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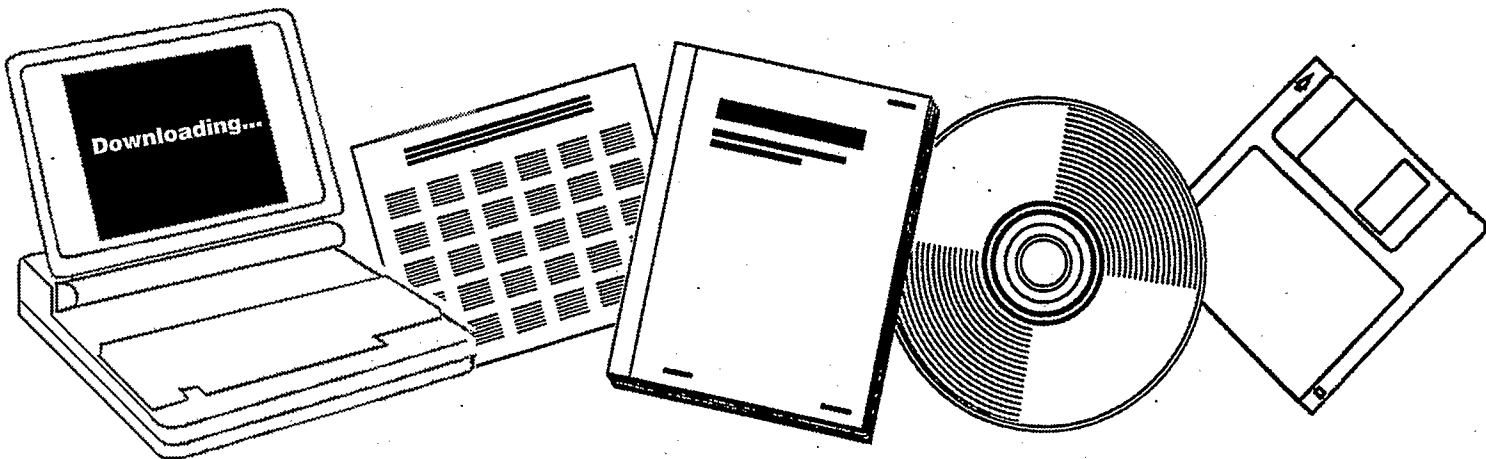
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**COAL CONVERSION PROCESSES. QUARTERLY
REPORT, MARCH 13, 1984-JUNE 12, 1984**

**PITTSBURGH UNIV., PA. DEPT. OF CHEMICAL
AND PETROLEUM ENGINEERING**

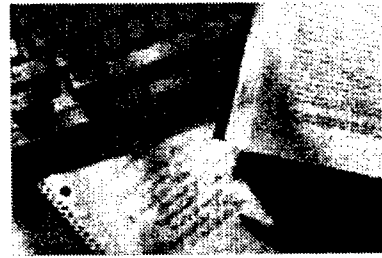
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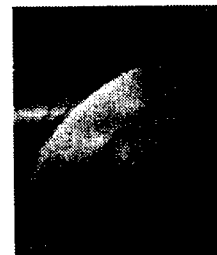
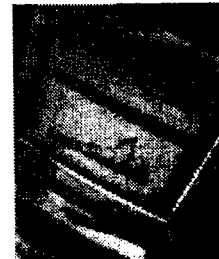
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COAL CONVERSION PROCESSES

Quarterly Report

For Period March 13, 1983 - June 12, 1984

James T. Cobb, Jr.

Paul Biloen

Gerald D. Holder

George E. Klinzing

John W. Tierney

Department of Chemical and Petroleum Engineering
University of Pittsburgh
Pittsburgh, PA 15261

August 1984

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I. ABSTRACT

Experimental work is continuing on four separate projects related to coal conversion processes.

The direct digital control of exothermic multiphase reactions is being studied in an experimental adiabatic flow reactor. A paper based on earlier results has been submitted for publication. The effect of step changes of important process variables on reactor performance has been determined.

Various absorbents for SO_2 and NO_x are being studied. Further data on the absorption of SO_2 and NO_x by a solution of N-cyclohexyl-2-pyrrolidone (CHP) have been obtained. Data on the absorption of NO in triethylene-tetraamine has also been obtained. Characterization of liquid membranes formed experimentally have been performed; the FeCl_2/CHP system will be examined first.

Isotopic switching is being used to study the way in which promoters affect supported metal catalysts. Non-statistical distributions of ^{13}C in Fischer-Tropsch products has been observed experimentally. A model for the ingrowth of ^{13}C in ethane has been developed.

A program for the study of the extraction of coal and oil shale using supercritical fluids is being carried out. The effect of stirrer speed, density and reaction time on the amount of toluene solubles and tetrahydrofuran solubles produced by supercritical extraction of Bruceton coal with toluene.

II. INTRODUCTION

Work continues on four subjects of importance in coal conversion:

- thermal behavior of slurry reactors for indirect coal liquefaction
- use of chromatographic techniques to explore absorbers for SO_2 and NO_x
- support and promoter effects on composite CO/H_2 conversion catalysts
- extraction and conversion of coal and oil shale using supercritical fluids.

This quarterly report has been prepared by Professors Paul Biloen (Section V), Gerald D. Holder (Section VI), George E. Klinzing (Section IV) and John W. Tierney (Section III). The overall project is coordinated by Professor James T. Cobb, Jr.

III. THERMAL BEHAVIOR OF SLURRY REACTORS USED

FOR INDIRECT COAL LIQUEFACTION (Task 1)

A slurry reactor especially designed to measure heat evolution has been built in our laboratories and is being used in this study of indirect coal liquefaction. Thermal effects are particularly important in slurry reactors where heat transfer is good and local hot spots may rapidly propagate throughout the reactor. The system being studied is the H_2/CO synthesis using a ruthenium catalyst. The liquid is a heavy oil, and the catalyst particles are finely divided and kept in suspension by a stirrer.

Experimental evidence for the existence of multiple steady states in the experimental reactor were presented in the last quarterly report. These results have important design implications because the reactor operation depends not only on the current values of process variables but on the reactor history as well. A paper based on these results has been submitted to Industrial and Engineering Chemistry, Process Design and Development. Work in the ensuing quarter has been focused primarily on determining the effects of important process variables on reactor performance as measured by the conversion of CO, heat liberated, and conversion to methane. The independent variables which have changed are temperature, stirrer speed, pressure, hydrogen/carbon monoxidized ratio, and gas space velocity. The effect of a step change in each of these variables is summarized in Table 1.

To investigate the effect of process variables on the existence of multiple steady states, runs were made in which the temperature was varied while all other variables were held constant. This was done at two levels of pressure, stirrer speed, feed composition, and feed rate. The results are being analyzed and will be presented in detail in the final report. Multiple steady states were found at other conditions, although the region of multiplicity was changed.

IV. USE OF CHROMATOGRAPHIC TECHNIQUES FOR EXPLORE

ABSORBERS FOR SO₂ and NO_x (Task 2)

During the past quarter a number of encouraging advances were made on the solution of an organic absorbent that can remove both SO₂ and NO_x.

N-Cyclo-Hexyl-2-Pyrrolidone

The initial tests were continued on N-cyclo-hexyl-2-pyrrolidone (CHP). The temperature behavior of SO₂ and CHP was established. Figure 1 shows a diagram of the activity coefficient at infinite dilution for the SO₂ and CHP system. In the past quarter it was also established that CHP could absorb NO₂. This was not done by the infinite dilution technique since the N₂/NO₂ chromatographic technique did not separate the two species sufficiently in order to calculate the activity coefficients. The NO₂ which is brown in color was injected into a closed vessel containing CHP. After mild agitation, the brown color disappeared indicating that NO₂ had been absorbed. The tests conducted with NO and CHP proved to be ineffective. Thus one can suggest CHP as an absorbent of SO₂ and NO₂. See Table 2 for absorption conditions.

