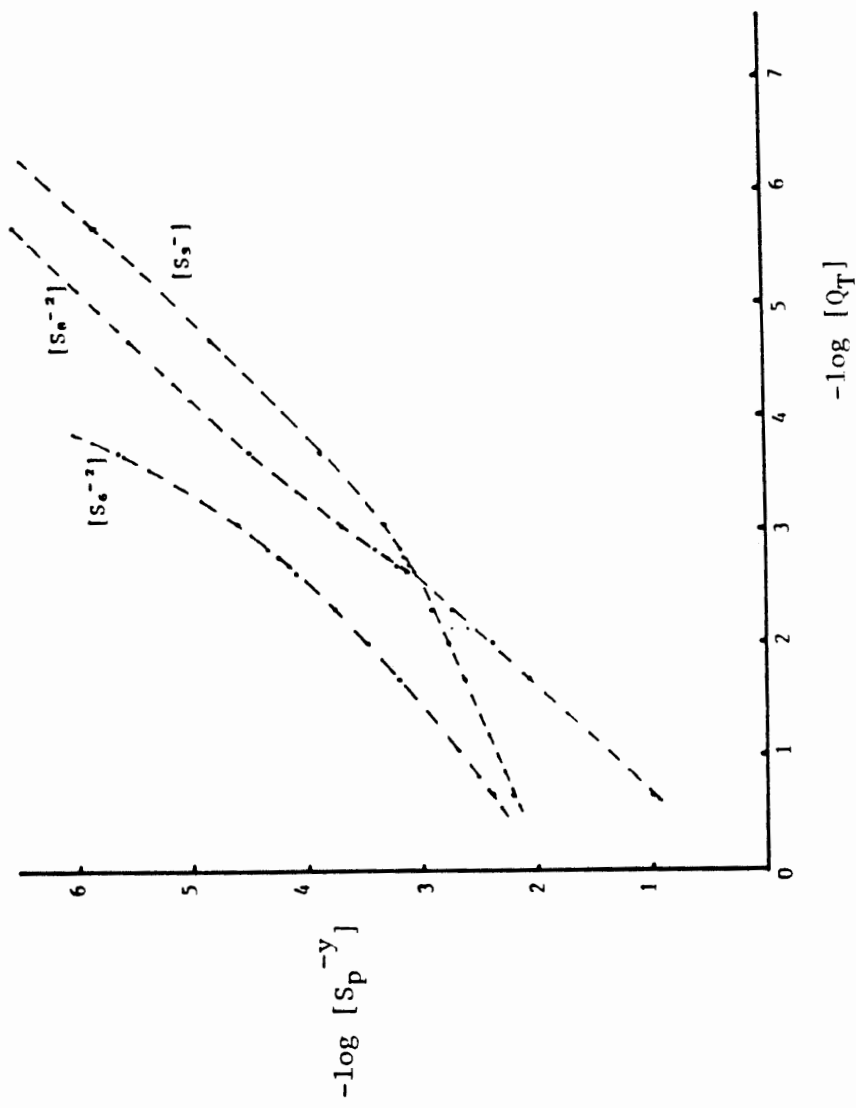


Figure 13. --- Theoretical values for polysulfide concentrations calculated with Sawyer's equilibrium equations where sulfur atom to charge ratio equals 4.78.

