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ADSORPTION STUDIES OF THE
 $\text{Ni}(4\text{-methylpyridine})_4(\text{SCN})_2 \cdot \text{C}_6\text{H}_6$ CLATHRATE SYSTEM

by

M. A. Brault

B. A., Northern Michigan University

A Thesis

Submitted in Partial Fulfillment of the
Requirements for the Degree of
Master of Arts in Chemistry

School of Graduate Studies
Northern Michigan University
Marquette, Michigan

August 1973

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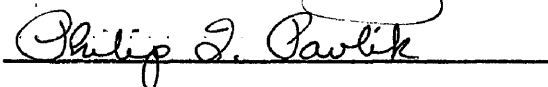
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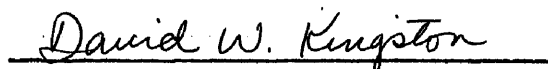
M. A. Brault

This thesis is recommended for approval

by the student's thesis committee:


Chairman





Approved by  Dean of Graduate Studies

Submitted in partial fulfillment of the

requirements for the Degree of

Master of Arts

Northern Michigan University

Marquette, Michigan

August 1973

ABSTRACT

A historical introduction to clathrate compounds is given. Adsorption studies were conducted using $\text{Ni}(4\text{-mepy})_4(\text{SCN})_2$ as host and benzene as guest. The consequences of varying the temperature, concentration of adsorbate and the surface area of the adsorbent were studied. In addition, reversibility tests were conducted and the degree of penetration of the guest molecules was determined. The results of these studies support a physical adsorption type process for the clathrate system under investigation. Clathration reactions were also found to occur between $\text{Ni}(4\text{-mepy})_4(\text{SCN})_2$ and toluene and p-xylene in the vapor state.

ACKNOWLEDGEMENTS

The author sincerely expresses her appreciation to Dr. Gerald D. Jacobs for the advice and guidance he so patiently gave during this research project and the preparation of this thesis and to the faculty and graduate students of the Chemistry Department for their helpful suggestions.

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4-Ethyltoluene, Toluene and p-Xylene as
Guest. 50

Ni(4-mepy)₄(SCN)₂
4-ethyltoluene
toluene
p-xylene

HISTORICAL BACKGROUND

HISTORICAL BACKGROUND

Clathrates may be described as single-phased solids containing two distinct components--the host which is considered to be the enclosing material and the guest which is enclosed by the crystalline structure of the host. Mylius (19), in 1886, was the first to suspect the existence of clathrate compounds. His work was concerned with complex molecules containing quinol. It was not until H. M. Powell (21) completed x-ray studies on a series of molecular compounds in 1948 that the term "clathrate" was introduced. Clathrate is derived from the Latin word "clathratus" and means enclosed or protected by the cross bars of a grating. Powell's work initiated intensive investigations of this new type of compound with work being concentrated in three areas:

- 1) Gas hydrates
- 2) Quinol complexes, and
- 3) $\text{Ni}(\text{CN})_2\text{NH}_3 \cdot \text{M}$ (M = organic adduct)

1) Gas hydrates

Gas hydrates can be thought of as inclusion compounds in which gas molecules are entrapped in crystals of ice. They are prepared by the dissolution of the gas in water under pressure and subsequent cooling until the solution freezes. Davy (8) reported the first gas hydrate of chlorine and water in 1810 and further work by Faraday (13)

resulted in the formula $\text{Cl}_2 \cdot 10\text{H}_2\text{O}$. Guests suitable for gas hydrates have been found to include Cl_2 , Br_2 , SO_2 , H_2S , CH_4 , CH_3Cl , Kr and Xe. X-ray crystallographic studies by Pauling and Marsh (20) revealed that gas hydrates contain water molecules that are bonded together through hydrogen bonds. The cavities, in which the trapped guest molecules are located, have the shape of dodecahedrons.

2) Quinol complexes

Wohler (26) and Clemm (7) reported the first hydroquinone complexes with H_2S and SO_2 . Powell (21) did a complete structural analysis by x-ray diffraction and proposed that hexagonal shaped cavities are formed by hydrogen bonds linked through oxygen atoms of the hydroquinone.

Evans and Richards (11) have reported thermodynamic and other related properties.

3) $\text{Ni}(\text{CN})_2\text{NH}_3$ complex

The first clathrate of an inorganic complex and an organic compound was announced in 1897. Single crystal investigations undertaken by Powell and Rayner (22) revealed that the organic molecules are simply trapped in the crystal lattice. Bhatnager (3) later did more extensive work on the benzene "clathrate".

The investigations of the clathrate compounds of $\text{Ni}(\text{CN})_2\text{NH}_3 \cdot \text{M}$ (M = organic adduct) led to studies on Werner complexes which differ from the above in having four neutral molecules in addition to an anion coordinated with

the metal ion. Schaeffer and Williams (23, 25) did extensive studies on these host molecules. Hart, Minton and Smith (14, 15, 18) reported constants, kinetic rate data, infra-red spectra and phase diagrams for the clathrates which have $\text{Ni}(4\text{-mepy})_4(\text{SCN})_2$ (4-mepy = 4-methylpyridine) as the host. Belitkus and co-workers (2) conducted single crystal investigations on cobalt and nickel tetra-4-methylpyridine-diisothiocyanate. Research studies by Lok (17), Vasantha (24), Chou (6), and Chick (5) indicated a correlation between guest/host sizes, temperature, guest concentration, and particle size of host during clathration.

It soon became evident that a classification scheme would be helpful in order to distinguish clathrates from substances unlike those defined by Powell. The following was proposed (28).

1) Complex molecules

A. Coordination Compounds

B. Inorganic Polymers

C. Molecular Compounds

i) Inclusion Compounds	<u>Type of Cavity</u>
a. Urea and Thiourea Adducts	Channels
b. Zeolite Complexes	Channels
c. Graphite and Silica Complexes	Layer
d. Dextrin-Iodine Type Complexes	Solution
e. Clathrates	Cage

Thus the distinction among inclusion compounds is in the type of cavity available for guest molecules.

INTRODUCTION

INTRODUCTION

The publication of the article "Separation of Xylenes, Cymenes, Methylnaphthalenes and Other Isomers by Clathration with Inorganic Complexes" by Schaeffer et. al. (23) in 1957 led to the preparation of several Werner complexes and investigations of their physical and chemical properties. Schaeffer's claim that more than 40 complexes of the first row transition metals formed clathrates could not be corroborated by Lok (17) for several of the complexes. Of the Werner complexes, $\text{Ni}(4\text{-mepy})_4(\text{SCN})_2$ has been studied most extensively. Infrared spectra, phase diagrams, calorometric and x-ray data were presented by Hart (15) for clathrates of $\text{Ni}(4\text{-mepy})_4(\text{SCN})_2$ while Minton (18) conducted additional kinetic, phase and calorometric investigations. Belitskus et. al. (2) conducted single crystal x-ray studies which showed that the complex has an octahedral configuration. Hart and Smith (14) detected a lattice change during clathration and initiated the designation of α for the lattice of the complex and β for the lattice of the clathrate.

Minton (18) described clathration as a first order reversible procedure but work by Lok (17) failed to support this theory. Allison and Barrer (1) were the first to propose that clathration might be an adsorption process and experimental evidence presented by Vasantha (24), Chou (6), and Chick (5) lends support to this theory.

Adsorption may be thought of as the adhesion of molecules of one component on the surface of another as opposed to absorption where a physical penetration occurs. Sorption refers to the two processes occurring simultaneously. The adsorbent refers to the substance adsorbing and the adsorbate is the substance being adsorbed. Physical or van der Waals adsorption indicates a weak, physical, attractive force between the adsorbent and the adsorbate and results when the valency requirements of the surface of the atoms of the adsorbent are satisfied by bonding with adjacent atoms. On the other hand, when these valency requirements are not satisfied, the surface tends to form chemical bonds with the adsorbate. This is chemisorption. Physical adsorption is reversible whereas chemisorption is not. Furthermore, physical adsorption does not depend on the concentration of the original solution and, as long as there is an excess of adsorbate, the amount adsorbed will be constant at a given temperature. Adsorption is an exothermic process and increasing the temperature decreases the amount adsorbed. Adsorption depends on (1) nature of adsorbent (2) nature of adsorbate (3) surface area of adsorbent (4) temperature and (5) the pressure of the gas.

In 1915 Langmuir (16) proposed that adsorption was a chemical process and that the adsorbed layer was monomolecular or one layer thick. In 1918 he published the Langmuir adsorption isotherm to explain the adsorption of

gases on solids. Although its use is limited, the Langmuir equation quite often serves as the basis for the derivation of other adsorption theories.

Adsorption is not always monomolecular and in 1929 deBoer and Zwikker (9) propounded the theory that physical adsorption could result in more than one layer thick (multimolecular). Their polarization theory of adsorption assumes that the adsorbent induces dipoles in the layers of the adsorbate causing a number of simultaneous Langmuir type adsorptions between each successive layer.

In 1938, Brunauer, Emmett, and Teller (4) introduced a theory of multimolecular adsorption which assumes that the forces required to produce adsorption are of the van der Waals type. Because of the assumptions used in its derivation, the BET theory has been the subject of frequent criticism and is generally used only in measuring the specific surface of a solid.

The Freundlich isotherm is often employed for a heterogeneous surface. An attempt was made to fit the data in this thesis to the Freundlich isotherm. The equation relates the amount of material adsorbed to the amount unadsorbed at equilibrium or

$$M = kc^{1/n}$$

where M = number of moles adsorbed per mole of adsorbent

c = number of moles unadsorbed at equilibrium

k and n = empirical constants

A constant value is obtained when the log of the number of moles adsorbed is plotted against the log of the number of moles unadsorbed.