In order to have CHP absorb NO a technique suggested by Ward has been proposed. Ferrous chloride (FeCl₂) has been employed in formamide as a carrier to actively transport NO across a liquid membrane of the solution while supported on a plastic porous membrane. Ferrous chloride thus is the active mover of NO and as such a solution of this and CHP will be tested in a cell similar to Ward's in order to assess the transport properties of this system. One then has a reasonable combination of CHP and ferrous chloride for simultaneous absorption of a SO₂/NO₂/NO system.

Of particular note in the FeCl₂/CHP system is that the CHP becomes insoluble in water by the addition of salts. This trait makes the FeCl₂/CHP system a good candidate for liquid membrane technology.

Triethylene Tetra-Amine

The other organic solvent showing very good promise is triethylene tetra-amine (TETA). The amine fits the category of a hindered amine. Initial testing was performed on TETA using NO gas since this is the most difficult to absorb. Figure 3 shows a chromatogram of N₂/NO using TETA as an absorbent. From the two peaks shown one can establish that there is absorption of NO in TETA. This series of experiments was run at three different temperature to establish a range of absorptivity. The Bureau of Mines had previously found TETA to be acceptable for SO₂ absorption. It is felt that TETA is an excellent candidate for SO₂/NO₂/NO absorption. See Table 3 for absorption conditions. Since the gas NO at room temperature is above its critical temperature, a Henry's law constant has been calculated and is shown in Table 1. Also see Figure 2. The gases SO₂/NO₂ will be explored for absorption details during the next quarter. It is of interest to note that TETA is very soluble in water. Liquid membranes probably can not be made from this solvent.

Other hindered amines to be tested in the next quarter are

N-Nitrosodipropylamine

N-Nitrosodiethylene amine

N,N,N^L,N^L tetraethylene diamine

N,N Dipropylacetamide

Liquid Membranes

The liquid membrane aspect of the absorption of SO₂/NO₂/NO has involved actual formations of the membranes. The heavy oil was used as the membrane material using Span 80 as the stabilizer. At 2000 rpm a oil/water emulsion was formed and the emulsion was viewed under the optical microscope. These emulsion drops were between 10 and 20µm in diameter. Using the marine

impeller at 500, 750 and 1000 rpm, the encapsulated emulsion droplets were formed within a large diameter liquid membrane, 150 μ m in diameter. Figure 4 shows a photograph of the encapsulating liquid membrane and the liquid emulsion droplets for 750 rpm. The membranes have been noted to be stable over a period of days. The present objective is to add the liquid absorbent to the oil or make the membrane out of the pure liquid absorbent depending on the solubility of the liquid absorbent.

V. SUPPORT AND PROMOTER EFFECTS ON COMPOSITE

CO/H₂ CONVERSION CATALYSTS (Task 3)

The preceding quarterly reports in this series described the methodology being used in this study:

- switching abruptly the isotopic constitution of the feed to working catalysts, and monitoring the rate of ingrowth of the "new" isotope into products.

We confirmed a surprising finding: A $^{12}\text{CO}/\text{H}_2$ -to- $^{13}\text{CO}/\text{H}_2$ switch leads to a non-statistical distribution of ^{13}C in C_3 and C_4 products. This is shown in Figure 5, which compares the theoretical prediction with our experimental observation.

Further to the sequence of elementary reaction steps on unpromoted cobalt, we have modelled the ingrowth of ^{13}C in C_2H_4 , taking t_1 , t_2 and t_b as the independent variables. (The parameters t_i are defined as the life times of the C_1 , the C_2 and the C_1 -building block intermediates, respectively, in the Fischer-Tropsch reaction.) Figure 6 and Figure 7, being the experimental observation and the computer simulation, respectively, demonstrate that our results can be described by $t_b < t_1$ and $t_2 > 0$.

VI. EXTRACTION AND CONVERSION OF COAL AND OIL SHALE

USING SUPERCRITICAL FLUIDS (Task 4)

Background

A program for the study of supercritical fluids for extraction of coal and oil shale is being carried out. Emphasis is placed on developing a fundamental understanding of supercritical phase behavior as applied to coal conversion and for coal liquid deashing. Initial experiments⁽¹⁾ which have used supercritical water to convert coal to gases, liquids and THF Soluble products at supercritical temperature have produced high conversion with brown coal (75%) and with bituminous coal (58%). Results obtained to date have shown coal rank; coal type, extraction (reaction) time, extraction temperature and density of the supercritical phase are important variables.

It has been hypothesized that when coal is contacted with a supercritical fluid, a portion of the coal dissolves instantaneously. The amount of coal which dissolves depends on the density and the temperature of the supercritical fluid and should increase with an increase in density and temperature of the supercritical fluid. It is further hypothesized that only the part of the coal which is dissolved in the supercritical fluid undergoes liquefaction reactions which results in the formation of oils, asphaltenes, preasphaltenes, gases and char. Consequently, short contact time liquefaction of bituminous coal in a non-donor solvent like toluene is being studied to determine if these effects actually exist. This report briefly describes the progress made during the period March 13 through June 12.

Progress for Period March 13 through June 12

Experiments were carried out with Bruceton coal and toluene at different stirrer speeds to find out at which stirrer speed the mass-transfer resistances are eliminated. The results are summarized in Table 4 and Figures 8 and 9 show the effect of stirrer speed on Toluene Solubles and THF Solubles respectively. It can be seen that the Toluene and THF Solubles vary linearly with stirrer speed in the range of 500 rpm-2000 rpm. It is not yet clear whether all the mass-transfer resistances are eliminated at the maximum stirrer speed of 2300 rpm. Two experiments are planned, one near zero stirrer speed and other at 2300 rpm to determine the nature of the plot of Toluene Solubles/THF Solubles versus stirrer speed.

Experiments were carried out with Bruceton coal and toluene at reduced densities of 1.0 and 1.5 and reaction time of two minutes to 60 minutes. The results are summarized in Tables 5 and 6 and Figures 10 and 11 show the effect of reaction time on Toluene Solubles and THF Solubles respectively at reduced density of 1.0 and 1.5. It can be seen that the initial rate of formation of Toluene Solubles and THF Solubles is higher when the reduced density is higher. This is consistent with the hypothesis that the solubility of coal increases with an increase in the density of the supercritical fluid. This part of the coal instantaneously dissolves in the supercritical fluid due to the high diffusivity of the supercritical fluid and the high stirrer speed employed during the experiment. The coal which has dissolved instantaneously undergoes liquefaction reactions resulting in the formation of Toluene Soluble and THF Soluble products. The experimental data at higher reaction time show a lot of scatter. Amestica and Wolf⁽²⁾ have reported a decrease in conversion after a reaction time of 30 minutes in case of Illinois #6 and toluene although their mode of contact was different from ours; in their experiments

the coal was not injected in the supercritical toluene phase but was heated with toluene to supercritical conditions and the reaction time was measured from the time the slurry attained the desired temperature. They also reported an increase in conversion with an increase in density of the fluid for reaction times of 1/2 hour.

Further experiments are planned at reduced density of 1.5 and higher reaction times (30 minutes to 60 minutes) to confirm the decrease in conversion with time.

A two variable regression is being done for Toluene Solubles and THF Solubles with density of the supercritical phase and reaction time as the two variables. After the data are smoothed by regression, the data will be tested for the model proposed in the last report.

Plans for the Next Quarter

Experiments will be carried out at temperature of 400°C and reduced density of 1.0 and 1.5 and reaction time of two minutes to ten minutes to confirm the higher solubility of coal at higher density at the higher temperature.