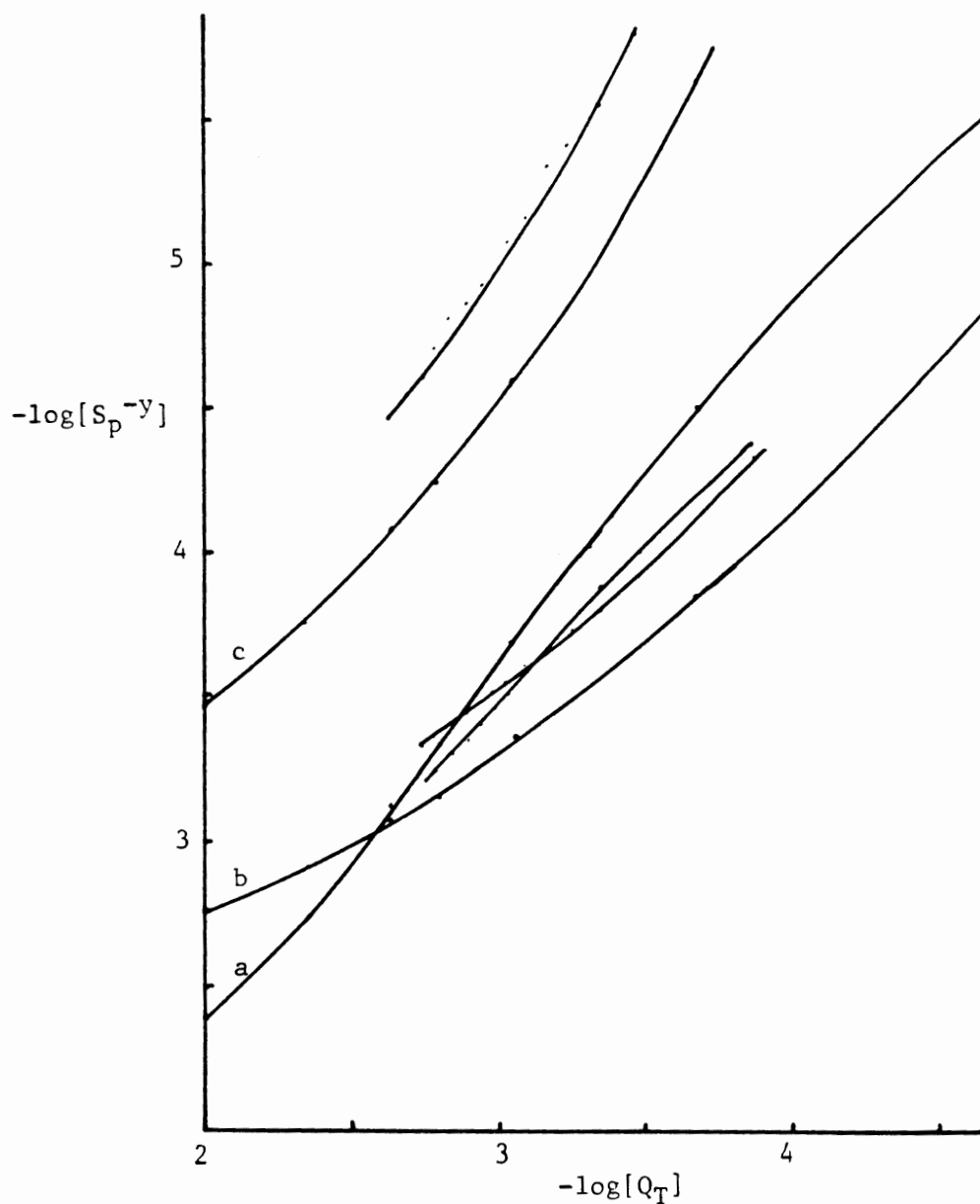


Figure 14. Expansion of Figure 13 with experimental values of  $[S_3^-]$ ,  $[S_6^{-2}]$ , and  $[S_8^{-2}]$  after each addition compared to the theoretical curves derived from Sawyer's equilibria equations.  $4.78 Q_T = M_T$ . Curves a, b and c are the expanded theoretical values from Figure 13.

TABLE VIII  
RELATIVE DEVIATION OF EXPERIMENTAL POLYSULFIDE CONCENTRATIONS  
FROM THEORETICAL POLYSULFIDE CONCENTRATIONS

For Spectra After Cadmium Addition	$[S_3^-]$ % Deviation	$[S_6^{-2}]$ % Deviation	$[S_8^{-2}]$ % Deviation
0	-37	-59	+26
1	-36	-61	+27
2	-38	-63	+26
3	-39	-60	+27
4	-40	-67	+27
5	-41	-66	+30
6	-41	-67	+26
7	-42	-69	+36
8	-39	-66	+37
9	-42	-70	+40
10	-40	-69	+47