In addition to monomolecular and multimolecular adsorption, condensation occurring in the capillaries or pores of a substance is considered to be physical adsorption.

Brunauer (27) presented five categories of physical adsorption isotherms (Figure 1) where

V_{ads} = Volume adsorbed per mole of adsorbent

P = Pressure, mm of mercury

P_0 = Vapor pressure of adsorbate

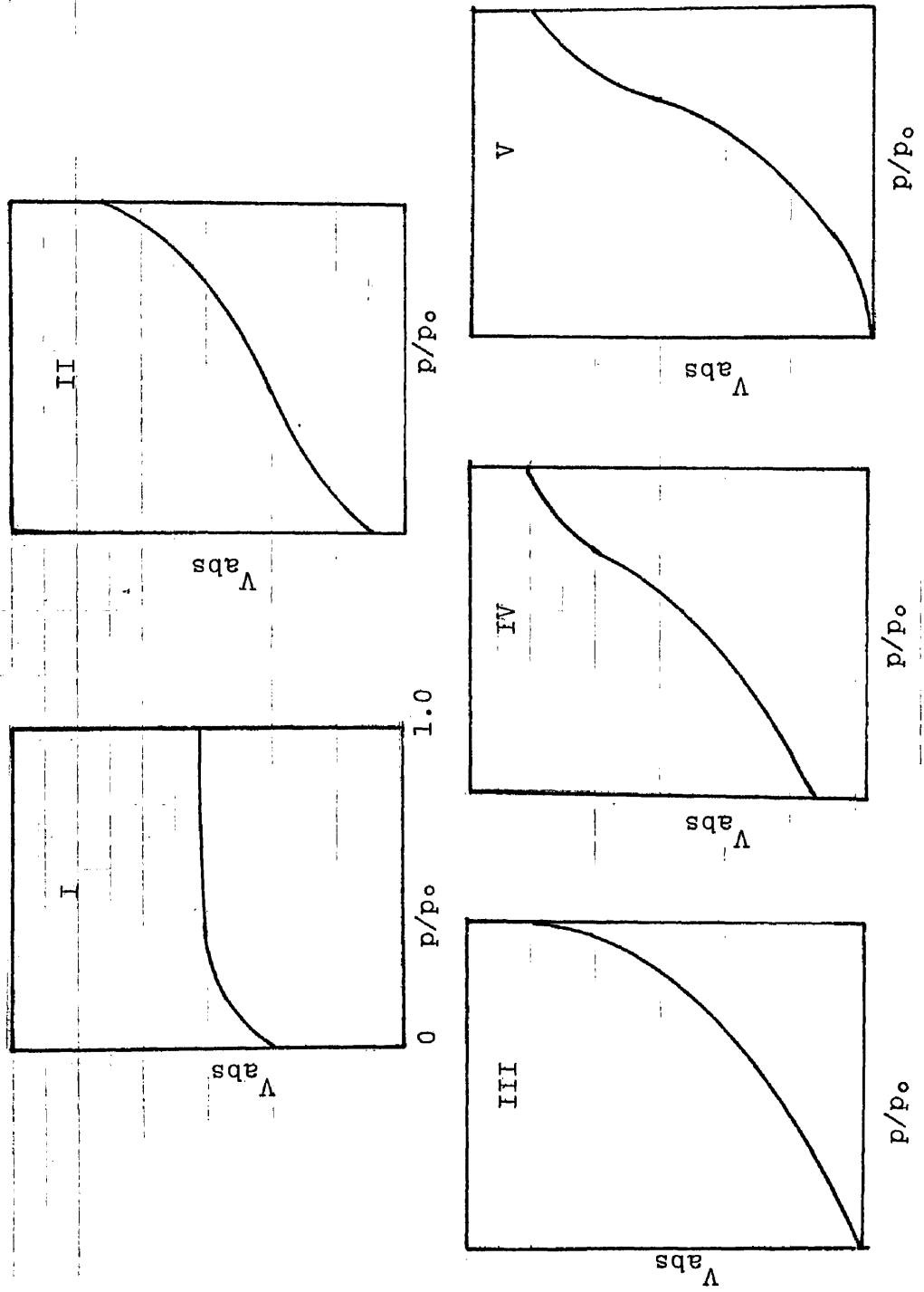
Type I, the Langmuir type, depicts monomolecular adsorption.

Type II, represents multimolecular adsorption and is the most frequently used.

Type III and V give the best results when adsorption is attained at a pressure lower than the vapor pressure of the gas.

Type IV and V includes, in addition to multimolecular adsorption, capillary condensation at pressures below the saturation value.

FIGURE I
BRUNAUER'S ADSORPTION ISOTHERMS



INSTRUMENTATION

INSTRUMENTATION

Temperature

The adsorption studies were conducted in a constant temperature bath which could be controlled to $\pm 0.2^\circ\text{C}$.

X-ray Measurements

A Siemens Kristalloflex 4, X-ray Diffractometer utilizing copper K-alpha radiation, 40 kV and 16mA was used for the powder diffraction patterns. Measurements of the powder patterns were made with a coincidence scale which has a reading error of ± 0.01 mm.

Spectral Measurements

A Beckman DB-G Grating Spectrophotometer and matched Beckman silica cells were employed to obtain ultraviolet spectra which were recorded on a Beckman Model 1005 Recorder.

Analytical Measurements

All weight determinations, except direct adsorption, were made on an Ainsworth Type 21N single pan automatic balance. Adsorption weighings were made with an Ainsworth Type DLB chainomatic balance.

Adsorption Study Apparatus

The adsorption study apparatus (Figure 2) required a reaction flask for the guest and the solvent, heptane, an adsorption bucket to contain the host, a balance and a constant temperature bath. A 30 ml beaker, cut in half lengthwise was utilized as the adsorption bucket and a

3-liter round bottom flask was used for the reaction flask.

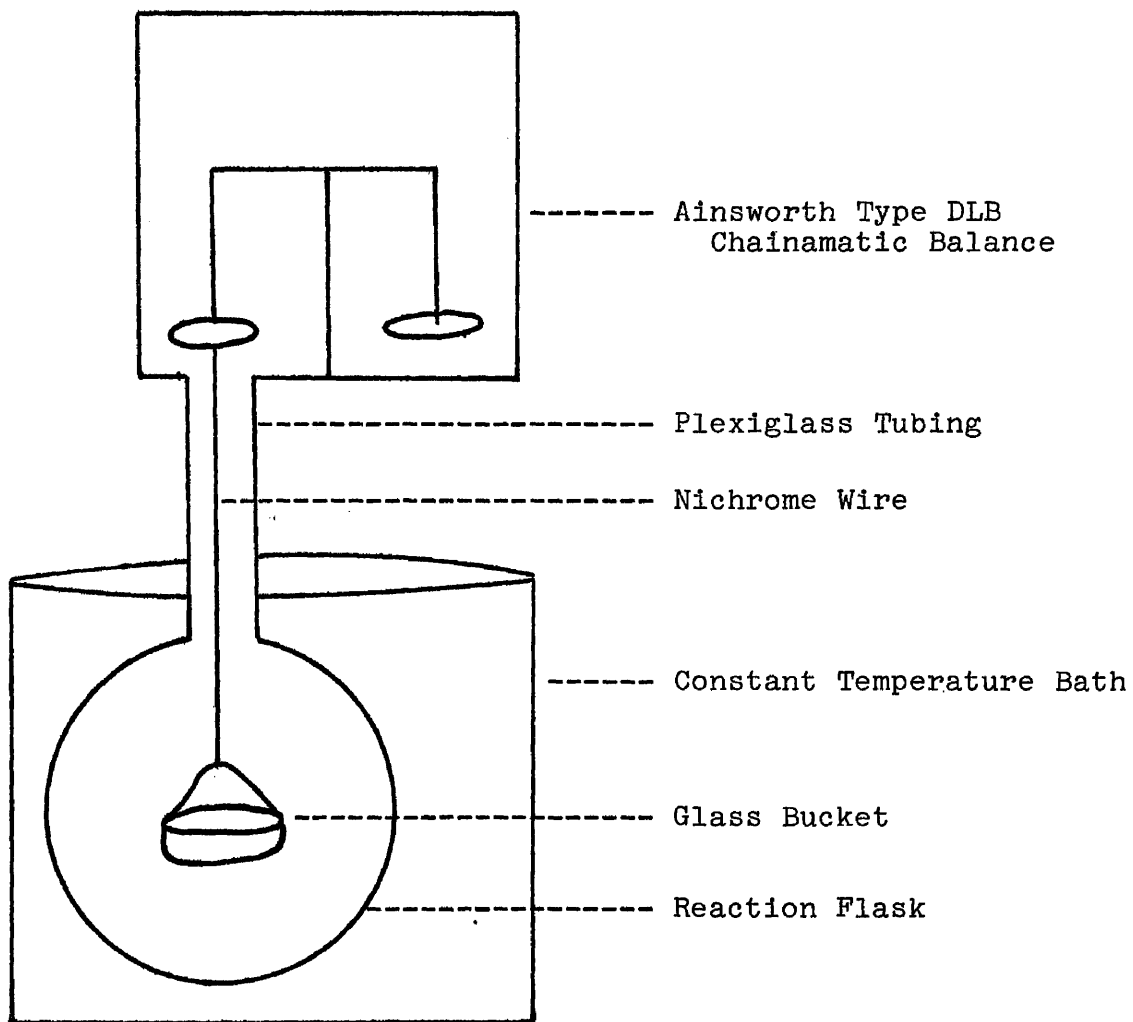


FIGURE II. Schematic of Adsorption Study Apparatus

EXPERIMENTAL

EXPERIMENTAL

Preparation of Ni(4-mepy)₄(SCN)₂

The complex was prepared by a simple precipitation method. Following the addition of 0.114 moles of Ni(SCN)₂ to 1500 ml of water, 0.455 moles of 4-mepy was added dropwise with constant stirring. After the addition of the 4-mepy was complete, the resulting suspension was stirred for another hour. The precipitate was then filtered, allowed to air dry for 24 hours, transferred to a dessicator and dried over potassium hydroxide pellets for one week. Analytical Reagent Grade chemicals were used in all preparations. Volumetric analysis for nickel was used to determine the purity of the complex.