VII. REFERENCES

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2. Amestica, L.A. and Wolf, E.E., "Supercritical Toluene and Ethanol Extraction of an Illinois No. 6 Coal," Fuel, 1984, 63, 227.

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Table 1
Effect of Changes in Reactor Operating
Conditions on Reactor Performance

Operating Conditions		Percent Change						
Variable	Base Value	Perturbed Value (+)	X_{CO} (84.42)*	N_{CO} (8.46)	n_{CH_4} (61.0)	N_{CH_4} (5.15)	Q_R (146.5)	Q_G (0.37)
T (K)	550.00	560.00	8.0 \neq	5.0	16.0	16.0	22.0	20.0
n_S (rpm)	2300.00	200.00	5.0	5.0	10.0	10.0	20.0	20.0
S_V (hr ⁻¹)	606.82	907.58	-9.0	40.0	17.0	50.0	13.0	50.0
P (MPa)	1.46	2.14	12.0	12.0	-10.0	-8.0	-25.0	-25.0
f_{CO} (mole percent)	21.31	61.62	-10.0	70.0	-40.0	60.0	-60.0	-10.0

*Base values for each variable are given in parenthesis.

+Effect of process variables were studied by changing one variable at a time.

\neq The number of the columns represent percent changes from the baseline conditions.

Table 2
 Typical Sample Amount of SO₂ and CHP Used for G.C.

T(°C)	Mix Gas (NO+Air)(ml)	CHP(g)	Flow Rate (cc/in)	Retention Time Difference (min)	γ^{∞}
70	0.3	4.93	161.3	13.82	0.0857
70	0.3	5.09	65.5	26.47	0.0839
100	0.3	5.00	27.0	16.74	0.1416
100	0.3	4.37	28.5	14.24	0.1379
130	0.3	5.37	49.6	4.99	0.2273
130	0.3	4.99	52.0	4.46	0.2292

Table 3
 Typical Sample Amount of NO and Triethylene-tetramine*

T(°C)	(NO+N ₂) ml	Amine (g)	Flow Rate (cc/in)	Time (min)	Henry's Law Constant,
18.6	0.3	16.98	9.33	2.42	126.6
50	0.3	16.98	3.73	4.58	177.8
80	0.3	16.98	3.73	3.86	213.1
100	0.3	16.98	3.74	3.21	256.4

+ γ^{∞} is not yet calculated

Table 4
 Summary of Batch Extraction/Reaction of Bruce-ton
 Coal Using Supercritical Toluene
 Effect of Stirrer Speed on Conversion

Run #	70	68	69	64	71	65	49
Toluene density, kg/m ³	304	304	304	303	301	302	301
Coal charged x10 ³ kg	41.5	41.0	40.1	39.7	42.2	41.7	38.9
Temperature, K	672.5	672.6	672.5	672.3	672.4	672.4	672.4
Pressure prior to injection, MPa	7.86	7.92	7.83	7.87	7.83	7.88	7.62
Pressure, MPa (Toluene + Argon)	12.43	11.69	12.45	12.76	12.40	12.48	11.87
Reaction time, min.	30	30	30	30	30	30	30
Stirrer speed, rpm	508	988	988	1627	2040	2110	2300
% Toluene Solubles	9.42	9.77	9.83	10.84	11.74	13.85	14.58
% THF Solubles	12.81	9.77	9.83	10.84	11.74	13.85	16.51

Table 5
 Summary of Batch Extraction/Reaction Bruceton Coal
 Using Supercritical Toluene
 Effect of Recation Time at Reduced Density of 1.0

Run #	72	76	74	67	66	25	29	46
Toluene density, kg/m ³	301	300	300	300	302	305	305	302
Coal charged x10 ³ , kg	41.1	40.2	40.0	39.0	42.7	34.9	35.6	31.7
Temperature, K	646.8	647.2	648.1	648.4	648.2	647.5	647.2	648.0
Pressure prior to injection, MPa	6.78	6.71	6.72	6.99	6.78	6.67	6.66	6.73
Pressure, MPa (Toluene + Argon)	10.93	11.12	11.33	11.45	11.54	14.74	15.45	11.09
Reaction time, min.	2	4	6	8	10	15	30	60
Stirrer speed, rpm	2300	2300	2300	2300	2300	2300	2300	2300
% Toluene Solubles	0.90	3.96	4.37	2.75	3.89	7.92	10.58	18.02
% THF Solubles	2.61	3.96	4.68	5.88	4.34	14.12	12.27	18.02

Table 6
 Summary of Batch Extraction/Reaction of Bruceton Coal
 Using Supercritical Toluene
 Effect of Reaction Time at Reduced Density of 1.5

Run #	73	75	77	28	60	59
Toluene density, kg/m ³	446	447	447	438	443	444
Coal charged x10 ³ , kg	36.8	33.9	37.1	29.0	34.9	38.3
Temperature, K	647.3	648.7	647.8	647.1	648.2	647.8
Pressure prior to injection, MPa	9.26	9.27	9.30	8.70	9.37	9.16
Pressure, MPa (Toluene + Argon)	12.77	13.48	13.96	16.92	13.78	14.15
Reaction time, min	2	6	10	15	30	60
Stirrer speed, rpm	2300	2300	2300	2300	2300	2300
% Toluene Solubles	4.45	7.89	8.69	19.85	7.85	13.08
% THF Solubles	5.08	7.89	9.80	22.16	11.89	13.53

