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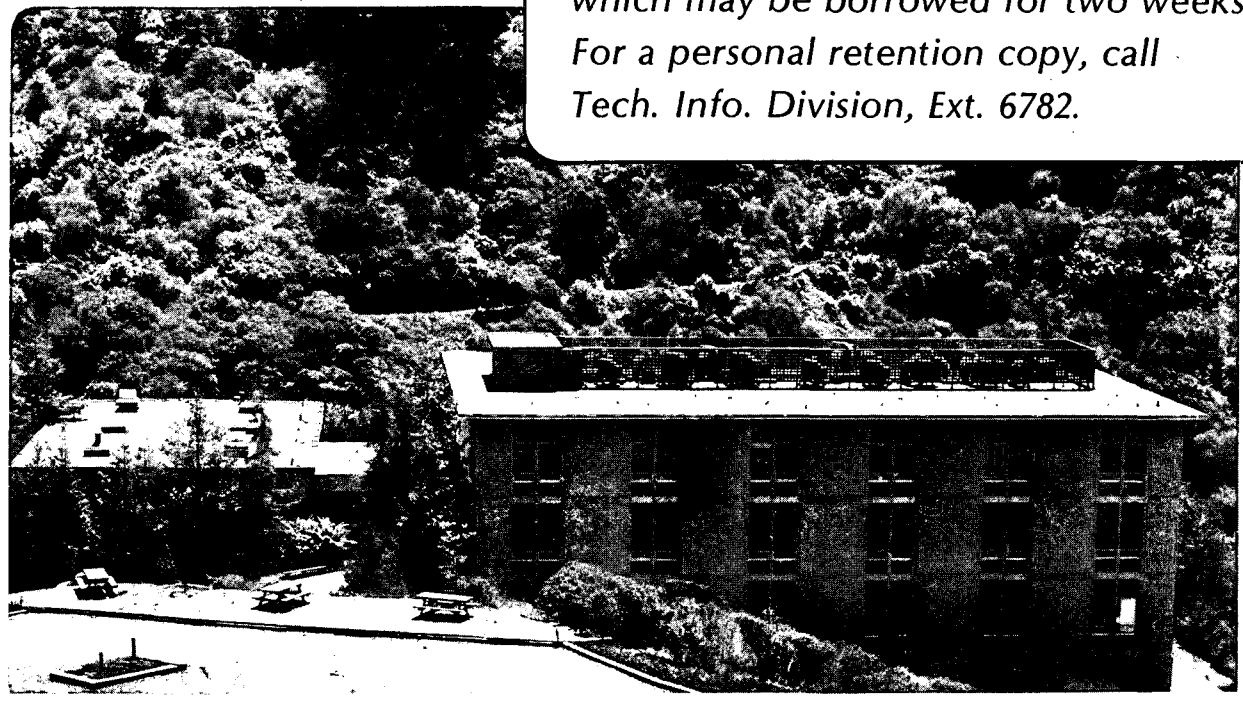

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Mutual Solubilities and Vapor Pressures for Hydrocarbon-Water Systems

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I. Abstract

An apparatus has been constructed for measuring mutual solubilities and vapor pressures for liquid-liquid systems in the region ambient to 200°C. Both phases are sampled and analyzed using gas chromatography.

The apparatus has been used to obtain data for binary water-hydrocarbon systems in the range 100 to 200°C. Special care must be taken to assure reliable sampling because mutual solubilities are very small; it is especially important to avoid entrainment, phase change (due to temperature gradients or pressure drop) and adsorption when removing samples for chemical analysis.

Experimental results are reported for binary aqueous mixtures containing benzene, toluene, and m-xylene. These results are in good agreement with diverse data reported in the literature.

II. Introduction

Liquid-liquid mutual solubility data are required for design of a variety of chemical engineering separation operations, especially those concerned with water-pollution abatement. The most common of these are single and multistage liquid-liquid extraction processes and vapor-liquid stripping. Extraction processes are based on equilibration of hydrocarbon-rich and water-rich liquid streams; these streams occur in petroleum processing, petroleum reservoir production, and coal gasification. Separation processes are often operated at elevated temperatures, where the vapor pressures of the mixtures may be significantly above atmospheric.