Purification of Heptane

Impurities in the Reagent Grade heptane made its purification necessary. This was done by first extracting with concentrated sulfuric acid. Frequent shaking was required over a 24 hour period. This was followed by neutralization of the heptane with 10% sodium carbonate solution and then treatment with a saturated solution of sodium chloride. The neutralization and salting out required 24 hours each with occasional shaking. Passing the heptane through a column of calcium chloride was required for final drying and was followed by fractional distillation. The heptane produced was determined to be of Spectroquality Grade as shown by ultraviolet spectra.

Adsorption Studies

The reaction flask containing 60 ml of heptane and a predetermined amount of guest component was placed in a constant temperature bath and allowed to come to equilibrium for 24 hours. The bucket was suspended over the solution by a nichrome wire. After equilibrium was established, a sample of the solution was withdrawn and 0.1 ml was transferred to a 25 ml volumetric flask and diluted with purified heptane. The empty bucket was weighed, removed from the flask, filled with complex, re-suspended above the solution and weighed immediately. At predetermined time intervals, a pipet was used to remove a sample from the reaction flask and was prepared for spectroscopic analysis. However, the Beckman DB-G Grating Spectrophotometer was not sensitive enough to detect the small change in the concentration of the guest and this step was discontinued. At the same time, the weight of the bucket and its contents was recorded.

An adsorption study was allowed to proceed for at least 48 hours or until there was no significant weight change in the bucket and its contents for 24 hours. At the completion of an adsorption study, an x-ray powder pattern was obtained of the solid and the percent nickel was determined by volumetric analysis.

X-ray Diffraction Patterns

An x-ray powder pattern was obtained for the complex and the compound remaining after the completion of each

adsorption study. The sample was prepared for x-ray analysis by mixing with collodion and then extruding the partially dried sample from a 0.5 mm diameter capillary tube.

A two-radian camera and exposure time of two hours was used to obtain the powder pattern.

Quantitative Analysis

The complex and clathrate, after being treated with dilute hydrochloric acid, were analyzed for percent nickel by titrating with EDTA using murexide as indicator (29).

RESULTS AND DISCUSSION

RESULTS AND DISCUSSION

Adsorption Studies

Allison and Barrer (1) conducted the first sorption studies on clathrate compounds. Preparation of the β -phase was brought about by the direct contact of the solid complex with the guest in the liquid phase. The emphasis in their research was on the stability of the β -phase. Their evidence indicated that clathration was a reversible process and that the rate of desorption was temperature dependent. They also concluded that there is a relationship between sorption and the size and shape of the guest molecule.

Preliminary studies by Vasantha (24), Chou (6), and Chick (5) indicated that clathration could be an adsorption process. Therefore, it was felt that more extensive adsorption studies should be made on the host Werner complex, $\text{Ni}(4\text{-mepy})_4(\text{SCN})_2$. The factors investigated were:

- (i) temperature
- (ii) reversibility
- (iii) concentration of adsorbate
- (iv) surface area of adsorbent
- (v) penetration of guest

Temperature Studies

Temperatures of 13°, 23°, 33°, and 43°C were used in the study of the adsorption of 0.06 moles of benzene by

TABLE I
 MOLES OF BENZENE ADSORBED PER MOLE OF ADSORBENT**

TIME (HOURS)	CLATHRATE			
	I*	II*	III*	IV*
$\frac{1}{2}$	0.0336±0.0003	0.0470±0.0003	-0.0170±0.0003	-0.2460±0.0003
1	0.0491	0.0578	-0.0069	-0.2583
2	0.0799	0.1156	0.0733	-0.1848
3	0.1364	0.1858	0.1786	-0.0801
4	0.2120	0.2977	0.3192	-0.0002
6	0.3498	0.4920	0.5462	0.2050
8	0.5234	0.6747	0.7240	0.3612
12	0.8161	0.9432	0.8546	0.5890
24	1.0540	1.1180	0.8811	0.6025
36	1.0830	1.1440		0.6110
48	1.0953	1.1490	0.8798	0.5948
60	1.0950	1.1490	0.8899	0.5948
72	1.1030	1.1490	0.8889	0.5948

*Clathrate I, II, III, and IV refers to temperatures of 13°, 23°, 33°, and 43° respectively.
 **Adsorbent refers to Ni(4-mepy)₄(SCN)₂.

TABLE II

INTERPLANAR SPACINGS (Å) FOR THE MORE PROMINENT REFLECTIONS FROM THE
 $N_1(4\text{-mep})_4(\text{SCN})_2$ COMPLEX AND THE BENZENE CLATHRATE

OBSD.	COMPLEX		CLATHRATE			
	LIT.**	I*	II*	III*	IV*	
8.65±0.05	8.64	13.06±0.05	13.06±0.05	12.98±0.05	12.98±0.05	
	8.37	8.46	8.30	8.25	8.34	
7.60	7.56					
	7.34	7.12	6.98	6.95	7.00	
	5.17	5.16	5.11	5.11	5.20	
5.09	5.03					
	4.98					
4.86	4.85					
4.45	4.50	4.61	4.79	4.52	4.56	
	4.36					
	4.27					
4.10	4.08	3.98	3.92	3.90	3.95	
3.89	3.90					

*Clathrate I, II, III, and IV refers to temperatures of 13°, 23°, 33°, and 43°C respectively.
 **M. I. Hart and N. O. Smith, J. Am. Chem. Soc., 84, 1816 (1962).

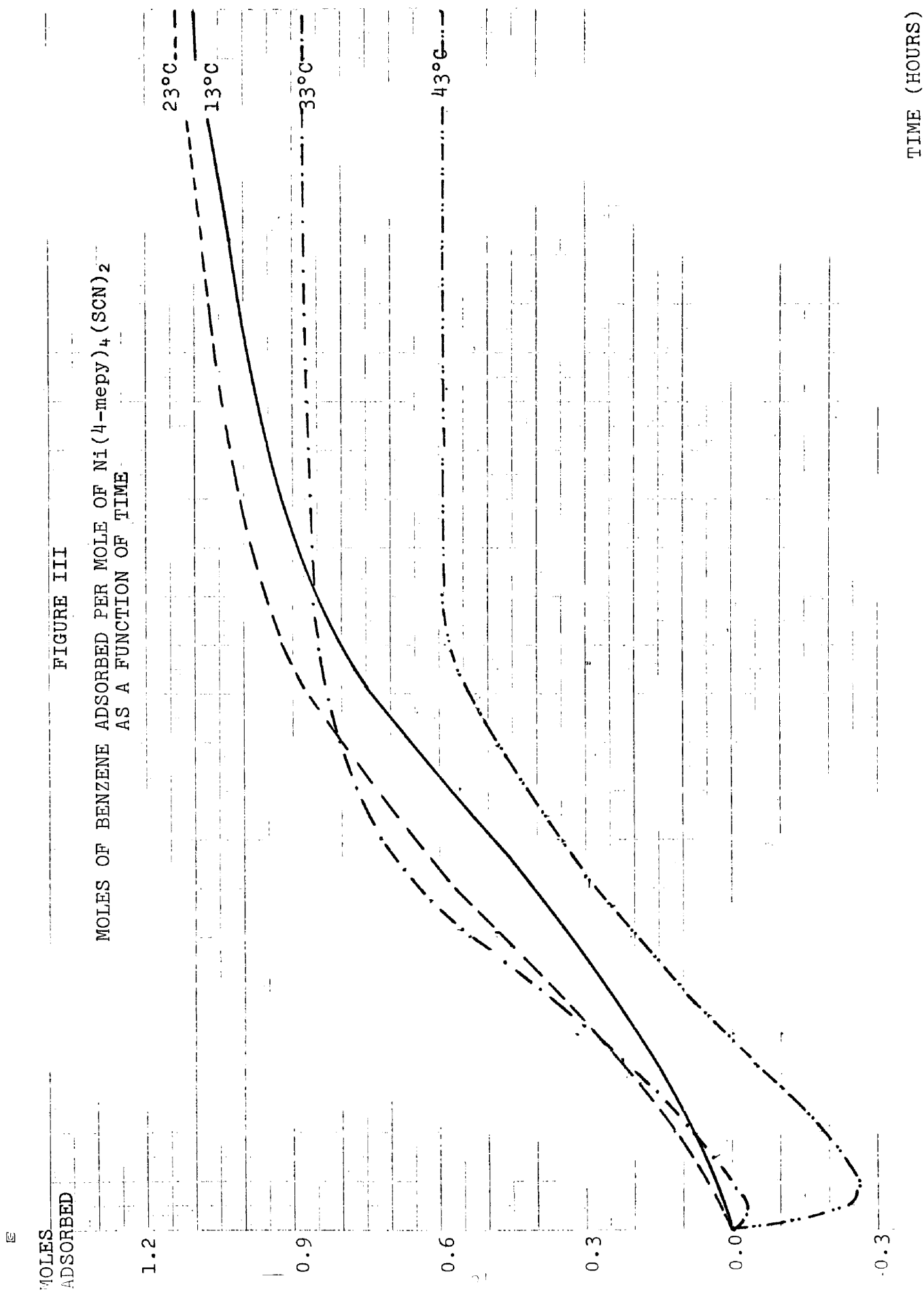
TABLE III
 VOLUMETRIC ANALYSES FOR PER CENT NICKEL IN
 THE BENZENE CLATHRATE

TRIAL	CLATHRATE	
	A*	B*
1	9.60±0.06%	9.89±0.06%
2	9.60	9.89
AVERAGE	9.60	9.89
THEORETICAL	10.73	
MOLE RATIO (GUEST/HOST)	0.843	0.627

*Clathrate A and B refers to clathrate formed at 23°C.
 Clathrate B was analyzed 30 days after clathrate A.