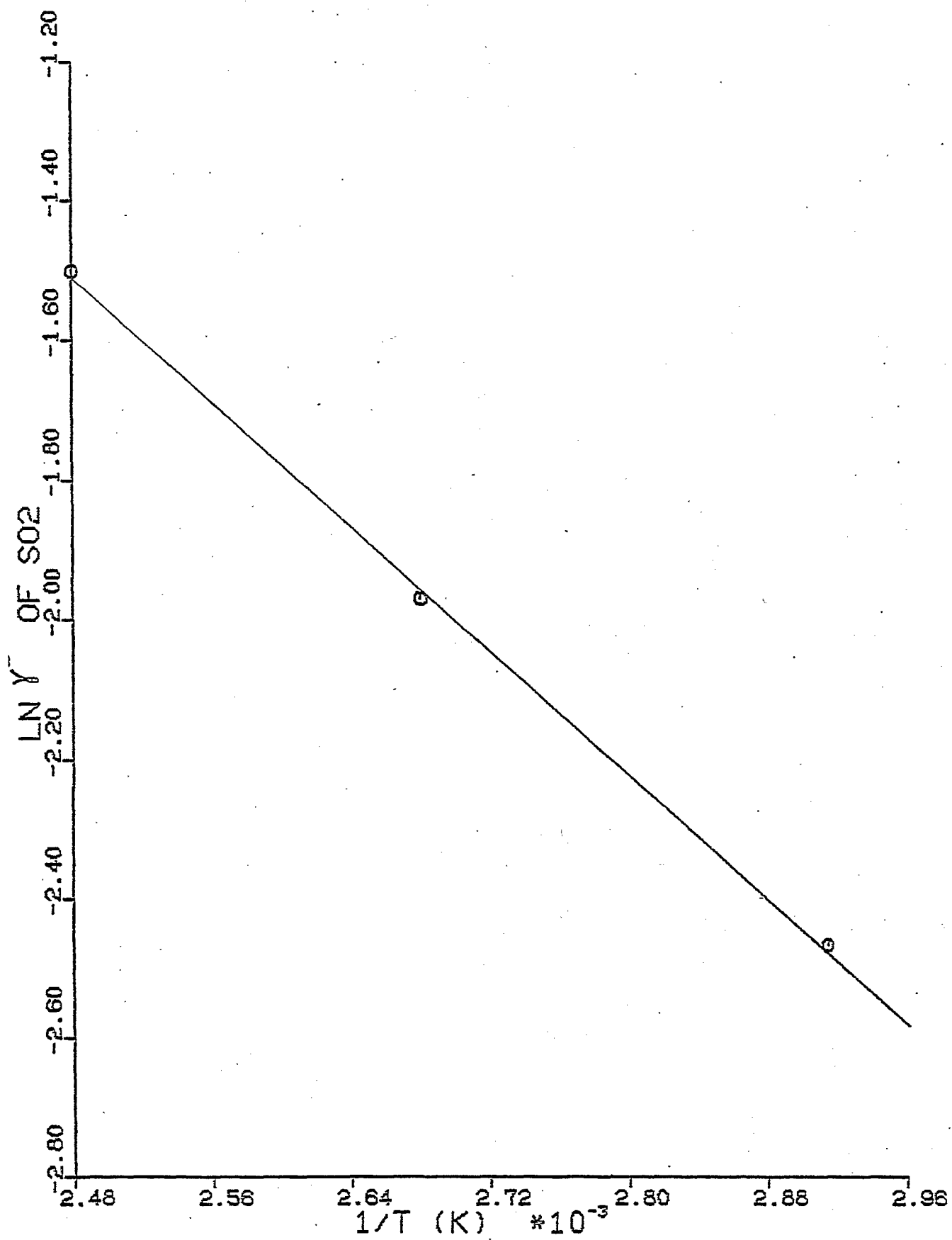


FIG. 1 γ° OF SO₂ IN CHP

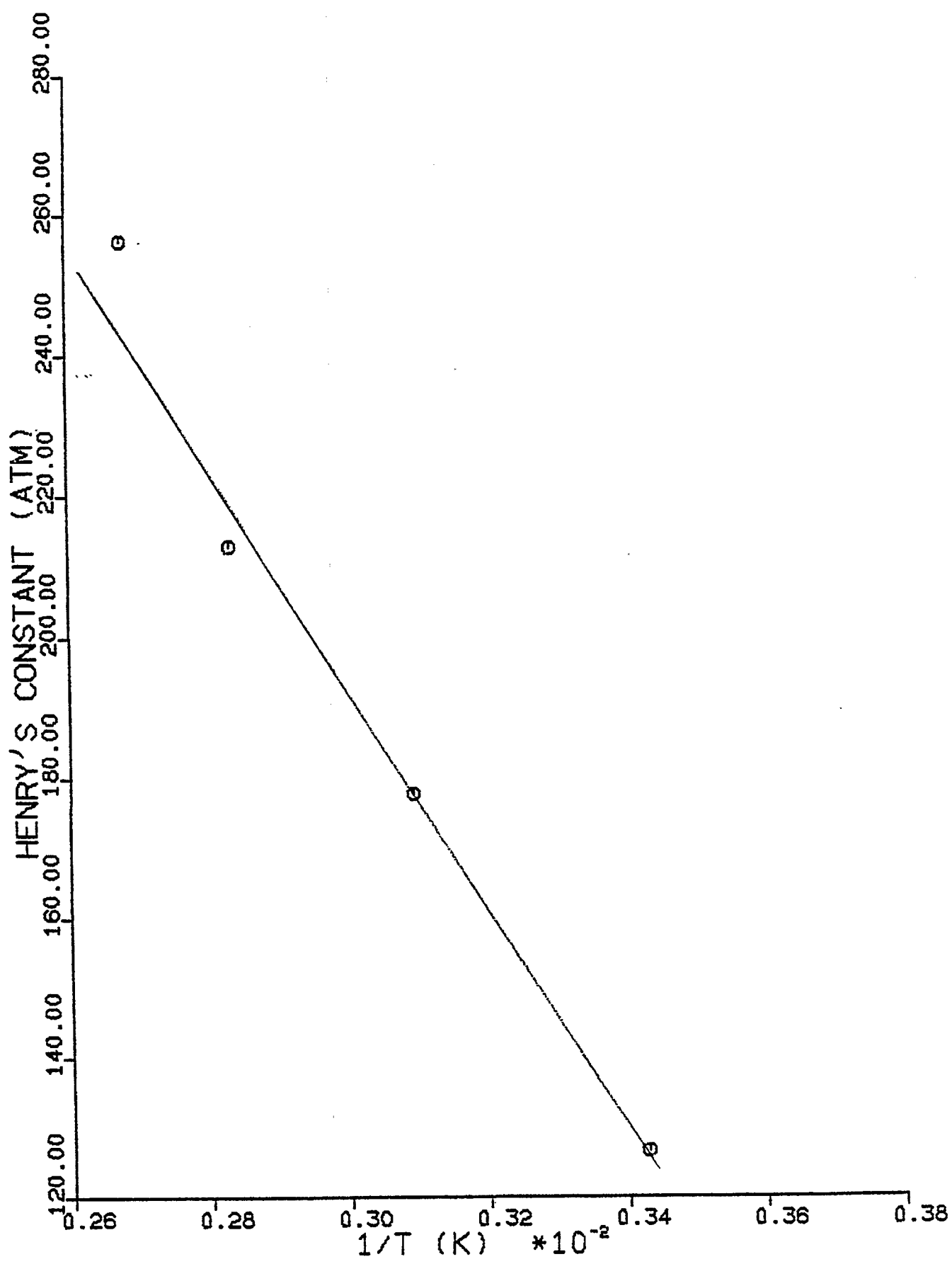


FIG. 2 HENRY'S CONSTANT OF NO IN TETA

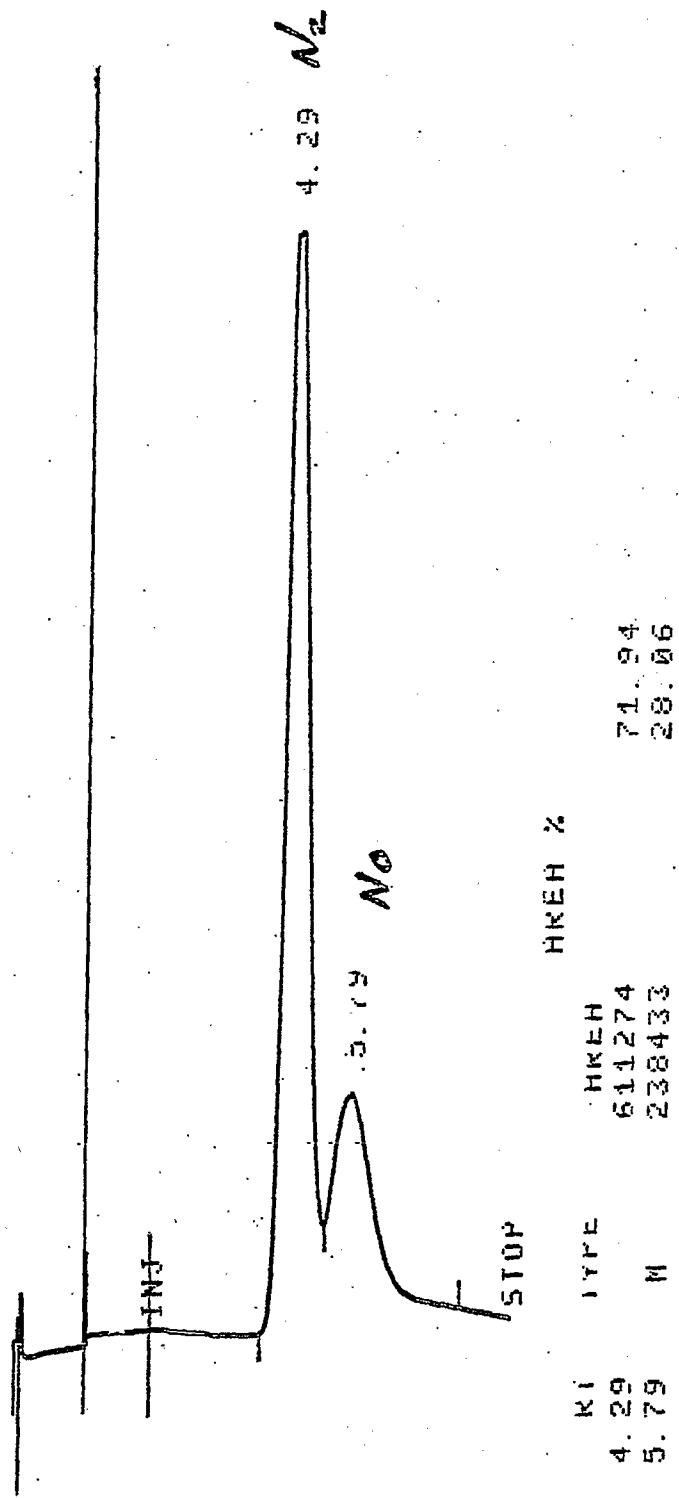


Figure 3.2

Chromatogram of NO/N_2

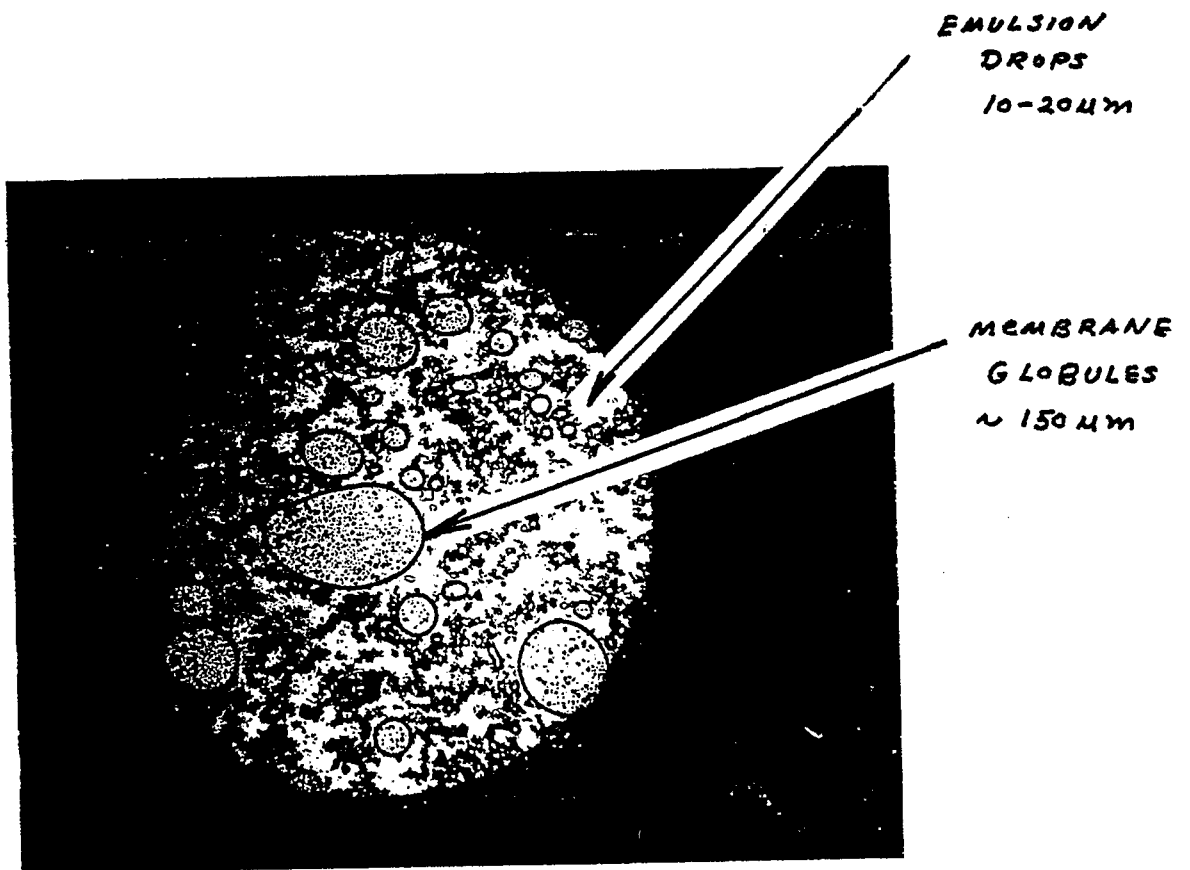