Coal gasification processes often include a quench step where the hot effluent gases from the gasifier are cooled quickly by contacting with water. This quench step is necessary to remove heavy tar components and entrained ash from the gases prior to further purification. Current designs for quench steps operate near or below 250°C. Figure 1 shows a schematic diagram of a typical quench step. Either three or four phases may be present in the quench vessel; these include a vapor phase, a light hydrocarbon or oil phase, an aqueous liquid phase, and a heavy hydrocarbon or tar phase. The oil and tar phases may mix to form one phase, especially at high temperature.

Typically, the contents of the quench vessel are a multiphase mixture of light and heavy components. Light components include hydrogen, methane, carbon monoxide, carbon dioxide, hydrogen sulfide, and ammonia. Heavy components include a wide variety of aromatic hydrocarbons, phenolics, furans, pyridines, thiophenes, and other organic compounds derived from

hydrocarbons. These components are present in coal tar in a diverse molecular-weight range. The presence of entrained ash may affect phase equilibria through soluble inorganic salts.

To design the quench operation and subsequent coal-tar/water separation, phase equilibria must be available. To estimate these equilibria, we require a molecular-thermodynamic model so that limited mutual solubility data may be correlated for extension to pressures and temperatures other than those where the data are acquired. Owing to the complexity of the multicomponent-multiphase mixture, we cannot hope to correlate multicomponent phase equilibria without first decomposing the problem into simpler parts. One method for achieving this simplification is to measure binary mutual solubilities of several well chosen model compounds with water. Based on these measured binary data, generalization to the multicomponent case may be accomplished by molecular-thermodynamic methods.

Fundamental to the understanding of the behavior of coal-tar/water systems is an understanding of the mutual solubilities of small aromatic hydrocarbons and water. In this report, mutual solubilities and vapor pressures are reported in the region 100 to 200°C for three aqueous binaries: benzene, toluene, and m-xylene.

This report presents design, construction and operation of an apparatus for measurement of binary hydrocarbon-water, liquid-liquid mutual solubilities and vapor pressures at elevated temperatures and pressures. While a large number of investigations have been reported for aqueous, binary, mutual solubilities of benzene(1-52), toluene (8-10, 14, 16, 18, 19, 21, 30, 32, 35-38, 42, 46, 53-55, 57) and m-xylene (14, 16, 35, 46, 54, 56), with few

exceptions, previous work has been limited to temperatures at or near ambient. Of the studies at elevated temperature, only five (22, 26, 27, 34, 52) present benzene-water data in the temperature range 100-200 °C measured along the three-phase line. No data are available in the literature for comparison with our toluene-water data. Two limited studies of the m-xylene-water system (34,56) allow comparison with some of our data.

III. Measurement of Phase Equilibria

To measure binary liquid-liquid equilibria for coal-derived-fluid/water systems, we fill an equilibrium cell with the mixture of interest, and equilibrate the contents at a given temperature. We withdraw a sample of each phase in the cell and determine the composition of each sample. Toward this end, our mutual solubility apparatus consists of three major parts, one for each of these steps: equilibration, sampling, and analysis.

Measurement of mutual solubilities is difficult (62), particularly at elevated temperatures and pressures. Analysis of the dilute compositions encountered in these systems is subject to large error. Most of the problems however, are associated with transferring a sample of the equilibrated mixture from the equilibrium cell to an appropriate analytical instrument without composition change. Since these samples are highly dilute, a small composition change can lead to serious error. Entrainment of small droplets of one phase in the other while sampling can lead to very large errors. In some cases (61), we encounter stable dispersions of very small droplets of one phase suspended in the other. Such suspensions often appear as fogged or misted phases. Adsorption of the dilute solute on the walls of the sample lines can lead to depletion of the solute from the phase sample, giving erroneous results. Changes in temperature and pressure while sampling can lead to phase changes in the sample lines which alter composition uniformity. Temperature drops along the sample line can lead to liquid-liquid phase splits, while pressure drops can lead to vapor-liquid flashing during sampling. Differential flows of one phase with respect to the other in the sample line can cause a physical separation, leading to erroneous results.