The examination of Sawyer's treatment of the experimental data revealed the possibility of an alternative treatment of his data in which different values of  $\epsilon_{618}^3$ ,  $K_d$ ,  $\epsilon_{475}^6$ , and  $K_2$  would result. Sawyer had calculated  $\epsilon_{618}^3$  and  $K_d'$ , where  $K_d'$  is the apparent dissociation



constant for the reaction  $S_6^{-2} \rightleftharpoons 2S_3^{-}$ , from absorbances of polysulfide solutions having the overall stoichiometry of  $Na_2S_6$ , or one sodium ion per three sulfur atoms. Specifically,

$$(17) \quad K_d' = \frac{(A_{618}/\epsilon_{618}^3)^2}{C_6 - 2 \frac{A_{618}}{\epsilon_{618}^3}} = \frac{[S_3^-]^2}{[S_6^{-2}]_A}$$

where  $\epsilon_{618}^3$  is the molar absorptivity of  $S_3^-$  at 618 nm,  $C_6$  is the overall concentration of  $Na_2S_6$ , and  $[S_6^{-2}]_A$  is the apparent concentration of  $S_6^{-2}$ . Rearrangement of equation 17 yielded

$$(18) \quad \frac{A_{618}^2}{C_6} = K_d' (\epsilon_{618}^3)^2 - [K_d' (\epsilon_{618}^3)] \frac{A_{618}}{2C_6}$$

In Figure 13, an additional point from Sawyer's data was added to the plot. At higher polysulfide concentrations the linear relationship failed to hold, and therefore, a better estimate of  $\epsilon_{618}^3$  and  $K_d'$  was obtained for overall  $[Na_2S_6] \leq 2 \times 10^{-3}$  M by using only the lower concentration data. A new slope and intercept were calculated for the lower concentrations using a least squares method. The corrected plot is graphed with Sawyer's original plot in Figure 15. Since  $[S_6^{-2}]_A > [S_6^{-2}]$  because of disproportionation of  $S_6^{-2}$ ,  $K_d > K_d'$ . Therefore, in this new interpretation of the data  $K_d > 1.05 \times 10^{-2}$  moles/liter and  $\epsilon_{618}^3 = 4220 \text{ l cm}^{-1} \text{ mole}^{-1}$ .

Spectral evidence in DMF and acetonitrile by Seel et al. (26) and Fujinaga et al. (27) respectively, suggest that  $\epsilon_{475}^6$  is 60-80% of Sawyer's value of  $3800 \text{ l cm}^{-1} \text{ mole}^{-1}$ . Since the absorbance attributed to  $S_6^{-2}$  is already very small in Figure 7, such a change in  $\epsilon_{475}^6$