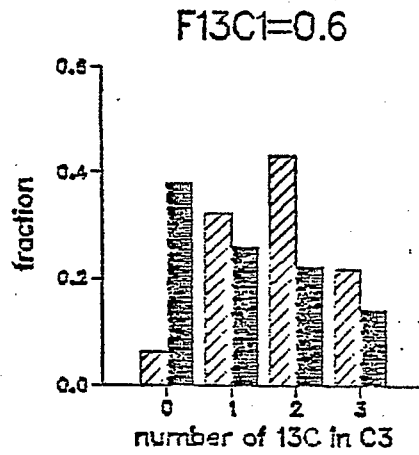
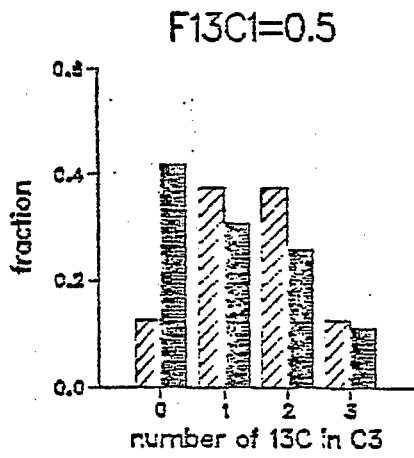
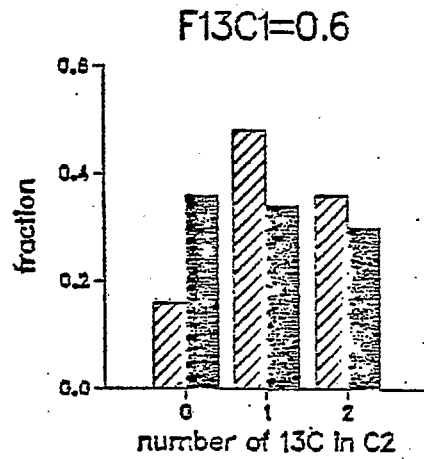
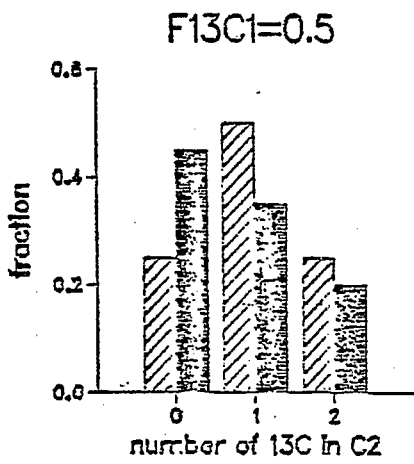


Figure 4.
Liquid Membrane Photograph



Legend
 ▨ static
 ▩ experimental

Figure 5.