A. Experimental Apparatus

Figure 2 shows a schematic diagram of our liquid-liquid phase equilibrium apparatus. All parts of the apparatus (unless otherwise specified below) are fabricated from 304-stainless steel. All apparatus part numbers given below refer to the labels specified in Figure 2.

Equilibrium Cell

The equilibration portion consists of an equilibrium cell suspended in a constant-temperature air bath. Since it is advantageous to see the contents of the cell during the equilibration process, we use a commercially available liquid-level sight gauge (Jerguson Gauge Co.; Model # 17-T-20) as our equilibrium cell. The pressure rating of this gauge is 1250 psi (86.2 bar) at 100°F (38°C), and 850 psi (58.6 bar) at 600°F (316°C). The volume of this cell is about 140 cm^3. The air bath is equipped with a window which allows viewing of the cell and the contents of the cell. The Jerguson gauge is provided with a 3/4" NPT female connection at either end. Each of two 3/4" NPT plugs is fitted with two tubes, which are welded into holes drilled through the plugs. One tube (1/8" OD by 0.035" WT) projects 2 1/2" beyond the inner face of the plug, while the other tube (1/4" OD by 0.028" WT) is welded in flush with the face of the plug. The end plugs are screwed into the female connector and welded into place. The entire assembly is hung in the air bath.

Pressure Measurement

The larger tube in the top plug is connected to two bellows assemblies (B1 and B2), and to a bellows valve(V2; Nupro Model #SS-4TW). Valve V2 allows

venting and degasing of the contents of the cell and the sampling system. In bellows assembly B1, a cap is welded over one end of a bellows (Robertshaw Controls Co., Model #A1014-A10), while the other end of the bellows is welded into a body fitted with 1/4" tube connectors at either end. Bellows system B1 acts as a pressure transducer for the 0-2000 psi (0-138 bar) pressure gauge (G1; Heise Gauge Co., Solid Front Model #C-68482). The gauge, associated tubing, and the gauge side of bellows system B1 is filled with degased Dow Corning 550 silicon oil. The silicon oil can be used to a maximum temperature of 315°C for closed systems. The bellows in B1 is sized such that it compensates for the large thermal expansion of the silicon oil (~3 cm^3 maximum for this line volume) as the temperature is raised. The vapor pressure of the mixture in the equilibrium cell is measured using gauge G1.

Pressure Drop Compensation During Sampling

Bellows assembly B2, is a similar arrangement to bellows assembly B1. A bellows (Robertshaw Controls Co.; Model #A2938-A14) is capped at one end and welded into a body provided with 1/4" tube connectors at either end. This bellows body and the body for B1 have been pressure tested to 3000 psig (207 bar). Bellows assembly B2 acts as a pressure transducer to gauge G2 and pressure generator PG3 (High Pressure Equipment Co.; Model #62-6-10). The gauge-pressure generator side of B2 is filled with degassed Dow Corning 550 silicon oil. The pressure generator is constructed such that by turning a handle, a piston is forced to move through a cylinder. This pressure generator displaces 30 cm^3 for 83 revolutions of the handle or 0.36 cm^3 per revolution. During filling of this system with oil, the piston in PG3 is retracted completely. This allows PG3 to be filled with oil.

During the sampling procedure, pressure generators PG1 and PG2 are pulled out, increasing the volume of the system. By turning the handle on PG3, oil is forced against the bellows in B2, which decreases the volume of the system. This arrangement allows sampling to be accomplished at constant volume. Gauge G2 is used to check against G1 for a pressure differential across the bellows in B2; such a differential could rupture the bellows. Valve V8 is used to decrease the amount of oil in B2 if necessary.