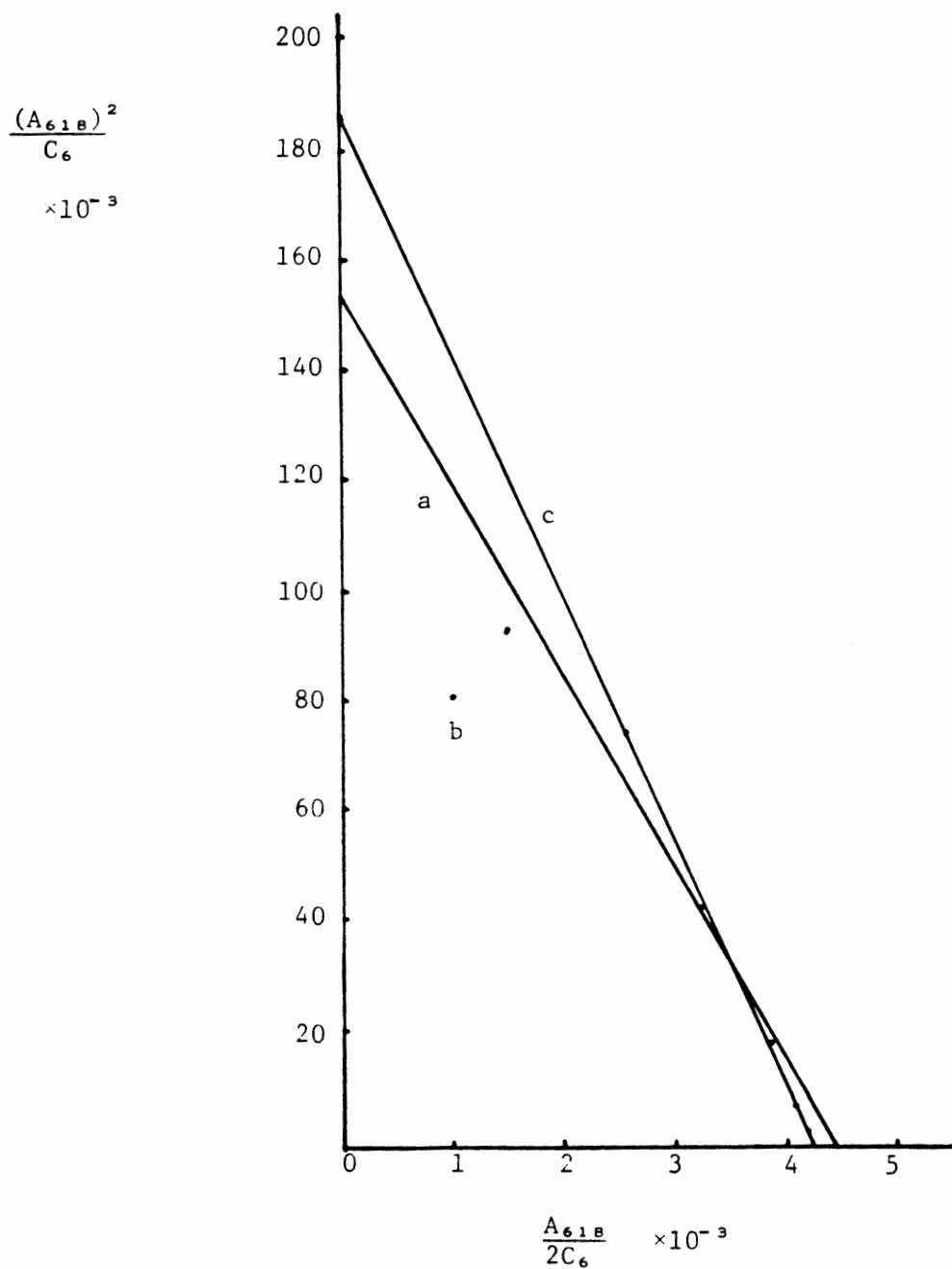


Figure 15. a) Sawyer's original plot (24). b) An additional datum point taken from Sawyer's data for an overall  $[\text{Na}_2\text{S}_6]$  of  $20 \times 10^{-3}$  M. c) Modified plot.

is of little significance. An examination of Sawyer's data and calculation of  $K_2$ , however, revealed that his calculated value of  $8 \times 10^{-8}$  moles/liter is applicable to a  $10 \times 10^{-3}$  M  $\text{Na}_2\text{S}_8$  solution alone. Values of  $K_2$  calculated by Sawyer's method from these sources of experimental data are listed in Table IX.

TABLE IX  
VALUES OF  $K_2$  CALCULATED FOR DMSO SOLUTIONS OF  $\text{Na}_2\text{S}_8$

$[\text{Na}_2\text{S}_8]/\text{M}$	$K_2/\text{moles/liter}$	Source of data
$1 \times 10^{-2}$	$8.73 \times 10^{-8}$	24
$1 \times 10^{-3}$	$8.49 \times 10^{-12}$	24
$1 \times 10^{-4}$	$1.4 \times 10^{-14}$	24
$1.2 \times 10^{-3}$	$7.1 \times 10^{-11}$	21
$8.8 \times 10^{-4}$	$5.3 \times 10^{-10}$	Present Work

These discrepancies in the values of  $\epsilon_{618}^3$ ,  $\epsilon_{475}^6$ ,  $K_d$ , and  $K_2$  suggest further work is needed to fully understand solutions of polysulfides in aprotic solvents. However, even when the new estimates of  $K_d$ ,  $\epsilon_{618}^3$ , and  $\epsilon_{475}^6$  were used to calculate  $\bar{n}_Q$  and  $\bar{n}_M$  for the present experimental data, their evaluation was again 4.8 and 18 respectively.