FIGURE III

MOLES OF BENZENE ADSORBED PER MOLE OF $\text{Ni}(4\text{-mepy})_4(\text{SCN})_2$
AS A FUNCTION OF TIME



TIME (HOURS)

5

-LOG MOLES
ADSORBED

FIGURE IV

ADSORPTION ISOTHERM
23°C

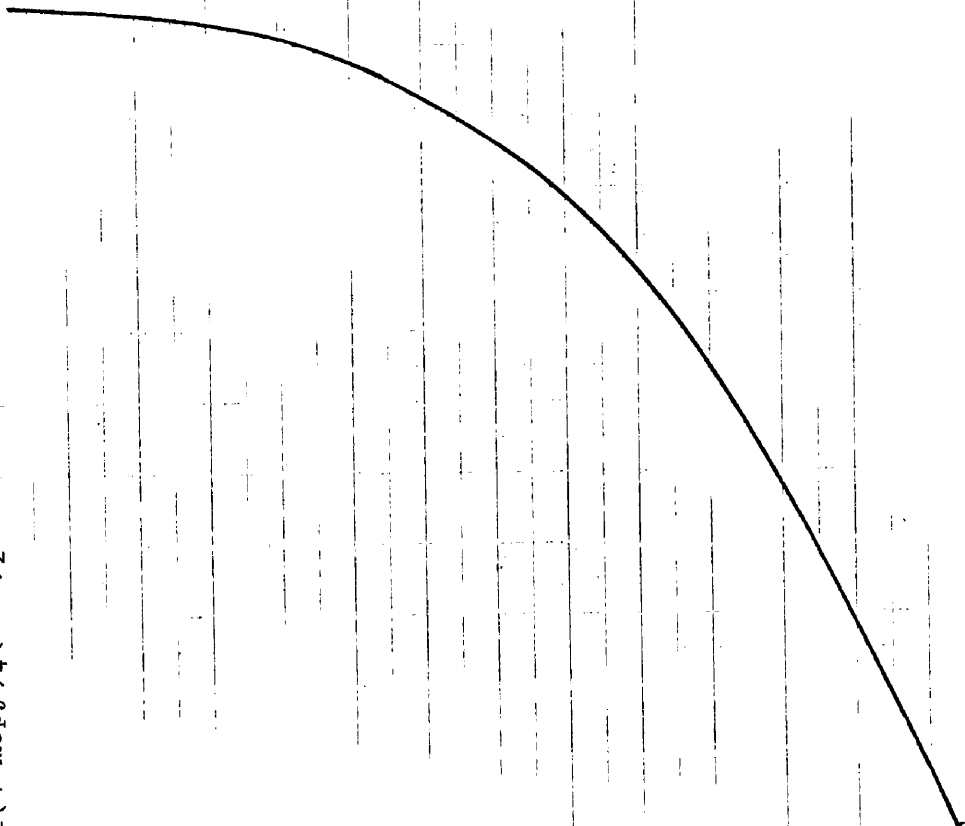
1.5

GUEST MOLECULE BENZENE
HOST MOLECULE Ni(4-mepy)₄(SCN)₂

1.0

0.5

0.5



LOG MOLES
UNADSORBED

0.004 moles of host (more exactly 15.4 moles of benzene per mole of complex). The results are presented in Tables I and III and Figures III and IV. Table I shows the number of moles of guest adsorbed per mole of host as a function of time. Table II gives the results of the x-ray analysis and Table III gives the results of volumetric analyses for the 23°C adsorption study. Figure III is a plot of Table I and Figure IV is an attempt to fit this data to the Freundlich isotherm.

Volumetric analyses for the per cent nickel (Table III) revealed that guest to host (G/H) ratios changed with time probably due to the loss of physically adsorbed guest molecule from the clathrate. A more accurate G/H ratio is obtained from the moles of guest adsorbed per mole of adsorbent which were calculated from the direct adsorption weighings and it is this figure which will be used as the G/H ratio in this thesis unless otherwise specified. From the data it can be seen that the number of moles adsorbed decreases with increasing temperature. The initial decrease in moles adsorbed at 43°C and 33°C can be attributed to the release of excess 4-mepy. It can also be seen that total adsorption at 23°C is slightly greater than that adsorbed at 13°C, but Table I indicates that maximum adsorption has occurred at 23°C and, therefore, an increase in moles adsorbed at 13°C is unlikely. A change in vapor

pressure could account for the slight difference in G/H ratios. However, the fact that G/H ratios decreased with increasing temperature is evidence supporting the theory that the clathration of benzene by $\text{Ni}(4\text{-mepy})_4(\text{SCN})_2$ is an adsorption process.

A plot was made of the log of moles adsorbed versus the log of the moles unadsorbed. It was found that the best initial conditions for these adsorption studies was a ratio of 15.4 moles of benzene/mole of host. This concentration produced an insignificant change in the moles unadsorbed and it is felt that Figure II is, therefore, of little value.

Reversibility

The reversibility of the clathration process was studied in the following manner. Clathration was first allowed to come to completion at 33°C after which time the temperature was adjusted to 43°C and the system allowed to reach equilibrium. The temperature was subsequently lowered to 33°, 23°, 13°, and 9°C allowing the system to come to equilibrium after each temperature adjustment. The results are presented in Tables IV and V and Figure V through X. The large initial drop in moles adsorbed in Figure VI can be attributed to a release of excess 4-mepy along with a liberation of guest due to the decrease in adsorption with an increase in temperature. This is to be expected in physical adsorption. Figures VII and VIII show a large increase in moles adsorbed

TABLE IV

MOLES OF BENZENE ADSORBED PER MOLE OF ADSORBENT**
DURING THE REVERSIBILITY ADSORPTION STUDY

TIME (HOURS)	CLATHRATE		
	I*	II*	III*
½	-0.1700±0.0003	0.8343±0.0003	
1	-0.0070	0.8320	0.8425±.0003
2	0.0730	0.8595	
3	0.1786	0.8556	0.8667
4	0.3192	0.8533	0.8683
6	0.5462		0.8428
8	0.7240	0.8500	
12	0.8546	0.8500	0.8301
24	0.8811	0.8441	0.8350
36		0.8412	0.8330
48	0.8798	0.8372	0.8347
60	0.8899	0.8340	0.8347
72		0.8311	0.8291
84		0.8226	0.8291
96		0.8226	0.8291
108		0.8150	
120		0.8131	
132		0.8098	

*Clathrate I, II, and III refers to temperatures of 33°, 43°, and 33°C respectively.

**Adsorbent refers to Ni(4-mepy)₄(SCN)₂

TABLE IV CONTINUED

TIME (HOURS)	CLATHRATE		
	IV*	V*	VI*
½	0.8254±0.0003	0.8428±0.0003	0.8677±0.0003
1	0.8533	0.8592	0.8752
2	0.8732	0.8716	0.8795
3	0.8827	0.8762	0.8804
4	0.8909	0.8772	0.8837
6	0.8834	0.8811	0.8863
8		0.8811	0.8880
12	0.8670	0.8772	0.8880
24	0.8719	0.8795	0.8880
36	0.8680	0.8765	0.8880
48	0.8723	0.8782	0.8880
60	0.8723	0.8782	0.8880
72	0.8723	0.8782	0.8880

*Clathrate IV, V, and VI refers to temperatures of 23°, 13°, and 9°C respectively.

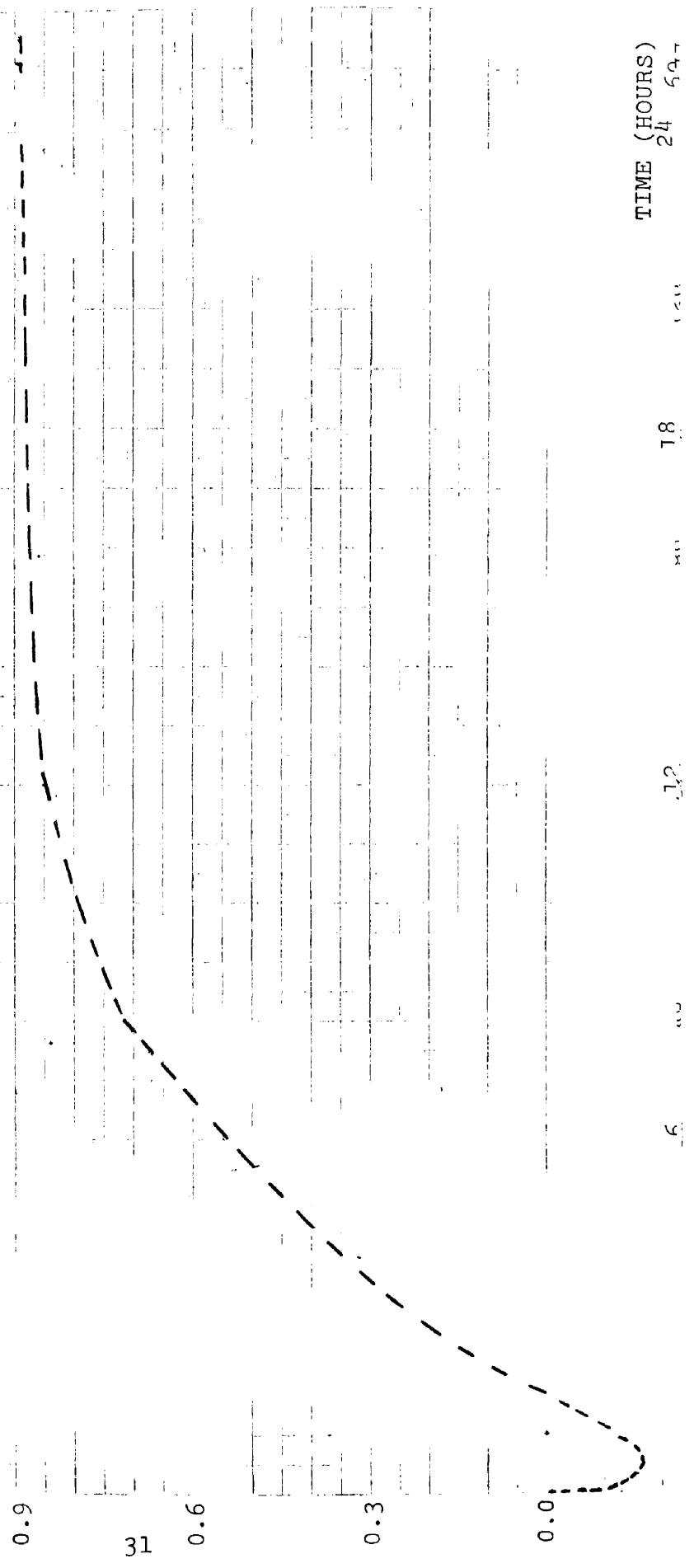
TABLE V
 INTERPLANAR SPACINGS (Å) FOR THE MORE PROMINENT
 REFLECTIONS FROM THE Ni(4-mepy)₄(SCN)₂ COMPLEX AND THE
 BENZENE CLATHRATE FORMED DURING THE REVERSIBILITY
 ADSORPTION STUDY