Sample Loading

The larger tube in the bottom plug is connected to two valves (V1 and V3), a rupture disc (RD1), and a recycle line from the sampling-pressure generators (PG1 and PG2; both High Pressure Equipment Co. Model #62-6-10). The line through valve V1 allows the cell to be filled and evacuated. The cell is loaded by forcing each component through V1 from nitrogen-pressurized feed vessels. The line through valve V3 allows the cell to be drained and vented. In case of excessive pressurization, rupture disc RD1 fails, venting the cell contents through a drain tank.

Phase-Sampling Lines

The smaller tubes which extend into the cell are used as sample-withdrawl ports. From the cell, these lines proceed out of the equilibration oven, through the temperature-controlled copper blocks (CB1 and CB2) and into the sampling-system oven. Each line is connected to a rotary 6-port sampling valve (RV1 and RV2; Valco Instruments Co., Model #V-6-UHTA-N60). The total line volume between the entrance to the sample line and the 6-port valve is about 1.0 cm^3. These rotary valves are rated to 250°C at 2500 psi (172 bar). Two ports on each valve are connected to a sample loop. The sample

loops are constructed from 8" of 0.035 WT by 1/8" tubing. The volume of each sample loop is 0.31 cm^3. One of the remaining ports on each valve is connected to a 1-liter flash vessel (F1 and F2). A second port is connected to a pressure-regulated helium line through bellows valves (V12 and V14; Nupro Model #SS-4H). The last port is connected to a line which proceeds out of the sampling oven to a pressure generator (PG1 and PG2) through the 3-way ball valve (V5 and V4; Whitey Model #SS-41XS2). By opening bellows valves V11 and V13 (Nupro Model #SS-4H), the flash vessels can be evacuated through the vacuum line.

Chemical Analysis

From the flash vessels, lines proceed through bellows valves (V10 and V9; Nupro Model #SS-4H), and rotary 3-port valves (RV3 and RV4; Valco Instruments Co. Model #V-3-HTA-N60) to the rotary 10-port gas-sampling valve (RV5; Valco Instruments Co. Model V-10-HTA-N60) on the gas chromatograph. The rotary 3-port valves are also connected to the injector ports IP1 and IP2. These injector ports allow injection of hydrocarbons and water to the flash vessels as required for the calibration procedure. Four ports on the gas-sampling valve are connected to two sample loops. Each loop has a volume of 0.75 cm^3. Of the remaining 4 ports on the 10-port valve, one is connected to the helium supply for the gas chromatograph, one leads to the gas-chromatograph column, and two lead to vacuum through regulating valves(V6 and V7; Whitey Model #SS-ORS2). The lines leading to the gas chromatograph and to the injector ports are all traced with heating tape and are insulated. All heating tapes are controlled with variable transformers.

All analyses are made using a gas chromatograph (Varian Instruments Co., Model 3700) equipped with a thermal-conductivity detector (TCD). The thermal-conductivity detector is used (rather than the more sensitive flame-ionization detector) because water is in the samples. The chromatograms are integrated using an electronic integrator (Perkin-Elmer Co.; Model #M-2). Chromatograms are also recorded on a chart recorder.

Materials

All hydrocarbons used in these experiments are of (commercially available) spectral-grade purity. Water used was purified and deionized. Water purification was accomplished by adsorption on activated carbon.

Temperature Measurement

Temperatures are measured at 32 locations scattered throughout the apparatus with 30 thermocouples and 2 platinum-resistance temperature detectors (RTD). The millivolt output of the thermocouples and the voltage drop across the platinum resistance temperature detectors is converted to a digital signal by a multichannel scanning datalogger (John Fluke Mfg. Co., Model 2200B). Ten thermocouples are placed at various locations in the equilibration oven. The maximum deviation between any two of these thermocouples is $4^{\circ}C$. Thermocouples placed on the sides of the cell show that the maximum temperature gradient across the cell is $2^{\circ}C$. The measurement of the equilibrium temperature is made by a resistance temperature detector placed in the equilibration oven. During sampling, the temperatures of the copper blocks (CB1 and CB2) and the sampling system oven are controlled to within $0.5^{\circ}C$ of the equilibration-oven temperature. The maximum temperature gradient in the sampling system oven is $5^{\circ}C$, as

indicated by another ten thermocouples. The remaining thermocouples are scattered along the heat-traced lines leading to the gas chromatograph and the injector ports.