The conclusions drawn from the present work are the following:

No evidence was found for fragmentation of  $\text{S}_8$  or for the formation of polysulfide in DMSO solutions at elevated temperatures. The predominant sulfur species at the beginning of electrodepositions described by Roe and Baranski appears to be  $\text{S}_8$ .

The reaction of metallic cadmium and  $S_8$  yields a  $CdS_p$  product in which  $p \geq 1$ ; that is, the formation of both CdS and sulfides of higher sulfur content may occur simultaneously. The formation of  $S_3^-$  during the reaction of the metal and  $S_8$  is supported by Raman evidence, but such formation must be listed with some doubt because of the inconsistency of the spectra of similar reaction products.

Cadmium ions react with polysulfides. Each cadmium ion has the capacity to react with an average of 4.8 units of polysulfide charge. Cadmium usually has a coordination number of four. The experimental value of 4.8 negative charges per cadmium ion suggests the existence of a mixed ligand complex. Nine different combinations of the predominant ligands could be considered and are listed in Figure 16.

If each ligand combination is considered to be equally probable, the average polysulfide charge contribution would be 5.4 and the average number of sulfur atoms per complex would be 20.3. However, since  $[S_3^-]$  and  $[S_8^{-2}]$  are about equal throughout the process of  $Cd^{+2}$  additions as measured from Figure 8, combinations containing both  $S_8^{-2}$  and  $S_3^-$  are more likely. If the improbable combinations a, e, and k are eliminated from consideration, and all other combinations are considered equally probable, the average charge ratio is 4.8, and the average S:Cd ratio is 19.2. These are very close to the experimental values.

Another possible pathway for the reaction of  $Cd^{+2}$  and  $S_p^{-y}$  is one in which cadmium plays the role of a catalytic center in which polysulfides come together and react with each other as well as with cadmium forming a complex  $CdS_p$  and  $S_8$ .