TRANSIENT EXPERIMENT

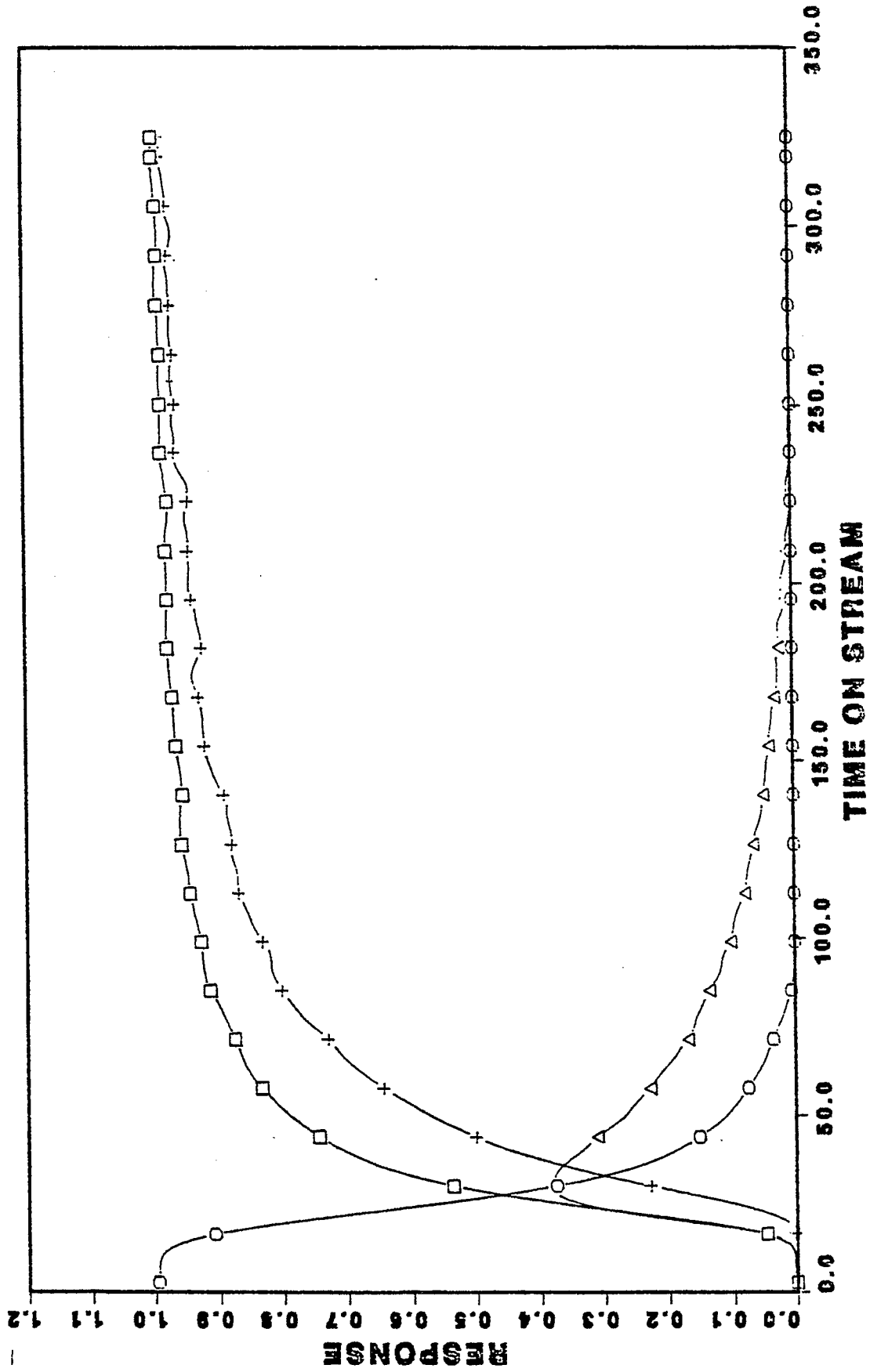


Figure 6.