B. Sampling Procedure

After loading the equilibrium cell with the mixture of interest, valves V1, V2, and V3 are closed. The temperature controller for the equilibration oven is set at the desired temperature. After thermal equilibrium has been reached in the equilibration oven, the temperatures of the copper blocks and the sampling-system oven are adjusted to within 0.5 ^{o}C of the same temperature. Valve V2 is opened slightly (to allow some of the vapor in the cell to bleed to the vent) and then closed. Repetition of this procedure accomplishes degasing.

Initial Valve Positions

Figure 3 gives in detail positions of the various rotary valves. For the components of the sampling system, initial positions are as follows: rotary valves RV1, RV2, RV3, RV4, and RV5 are all set to positions A, given in Figure 3. Ball valves V5 and V6 are positioned such that flow is between the recycle line and the pressure generators. The piston in the pressure-compensating pressure generator (PG3) is pulled back, while the pistons in the sampling-pressure generators (PG1 and PG2) are pushed forward. Helium line valves V12 and V14 are closed. Vacuum valves V11, V13, V10, V9, V6, and V7 are all open, allowing evacuation of the flash vessels and associated lines.

Equilibration

Equilibration of the contents of the cell is relatively rapid after thermal equilibration is accomplished. Three hours are usually sufficient for compositional equilibration, while complete thermal equilibration requires more time, typically overnight.

Sampling

Sampling of the equilibrated cell contents is accomplished in the following manner: Ball valve V5 is turned to allow flow between RV1 and PG1. The piston in PG1 is cranked (out) 5 turns, and subsequently PG3 is cranked (in) 5 turns. This procedure moves equilibrated fluid from the upper liquid phase through the sample line, through RV1, and out to PG1. Pushing in the piston in PG3, pushes oil against the bellows in B2, and hence forces vapor back into the equilibrium cell. The bellows-pressure-generator system (B2 and PG3) allows sampling of the liquid phases at relatively constant system volume. Note that the sample loop is not in line with the fluid flow, but is still evacuated along with F1. The piston in PG1 is again cranked (out) 5 turns, and PG3 is again subsequently cranked (in) 5 turns. The sample line between the equilibrium cell and RV1 has now been flushed with about 3.5 times its volume of equilibrated upper liquid phase. This has removed any non-equilibrated fluid from the sample line. Rotary valve RV1 is now turned to position B in Figure 3. The sample loop is now in line with the equilibrium cell and PG1. Pressure generators PG1 and PG3 are again cranked (out) and (in) respectively, using 5-turn increments. This is repeted until each pressure generator has moved a total of 25 turns. The sample loop now contains equilibrated liquid.

Vaporization

Valves V11 and V10 are closed, isolating the evacuated flash vessel. The rotary 6-port valve RV1 is turned back to position A in Figure 3. The contents of the sample loop are injected into the flash vessel to vaporize completely. An identically analogous procedure is used to sample the lower liquid phase. The contents of the sample loops and flash vessels are allowed to vaporize completely over the course of half of an hour.

Replacement of Valves to Initial Positions

Valves V5 and V4 are now tured such that flow once again is between the sampling-pressure generators and the recycle line. The sampling-pressure generators are each cranked (in) 25 turns. The pressure compensating pressure generator is cranked (out) 50 turns. This procedure replaces all components to their initial positions. Note that the sampling-pressure generators act as pumps to force fluid in a circulatory manner from the cell through the sample lines and back to the cell through the recycle lines. Repetition of this pumped circulation during the preliminary equilibration accomplishes agitation of the cell contents by bubbling the less-dense phase through the dense phase. The apparatus is in this sense circulatory. The level of the contents in the cell is observed, and the cell is refilled if necessary. The cell contents are degased, and are left to re-equilibrate.