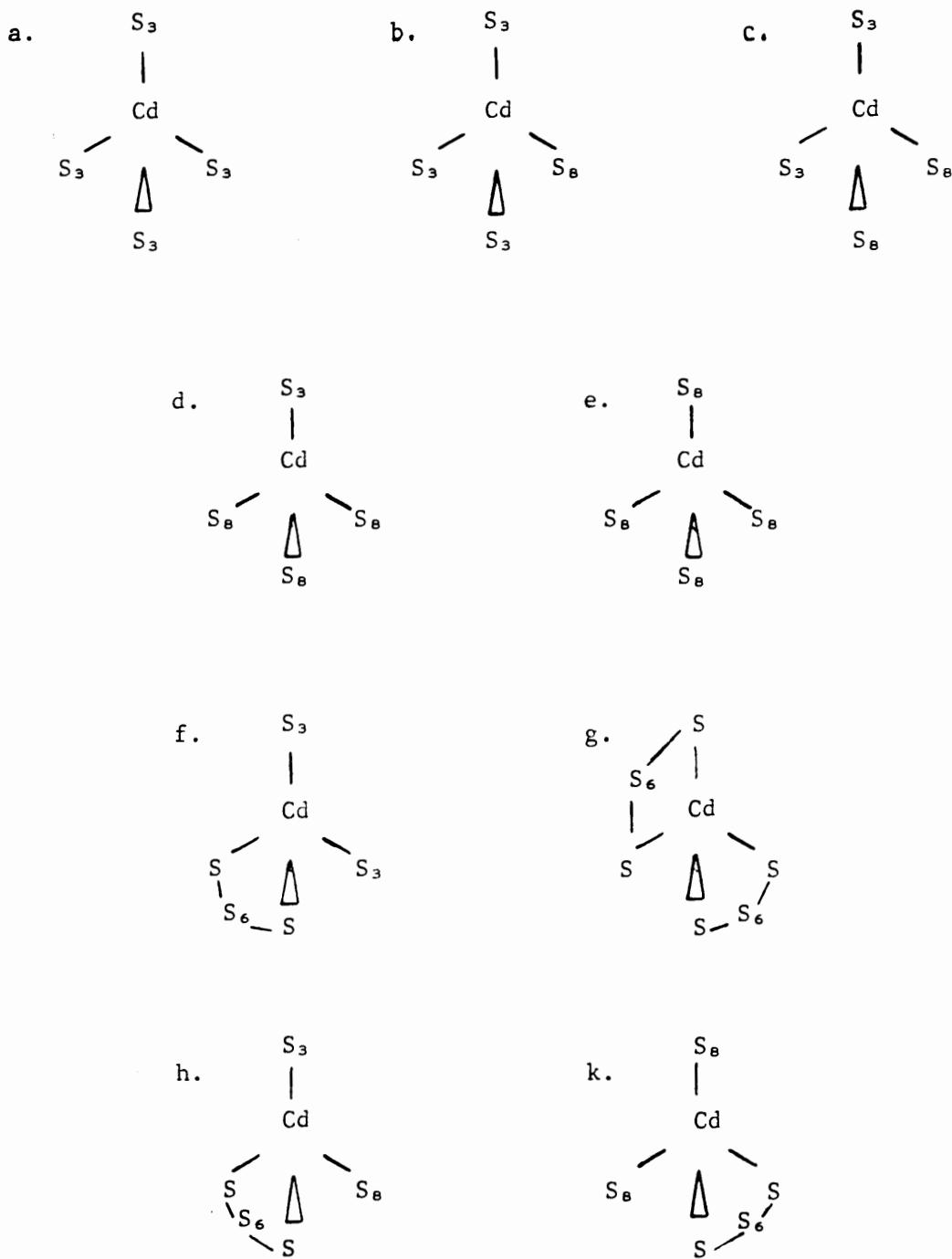


Figure 16. Possible ligand combinations involving only  $S_3^-$  and  $S_6^{2-}$ . Charges are omitted for clarity.

Finally, the significance of the results of the present work upon the two possible mechanisms (page 3) for the electrodeposition process are as follows: For the second mechanism to succeed, the most likely reduction product of  $S_8$ ,  $S_8^{-2}$ , must react with  $Cd^{+2}$  to form CdS. The present experimental results suggest that the reaction of  $Cd^{+2}$  and  $S_8^{-2}$  yields a product having a higher ratio of sulfur to cadmium.  $Cd^{+2}$  has been shown to have the capacity to react with four or more polysulfide charges. The formation of CdS by such a reaction is unlikely. Possible precipitation of  $CdS_p$  on the electrode surface, where  $p \gg 1$ , is not supported by Baranski's analysis of the actual electrodeposit where Cd:S is approximately one to one. Furthermore,  $CdS_p$  complexes have a greater solubility than CdS in DMSO, and would tend to stay in solution.

Cadmium metal, on the other hand, has been shown to react with  $S_8$  to form a  $CdS_p$  species. The first mechanism, in which cadmium is first electrodeposited and then reacts with  $S_8$  in solution to form CdS, is a similar reaction. However, a sulfur fragment is also formed. This fragment at the surface of the electrode may react again with additional freshly deposited cadmium to form additional CdS. A similar mechanism was proposed by Bartlett (39) in the nucleophilic attack of  $S_8$  by  $CN^-$  to form  $SCN^-$ . Once the ring is opened, the remaining chain was proposed to be further attacked by  $CN^-$  until the chain is completely consumed. A similar process may occur with an opened sulfur chain against the electrode surface of freshly deposited cadmium.

The increasing intensity of yellow-brown color of the electrolyte during electrolytic deposition may indicate the formation of cadmium polysulfide complexes which can form by either the reduction of  $S_8$  to  $S_8^{-2}$  and its subsequent reaction with  $Cd^{+2}$ , or by the dissolution of CdS which would further react with  $S_8$  to form soluble complexes. In either case complex formation may occur. The utilization of such complexes in the electrodeposition process is possible and an area which could be studied in the future to gain further insight into the mechanism and formation of CdS films.