COMPLEX		CLATHRATE
OBSD.	LIT.**	
8.65±0.05	8.64	13.13±0.05
	8.37	8.39
7.60	7.56	
	7.34	7.04
	5.17	5.95
5.09	5.03	5.19
	4.98	
4.86	4.85	
4.45	4.50	4.56
	4.36	
	4.27	
4.10	4.08	
	4.05	
3.89	3.90	3.94
	3.85	
	3.65	
	3.55	3.59
	3.27	
	3.16	

**M. I. Hart and N. O. Smith, J. Am. Chem. Soc., 84, 1816 (1962).

MOLES
ADSORBED

FIGURE V
MOLES OF BENZENE ADSORBED PER MOLE OF $\text{Ni}(\text{4-mepy})_4(\text{SCN})_2$
AS A FUNCTION OF TIME
(TEST OF REVERSIBILITY)
33°C

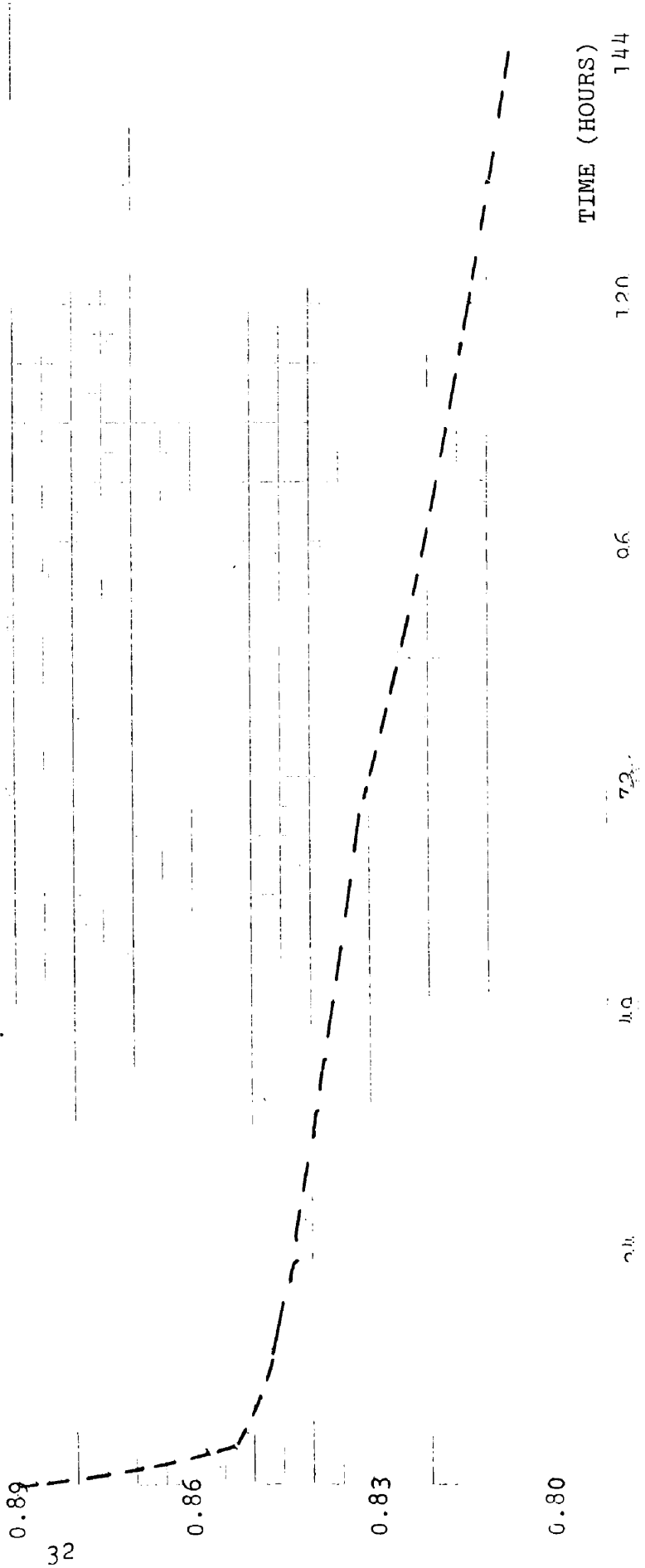


TIME (HOURS)
24 597

MOLES ADSORBED

FIGURE VI

MOLES OF BENZENE ADSORBED PER MOLE OF $Ni(4\text{-mepy})_4(SCN)_2$
AS A FUNCTION OF TIME
(TEST OF REVERSIBILITY)
43°C



MOLES
ADSORBED

FIGURE VII

MOLES OF BENZENE ADSORBED PER MOLE OF $\text{Ni}(\text{4-mepy})_4(\text{SCN})_2$
AS A FUNCTION OF TIME
(TEST OF REVERSIBILITY)
33°C



0.89

33

0.86

0.83

0.80

TIME (HOURS)

120

60

30

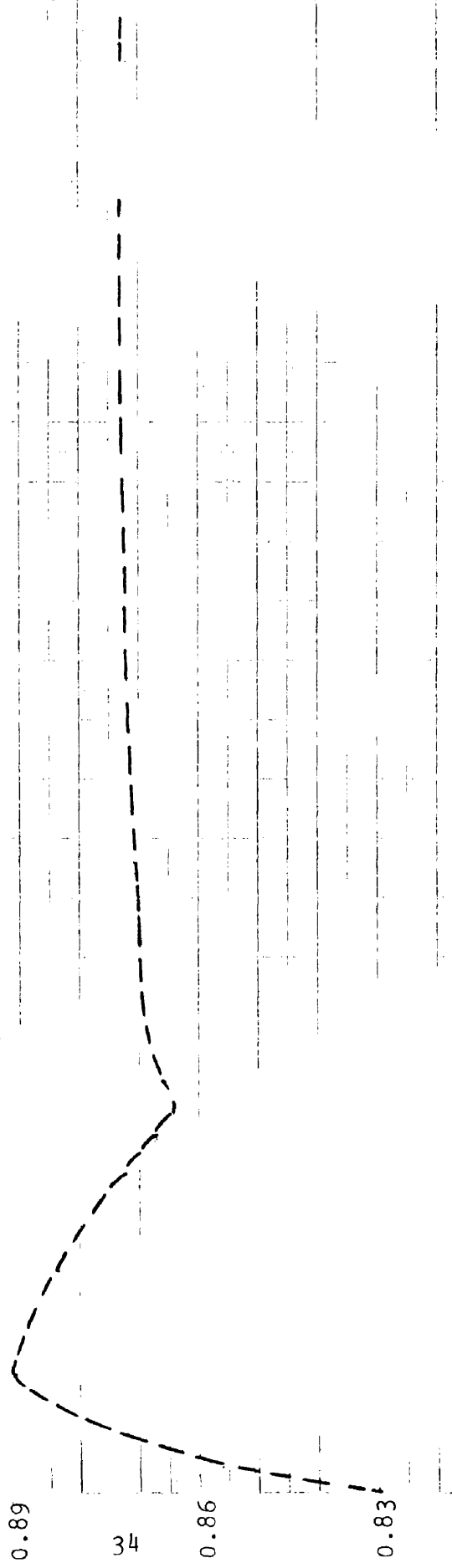
10

0

MOLES ADSORBED

FIGURE VIII

MOLES OF BENZENE ADSORBED PER MOLE OF $\text{Ni}(\text{4-mepy})_4(\text{SCN})_2$
AS A FUNCTION OF TIME
(TEST OF REVERSIBILITY)
23°C



0.80

0.89

34

0.86

0.83

TIME (HOURS)