Analysis of Vaporized Samples

The contents of the flash vessels are alternatly analyzed in the following manner. Valve V6 is closed, V10 is opened, and the contents of F1 flow

through the previously evacuated line to fill the upper liquid sample loop on the 10-port gas-sampling valve (RV5). Valve V10 is closed after 30 seconds, and RV5 is turned to Position B in Figure 3 to inject the sample-loop contents into the gas-chromatograph column. Valve V6 is opened to allow evacuation of the sample lines back to V10. To sample the lower liquid-phase flash vessel, V7 is closed, V9 is opened for 30 seconds, V9 is closed, and RV5 is turned back to Position A in Figure 3. Valve V7 is opened to allow evacuation of the sample line back to V9. This sequence is repeated so that the contents of each flash vessel are analyzed twice. Normally, about 15 minutes are required for elution of the injected samples from the gas chromatograph. The integrated chromatogram allows computation of the area percent of each component in the sample. From our calibration of the chromatograph, we can translate this area percent to mole percent of each component in each phase.

C. Chromatograph Calibration Procedure

Hydrocarbons and water are sparingly soluble at room temperature, but mutual solubilities rise at elevated temperatures. It is therefore not possible to construct a single liquid-phase mixture of the components with a composition comparable to the compositions encountered at elevated temperature. Such a mixture can however be prepared in the gas phase. The injector ports (IP1 and IP2) are used for this purpose.

The procedure used to calibrate the gas chromatograph follows. All valves are in the initial positions outlined under the sampling-procedure section. For purposes of calibration, the temperature of the sampling oven is typically set at least 20°C higher than the normal boiling point of the

least volatile component. Rotary valves RV3 and RV4 are both turned to Position B in Figure 3. All associated lines are evacuated.

Sample Injection for Calibration

The injector ports allow direct injection of measured amounts of hydrocarbon and water to the flash vessels. Valve V11 is closed, isolating the injector-flash vessel system from the vacuum line. A measured volume of liquid water (typically on the order of 1.0 to 10.0 microliters) is injected through the injector port to the flash vessel. This injection is followed by injection of a weighed amount of liquid hydrocarbon. About 0.3 cm^3 of hydrocarbon is injected, this quantity being chosen to correspond to the sample-loop size on the 6-port liquid-sampling valves. A variety of microliter syringes (Hamilton Syringe Co., Series 7000 and Series 700) is necessary to span a reasonable composition range. These microliter syringes are generally accurate to better than 5 % of full scale. Care must be taken to correct for the volume contained in the needle in injections to vacuum. Valve V13 is closed; a measured microliter quantity of liquid hydrocarbon, followed by a weighed amount of liquid water, are injected to F2 through IP2. Total vaporization of these injected compounds occurs during one half of an hour. Valves V10 and V9 are closed and rotary valves RV3 and RV4 are turned back to Position A in Figure 3. The lines between the rotary valves and V9 and V10 are evacuated and then the contents of the flash vessels are analyzed using the same procedure as that described under Sampling Procedure, above.

The integrated output from the gas chromatograph allows computation of the area percent of each component in the samples. Moles of the lesser

component injected is computed from the measured microliter volume, the molecular weight and the room temperature density of the lesser component injected. The moles of the major component injected to each flash vessel follows directly from the molecular weight of that component and the measured mass injected. Mole percent may be plotted versus area percent for the lesser component to yield the desired calibration curve.

D. Constraints on Apparatus Applicability

For our apparatus, applicable hydrocarbon-water systems are limited by two constraints. First, all components must flash completely during the vaporization step. Second, mutual solubilities must be large enough so that the mixtures may be analyzed by thermal-conductivity-detector gas chromatography. These constraints prohibit use of our apparatus with low-volatility hydrocarbons (e.g. hydroxypyrene), and very dilute (e.g. octane-water) systems.