COMPUTER SIMULATION

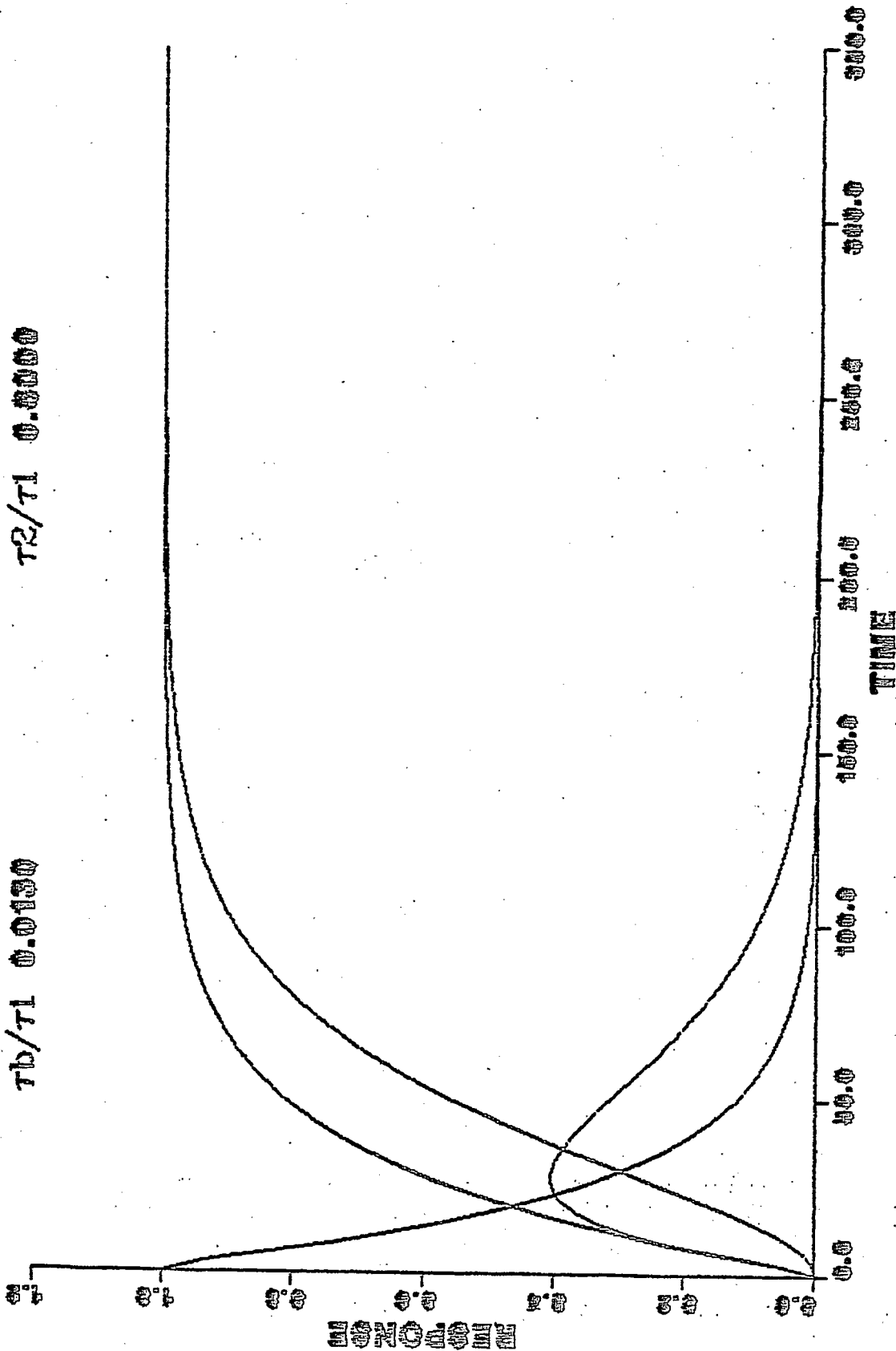
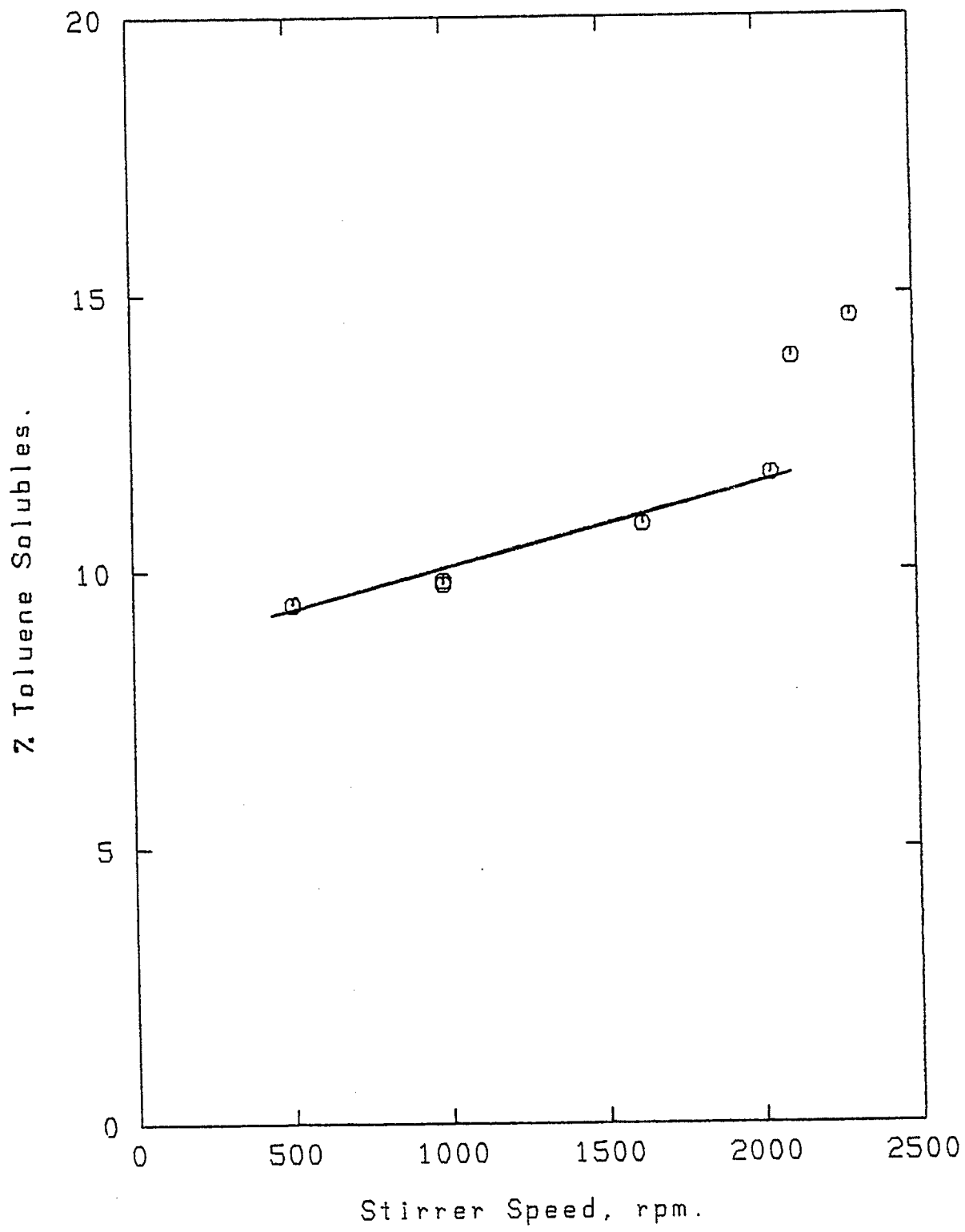
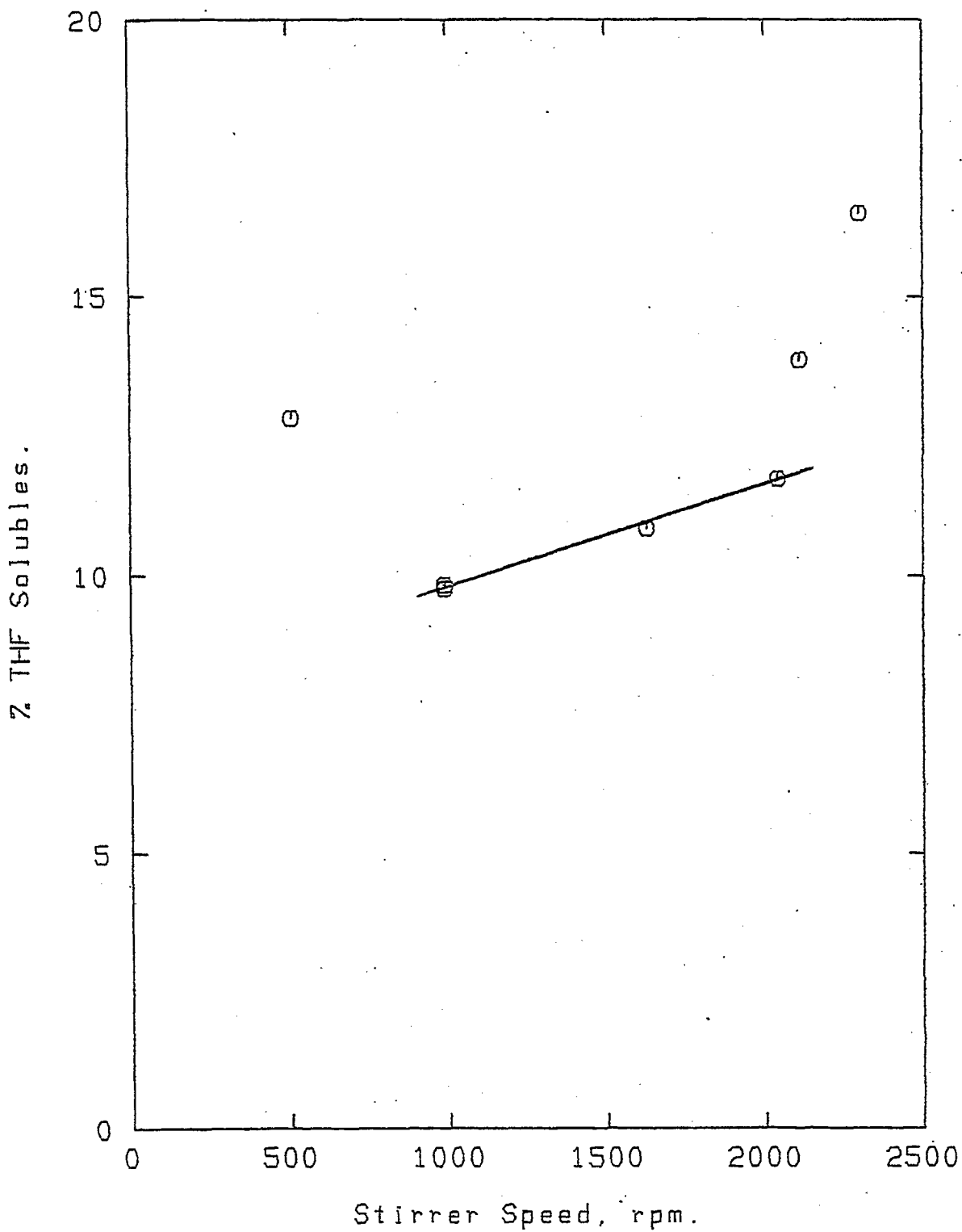


Figure 7.