44

26

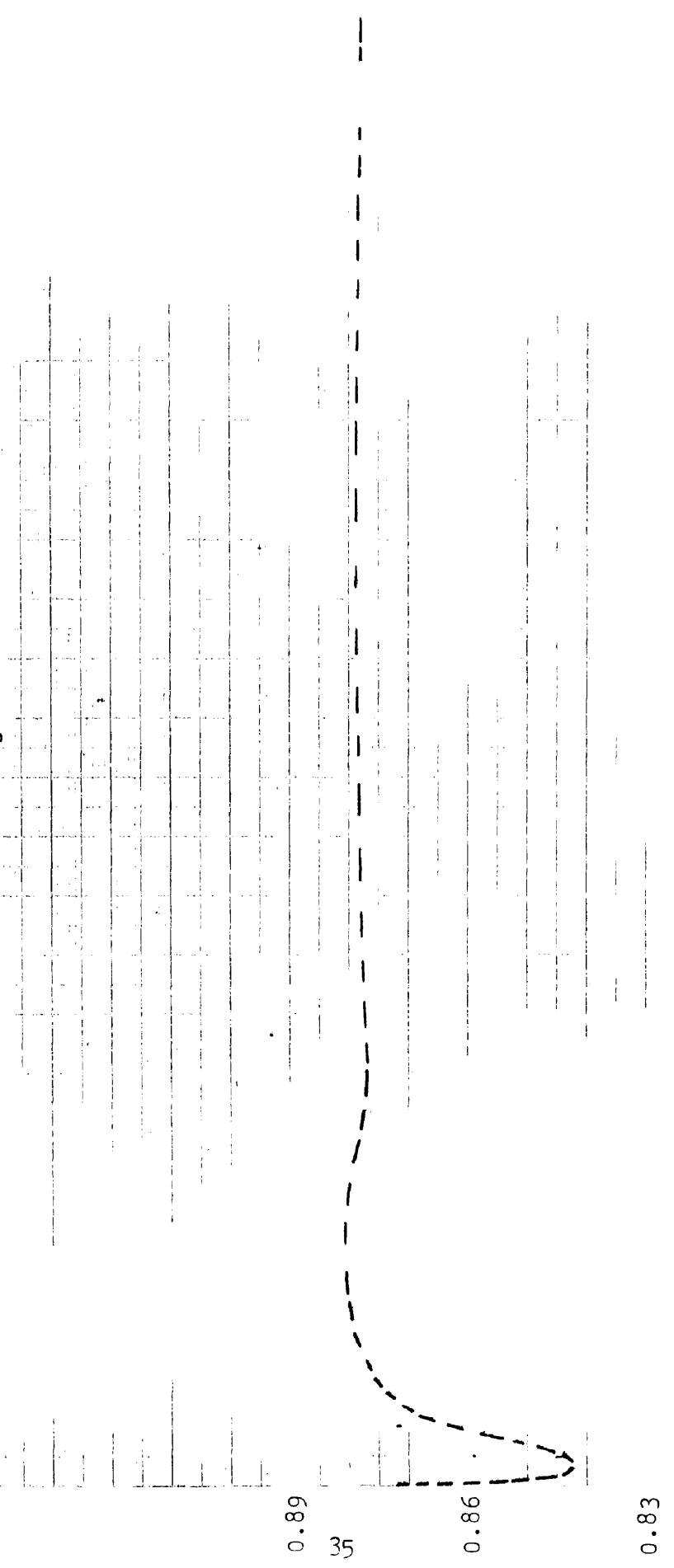
20

60

MOLES ADSORBED

FIGURE IX

MOLES OF BENZENE ADSORBED PER MOLE OF Ni(4-mepy)₄(SCN)₂
AS A FUNCTION OF TIME
(TEST OF REVERSIBILITY)
13°C



TIME (HOURS)

11.5 7.5

2.5

2.0

1.0

0.80

0.83

0.86

0.89

35

MOLES ADSORBED

FIGURE X

MOLES OF BENZENE ADSORBED PER MOLE OF Ni(4-mepy)₄(SCN)₂
AS A FUNCTION OF TIME
(TEST OF REVERSIBILITY)
9°C



TIME (HOURS)
116 72

followed by a drop which is due to an increase in adsorption with a decrease in temperature. This is again indicative of physical adsorption. The curves tend to straighten out with time as equilibrium is established. Figures IX and X show an initial drop in moles adsorbed. At this point, it would seem that the entrapped guest molecules are not free to move and, as the sites which a guest can occupy fill up, lowering the temperature decreases the number of guest molecules in the vapor state and simply removes some of the guests adsorbed by the surface. From the data, it can be concluded that this clathration process is reversible and, also, of a physical adsorption type.

Concentration of Adsorbate

The change in adsorption with concentration was studied. Table VI gives the concentration of benzene in the liquid and vapor states, Table VII the moles adsorbed and Table VIII the x-ray analysis. Figure XI is a plot of Table VII. As would be expected, decreasing the concentration of the guest decreases the rate of clathration. The larger number of moles adsorbed for clathrate iii is attributed to the fact that a slightly larger amount of host was used during the experiment. This increased the amount of exposed surface area and, in turn, the amount adsorbed by the surface. Time necessitated that the adsorption study for clathrate i be terminated after 98 hours. It can be concluded from

TABLE VI
MOLE FRACTION OF BENZENE IN LIQUID AND VAPOR STATES

MILLILITERS OF BENZENE*	MOLE FRACTION BENZENE IN LIQUID	MOLE FRACTION BENZENE IN VAPOR
1	0.026	0.095
5	0.121	0.344
10	0.216	0.512
20	0.355	0.677

*Benzene added to 60 milliliters of heptane

TABLE VII
 MOLES OF BENZENE ADSORBED PER MOLE OF ADSORBENT**
 CLATHRATE

TIME (HOURS)	i*	ii*	iii*	iv*
½	0.0018±0.003	0.0470±0.0003	0.2378±0.0003	0.5529±0.0003
1	0.0241	0.0578	0.4714	0.8310
1½		0.0790	0.6477	0.9337
2	0.0369	0.1156	0.7937	
2½				0.9758
3	0.0462	0.1858	1.0100	
3½				0.9931
4	0.0554	0.2977	1.1072	0.9986
6	0.0747	0.4920	1.1270	1.0230
8	0.0811	0.6747	1.1460	1.0400
12	0.1108	0.9432	1.1750	1.0610
24	0.1570	1.1180	1.2300	1.1180
36	0.1747	1.1440	1.2520	1.1280
48	0.1932	1.1490	1.2800	1.1430
60	0.2048	1.1490	1.2600	1.1430
72	0.2217			
84	0.2325			
98	0.2253			

*Clathrate i, ii, iii, and iv refers to 1, 5, 10, and 20 ml of benzene added to 60 ml of heptane respectively.

**Adsorbent refers to Ni(4-mepy)₄(SCN)₂.

TABLE VIII

INTERPLANAR SPACINGS (\AA) FOR THE MORE PROMINENT REFLECTIONS FROM THE
 $\text{Ni}(4\text{-mep})_4(\text{SCN})_2$ COMPLEX AND THE BENZENE CLATHRATE

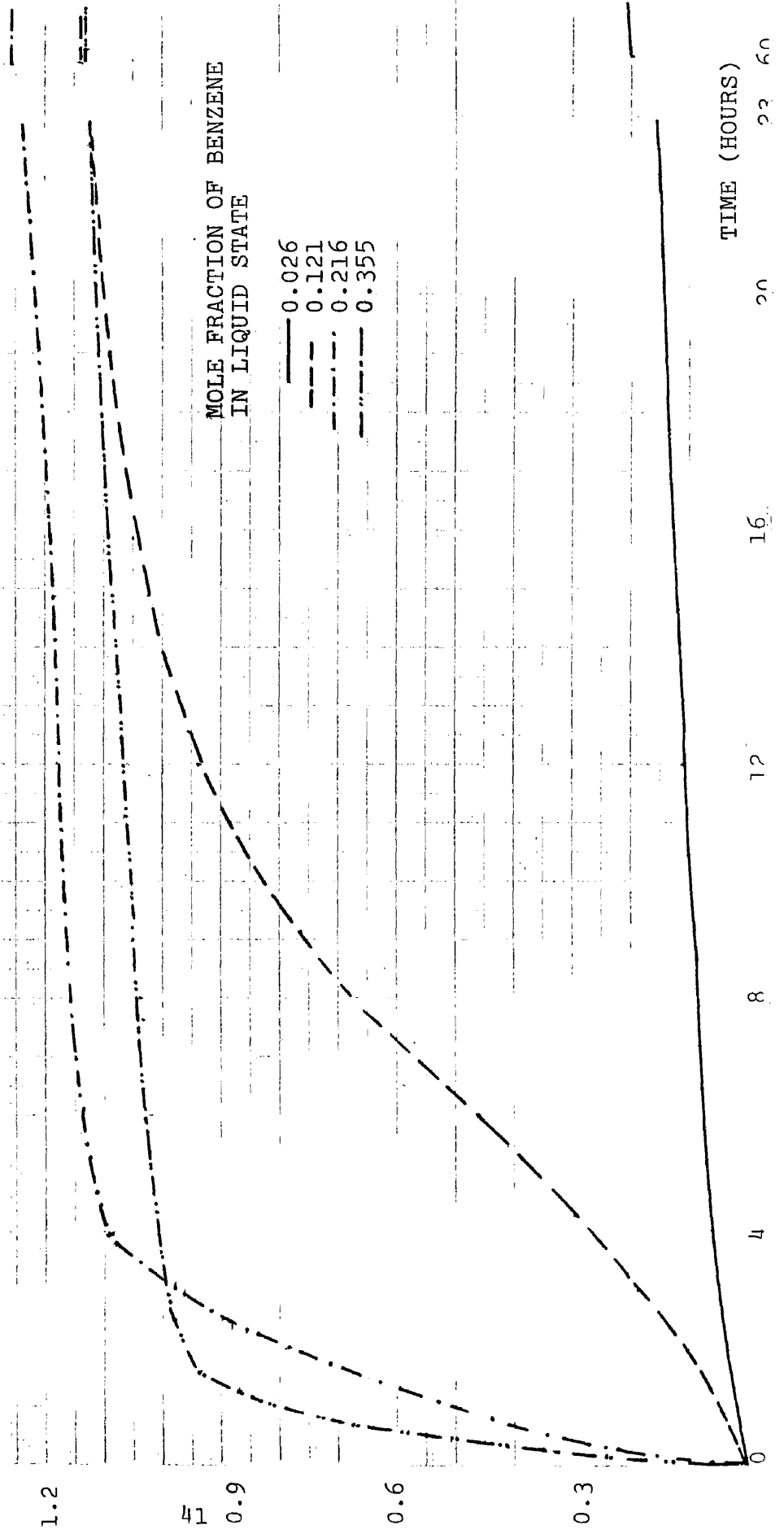
COMPLEX	CLATHRATE			
	i*	ii*	iii*	iv*
	13.05±0.05	13.06±0.05	12.78±0.05	13.19±0.05
8.65±0.05	8.34	8.30	8.36	8.35
7.60	7.02	6.98	7.14	7.04
	5.94	5.29	6.00	5.94
5.09	5.14	5.11	5.10	5.14
4.86				
4.45	4.53	4.53	4.58	4.56
4.10				
3.89	3.92	3.92	3.95	3.94
	3.57	3.56	3.61	3.59