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## APPENDIX A

### FORMATION OF POLYSULFIDE SOLUTIONS

There have been three methods described to produce polysulfide solutions in aprotic solvents. Giggenbach added  $S_8$  to a  $Na_2S \cdot 9H_2O$  solution of DMF (20). Seel added  $S_8$  to a solution of  $Na_2S_4$  in DMF or HMPA (26). Sawyer formed stoichiometric solids  $Na_2S_4$ ,  $Na_2S_6$ ,  $Na_2S_8$  by the reaction of metallic sodium and  $S_8$  in ammonia. The solids were then dissolved in DMSO and DMF (24). (Raman spectral studies of sodium polysulfides, of the general stoichiometry  $Na_2S_x$  where  $x > 4$ , which have been formed in this manner, have suggested the solid formed consisted of  $Na_2S_4$ ,  $S_8$ , and perhaps some  $Na_2S_5$  (33).) Both Sawyer and Cauquis formed polysulfide solutions by electrolysis at a controlled potential in DMSO with a supporting electrolyte (21,24). Fujinaga et al. (27) and Paris & Plichon (28) also used this method, but the electrolysis was performed in acetonitrile and DMA respectively.

There is very good agreement between spectra of a specific overall stoichiometry,  $Na_2S_x$ , prepared by two different methods. For example, spectra of Giggenbach in DMF coincide with those prepared by Seel in DMF. Likewise, Sawyer found that the measured electrolytic reduction of elemental sulfur in DMSO yielded spectra similar to those prepared by solution of the corresponding solid  $Na_2S_x$ . For DMSO, this point is further confirmed by a comparison of Cauquis' spectra

obtained by electrolysis and Sawyer's spectra obtained by dissolution. Stoichiometrically equivalent solutions of  $\text{Na}_2\text{S}_6$  or  $\text{Na}_2\text{S}_8$  prepared by two different methods have UV-visible maxima at identical wavelengths (21,24).

For the present work, a solution with  $\text{S}_8^{-2}$  as its major polysulfide was prepared, for our interest lay in the reduced form of  $\text{S}_8$ ,  $\text{S}_8^{-2}$ , its competition with the reduction of  $\text{Cd}^{+2}$  at the electrode surface, and its reactivity with  $\text{Cd}^{+2}$ . This was done by preparing a solution having the overall stoichiometry of  $\text{Na}_2\text{S}_8$  by the addition of appropriate amounts of  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$  and  $\text{S}_8$  to deoxygenated DMSO. The UV-visible spectra of these solutions are very similar to the spectra of  $\text{Na}_2\text{S}_8/\text{DMSO}$  solutions prepared by Cauquis and Sawyer. A measurement of the sodium concentration by AAS was used to estimate the actual ratio of sulfur atoms to charge. This was found to be 4.78; therefore, the actual stoichiometry of experimental polysulfide was then  $\text{Na}_2\text{S}_{9.6}$ .

## APPENDIX B

### DERIVATION OF EQUILIBRIUM EQUATION USING

#### SAWYER'S CONSTANTS

Beginning with a set of four equations containing four unknown concentrations, a polynomial containing only one unknown was formed through a series of algebraic operations. The four original equations are

$$(1) \quad \frac{[S_3^-]^2}{[S_6^{-2}]} = K_d$$

$$(2) \quad \frac{[S_6^{-2}]^4 [S_8^0]}{[S_8^{-2}]^4} = K_2$$

$$(3) \quad 8[S_8^0] + 8[S_8^{-2}] + 6[S_6^{-2}] + 3[S_3^-] = M_T$$

$$(4) \quad 2([S_8^{-2}] + [S_6^{-2}]) + [S_3^-] = Q_T$$

where  $Q_T$  is the total charge concentration and  $M_T$  is the total concentration of sulfur atoms.

Then

$$(5) \quad [S_8^{-2}] = \frac{Q_T - \frac{2[S_3^-]^2}{K_d} - [S_3^-]}{2}$$

$$(6) \quad [S_8^0] = \frac{K_2 K_d^4}{16[S_3^-]^8} \left\{ Q_T - [S_3^-] - \frac{2[S_3^-]^2}{K_d} \right\}^4$$