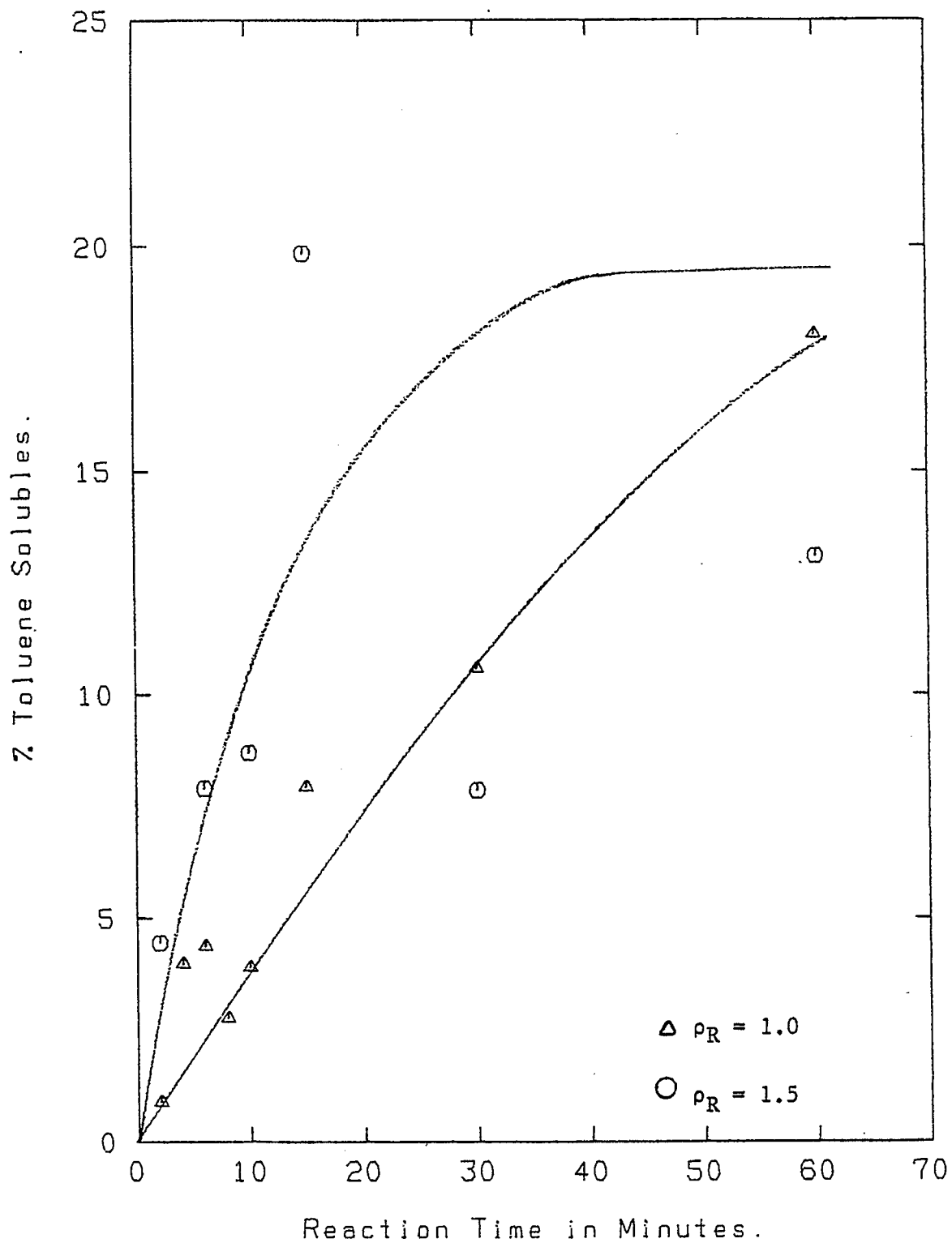
Effect of Stirrer Speed on Tol. Sol. @ 672.5 K.

Figure 8.



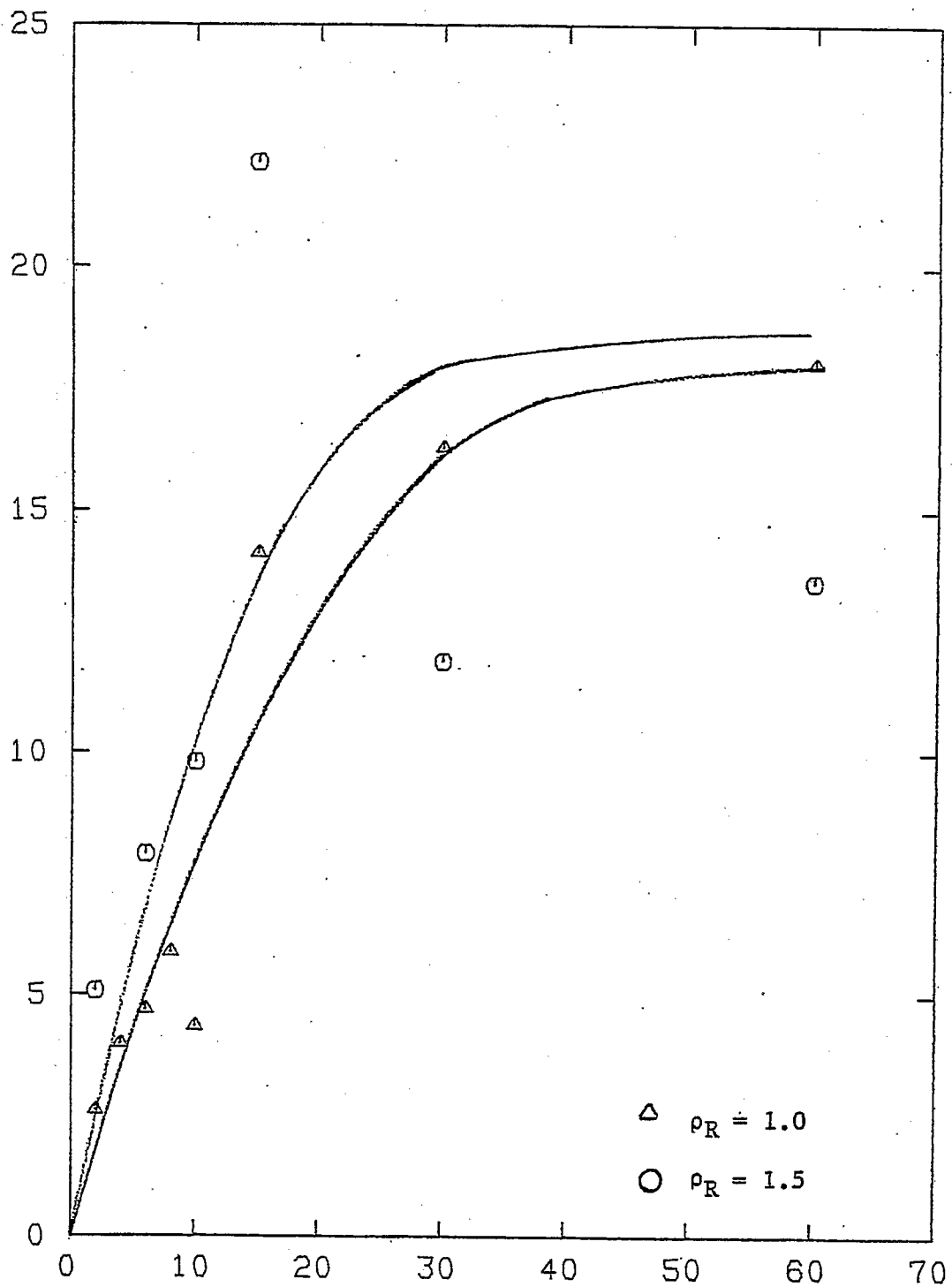
Effect of Stirrer Speed on THF Sol. @ 672.5 K.

Figure 9.



Effect of Rxn. Time & Dens. of SQ Toluene on % Toluene Sol. @ 647.8 K.

Figure 10.



Reaction Time in Minutes.

of Rxn. Time and Dens. of SC Toluene on % THF Sol. @ 647.8 K.

Figure 11.

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