*i, ii, iii, and iv refers to 1, 5, 10, and 20 ml of benzene added to 60 ml of heptane respectively.

MOLES
ADSORBED

FIGURE XI

MOLES OF BENZENE ADSORBED PER MOLE OF $\text{Ni}(\text{4-mepy})_4(\text{SCN})_2$
AS A FUNCTION OF TIME



MOLE FRACTION OF BENZENE
IN LIQUID STATE

- 0.026
- - - 0.121
- · - · 0.216
- - - - 0.355

TIME (HOURS)

0 4 8 12 16 20 24

clathrates ii, iii, and iv that the number of moles adsorbed is a constant and the adsorption theory is further supported.

Surface Area

The exposed surface areas studied were 12.80 and 8.03 square centimeters. Table IX gives the moles adsorbed with time, Table X the results of the x-ray analysis and Figure XII is a plot of Table IX. The data indicates that a change in surface area changes the rate of clathration. It should also be noted that the larger exposed surface area adsorbed a larger number of moles and is due to an increase in area for benzene-benzene and benzene-heptane type adsorption on the exposed surface of the clathrate.

Penetration of Guest

An x-ray powder pattern and volumetric analyses of the bottom, middle and top layers of the sample were obtained after the adsorption study at 23°C. The data are presented in Tables XI and XII. Evidence indicates that clathration occurs at all levels.

Guests other than Benzene

Attempts were made to obtain clathrates with guests other than benzene in the vapor state. Adsorption studies were conducted with toluene, p-xylene and 4-ethyltoluene. Tables XIII and XIV show the moles adsorbed and x-ray data respectively. Figure XIII is a plot of Table XIII. Schaeffer (23) reported clathrate formation with benzene,

TABLE IX
 MOLES OF BENZENE ADSORBED PER MOLE OF ADSORBENT**
 CLATHRATE

TIME (HOURS)	C*	D*
½	0.0470±0.0003	0.0250±0.0003
1	0.0578	0.0526
2	0.1156	0.1098
3	0.1858	0.2060
4	0.2977	0.2899
6	0.4920	0.5022
8	0.6747	0.6227
12	0.9432	0.8378
24	1.1180	0.9907
36	1.1444	0.9907
48	1.1490	0.9907

*Clathrate C and D refers to a surface area of 12.80 and 8.03 square centimeters respectively.

**Adsorbent refers to Ni(4-mepy)₄(SCN)₂

TABLE X
 INTERPLANAR SPACINGS (\AA) FOR THE MORE PROMINENT
 REFLECTIONS FROM THE $\text{Ni}(\text{4-mepy})_4(\text{SCN})_2$ COMPLEX AND THE
 BENZENE CLATHRATE

COMPLEX	CLATHRATE	
	C*	D*
	13.06 ± 0.0003	12.98 ± 0.0003
8.65	8.30	8.32
7.60	6.98	6.98
	5.92	5.93
5.09	5.12	5.14
4.86		
4.45	4.53	4.53
4.10		
3.89	3.92	3.92
	3.56	3.57

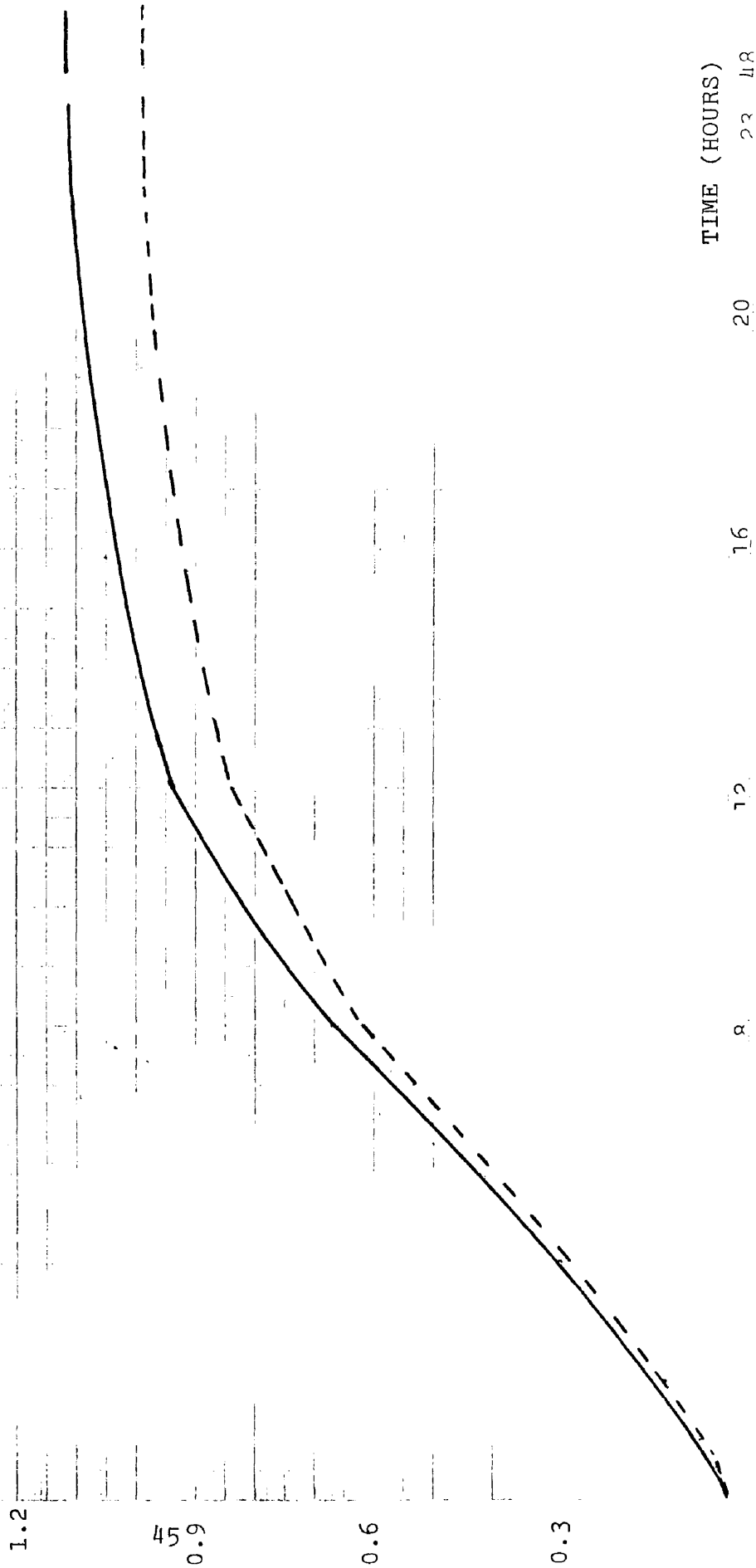
*Clathrate C and D refers to a surface area of 12.80 and 8.03 square centimeters respectively.

MOLES
ADSORBED

FIGURE XII

MOLES OF BENZENE ADSORBED PER MOLE OF $\text{Ni}(\text{4-mepy})_4(\text{SCN})_2$
AS A FUNCTION OF TIME

— 12.80 square centimeters
- - - 8.03 square centimeters



TIME (HOURS)
23 48

TABLE XI

INTERPLANAR SPACINGS (\AA) FOR THE MORE PROMINENT REFLECTIONS FROM THE $\text{Ni}(4\text{-mepy})_4(\text{SCN})_2$ COMPLEX AND THE BENZENE CLATHRATE

COMPLEX	CLATHRATE		
	E*	F*	G*
	13.11 \pm 0.05	13.19 \pm 0.05	13.27 \pm 0.05
8.65 \pm 0.05	8.56	8.35	8.33
7.60	7.03	7.04	7.02
	5.96	5.94	5.94
5.09	5.13	5.14	5.15
4.86			
4.45	4.56	4.56	4.56
4.10			
3.89	3.94	3.94	3.95
	3.58	3.59	3.58

*Clathrate E, F, and G refers to the top, middle, and bottom layers respectively of the solid remaining in the bucket after the 23°C adsorption study.

TABLE XII
 VOLUMETRIC ANALYSES FOR PER CENT NICKEL IN
 THE BENZENE CLATHRATE

	CLATHRATE		
TRIAL	E*	F*	G*
1	9.62±0.06%	9.76±0.06%	9.73±0.06%
2	9.57	9.72	9.65
3	9.52	9.74	9.86
AVERAGE	9.57	9.74	9.75
THEORETICAL	10.73		
MOLE RATIO (GUEST/HOST)	0.866	0.738	0.731

*Clathrate E, F, and G refers to the top, middle, and bottom layers respectively of the solid remaining in the bucket after the 23°C adsorption study.

TABLE XIII

MOLES OF GUEST ADSORBED PER MOLE OF ADSORBENT*

TIME (HOURS)	CLATHRATE		
	TOLUENE	p-XYLENE	4-ETHYLTOLUENE
½	0.0164±0.0003	0.0158±0.0003	0.0050±0.0003
1	0.0204	0.0204	0.0094
2	0.0269	0.0293	0.0153
3	0.0322	0.0343	0.0231
4	0.0353	0.0413	
6	0.0471	0.0569	0.0342
8	0.0548	0.0775	0.0420
12	0.0879	0.1238	0.0420
24	0.2857	0.2810	0.0796
36	"	0.4075	0.0796
48	0.4752	0.5277	0.1026
60	0.6231	0.7170	0.0859
72	0.7550	0.7254	0.0909
84	0.8355	0.8027	
96	0.8638	0.8725	0.1253
108	0.8836	0.9145	
120		0.9510	0.1319
132	0.9104	0.9428	
144	0.9104	0.9608	0.1167

*Adsorbent refers to $\text{Ni}(4\text{-mepy})_4(\text{SCN})_2$

TABLE XIV

INTERPLANAR SPACINGS (\AA) FOR THE MORE PROMINENT REFLECTIONS FROM THE $\text{Ni}(4\text{-mepy})_4(\text{SCN})_2$ COMPLEX AND SOME CLATHRATES

COMPLEX	CLATHRATE		
	TOLUENE	p-XYLENE	4-ETHYLTOLUENE
	13.05 \pm 0.05	13.21 \pm 0.05	
8.65 \pm 0.05	8.31	8.60	8.61 \pm 0.05
7.60	6.95	7.29	7.60
	5.95	5.39	
5.09	5.13		5.05
4.86	4.82	4.64	
4.45	4.53		4.43
4.10	3.94	4.02	4.10
3.89	3.67	3.82	3.88
		3.64	

MOLES ADSORBED

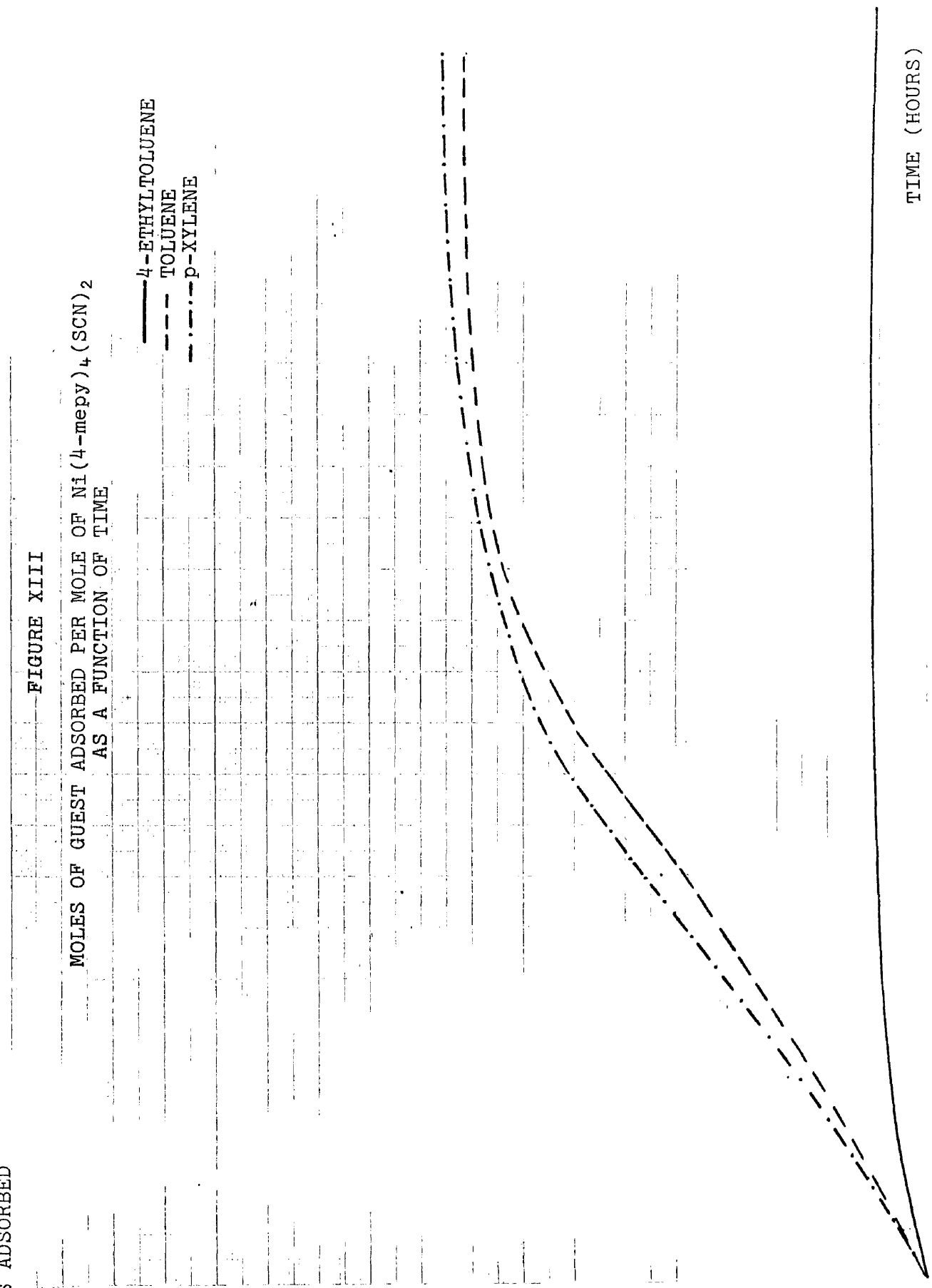
FIGURE XIII

MOLES OF GUEST ADSORBED PER MOLE OF Ni(4-mepy)₄(SCN)₂
AS A FUNCTION OF TIME

— 4-ETHYLTOLUENE
- - - TOLUENE
- · - · - p-XYLENE

1.2
0.9
0.6
0.3

TIME (HOURS)
100
110



toluene, p-xylene, 4-ethyltoluene and p-cymene. Lok (17) confirmed clathration for benzene, toluene and p-xylene but not for 4-ethyltoluene.

The data presented agrees with Lok's observations. However, preliminary kinetic studies with p-cymene were in agreement with Schaeffer and x-ray analysis and volumetric analysis confirmed the formation of a clathrate with the $\text{Ni}(4\text{-mepy})_4(\text{SCN})_2$ complex.

$\text{Ni}(4\text{-vinylpyridine})_4(\text{SCN})_2$

Preliminary kinetic studies were conducted with $\text{Ni}(4\text{-vinylpyridine})_4(\text{SCN})_2$ as host and benzene, toluene, p-xylene, 4-ethyltoluene, p-cymene and styrene as guests. Failure to form clathrates was confirmed by x-ray powder patterns and volumetric analyses.

etc

part 1

4

GENERAL SUMMARY

GENERAL SUMMARY

Work by Allison and Barrer (1) in England and studies conducted in this laboratory by Lok, Vasantha, Chou, and Chick (17, 24, 6, 5) led to the proposal that clathration could be explained as an adsorption process, at least in the case of a limited number of guest-host combinations. $\text{Ni}(4\text{-mepy})_4(\text{SCN})_2$ and benzene as host and guest, respectively, were used to further test this hypothesis. The effects of temperature, concentration of adsorbate and surface area of adsorbent were all examined. In addition, the reversibility of the process was studied as well as the degree of penetration of the guest molecules.

The results of the temperature study revealed that the extent of clathration between $\text{Ni}(4\text{-mepy})_4(\text{SCN})_2$ and benzene decreased with increasing temperature, thus supporting a physical adsorption theory. Further evidence favoring physical adsorption was obtained from reversibility tests and volumetric analyses. It was found that varying the concentration of the guest had no effect on the extent of clathration. This result would also be expected if the process is simple adsorption. Additional support for the proposed adsorption theory was obtained by observing that an increase in the exposed surface area of the host resulted in an expected increase in the guest/host ratio. In addition, the guest molecules were found to have penetrated

to the innermost layers of the host in the glass "bucket" which was constructed to hold the host crystals. The conclusion drawn from these studies is that the clathration reaction for this system may indeed be a physical adsorption process.

Clathration reactions were also found to occur between $\text{Ni}(\text{4-mepy})_4(\text{SCN})_2$ and toluene and p-xylene in the vapor state.

X-ray powder patterns indicated a lattice change in going from complex to clathrate for all studies.

Suggestions for further studies include:

- i) Adsorption study using p-cymene as guest.
- ii) Use guest only--no heptane. Since adsorption studies cannot be followed spectrophotometrically, it is unnecessary to use heptane.
- iii) Evacuate the system. This purifies the surface of the adsorbent prior to adsorption studies. It also allows for low pressure adsorption studies.
- iv) Use a quartz balance. This allows for frequent weight determinations and, at the same time, the complete enclosure of the system.
- v) After completion of an adsorption study, introduce a second guest to study competitive clathration.
- vi) After completion of an adsorption study, remove all unadsorbed guest and follow desorption gravimetrically.
- vii) Use radioactive guest molecules to measure changes in concentration during competitive clathration.
- viii) Use a Cahn Electrobalance. This allows for complete enclosure and evacuation of the system.

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LIST OF REFERENCES

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