Separate sampling and equilibration ovens are used in an effort to increase the range of applicability of the apparatus to low-volatility systems. After sampling in the conventional way, low-volatility samples can be further heated in the sampling oven to a temperature above the equilibration temperature. The valves in the sampling oven limit this temperature to a maximum of 250°C. This increases the vapor pressure of the mixture allowing complete flashing. Use of the second oven eliminates the necessity of raising the temperature of the equilibrium cell to higher values. High temperatures would both supersaturate the system with respect to the original temperature and destroy equilibrium in the cell. Saturation at a higher temperature is bad because subsequent cooling often

forms a stable fogged phase.

The relative volumes of the liquid-phase sample loops and the flash vessels are such that after complete flashing of the samples, the pressure in the flash vessels is subatmospheric. This further extends the range of applicability of our apparatus toward low-volatility systems. For the systems studied here, the pressure in the hydrocarbon-phase flash vessel is on the order of 0.10 bar, while the pressure in the water-phase flash vessel is about 0.50 bar.

IV. Results and Discussion

Tables 1-3 and Figures 4-9 sumarize our results for the mutual solubilities and vapor pressures of the benzene, toluene, and m-xylene-water systems. Each measurement was replicated 7 times for benzene, and at least 5 times for toluene and m-xylene. The tables report mean values and standard deviations (s).

Measured temperatures are accurate to about ± 0.3 C. In tables 1-3, the larger standard deviations in temperature result from a slight drift in the equilibration-oven temperature controller.

Pressures were measured to within ± 1 psi (0.069 bar) with the presision pressure gauge. At the start of a series of runs, the cell often contains some nitrogen, air and carbon dioxide. Since the cell is loaded by forcing each component through the feed line with nitrogen pressure, the primary contaminant is nitrogen. Owing to the large solubility of carbon dioxide in water, a significant amount of carbon dioxide is initially present in the cell. As degasing is accomplished at a given temperature, the equilibrium-cell pressure drops and then levels off. The final equilibrium pressure is reported.

Errors in composition are a function of composition; as smaller and smaller mass fractions are measured, the percent error increases. The percent scatter of the data (standard deviation divided by mean) increases as solubility decreases. Using thermal-conductivity gas chromatography, the lower limit for measuring composition is in the neighborhood of 10^{-4} mass percent.

At least five previous studies of the benzene-water sysyem have been reported in this temperature range. Several studies of this system are at higher temperatures. With the exception of the work by Guerrant (34), agreement of our results with literature values is very good. The discrepancy between our results and those of Guerrant are possibly due to Guerrant's analytical technique; Guerrant measured compositions by cooling phase samples from high-temperature equilibration to low-temperature. The volumes of hydrocarbon and water in the low-temperature samples were measured. Mole fractions of each component were computed using the known densities of the hydrocarbon and water at the low temperature. Guerrant's technique is good at very high temperatures, but is probably not applicable to intermediate temperatures where solubilities are very small.

Prior to this work, no studies have been reported for the toluene-water system in this temperature range. Studies of the m-xylene-water system have been made by Guerrant(34) and Pryor and Jentoft(56). The work by Pryor and Jentoft includes only the solubility of m-xylene in water, and therefore is of limited use for determination of molecular-model parameters. Our results compare well with those of Pryor and Jentoft, but (as for the benzene-water system) are somewhat different from those of Guerrant. In general, agreement of our vapor pressures with previous work is very good.

Solubilities of the hydrocarbons in water differ appreciably from each other. As CH_3 groups are added to the aromatic ring, the solubility in water falls strongly, probably because the interaction of the ring pi electrons with the water molecule is appreciably stronger than that of the water-CH_3 interaction. Low solubilities are probably related to the

inability of hydrocarbon molecules to penetrate the highly hydrogen-bonded liquid structure of water. Solubilities of water in the hydrocarbons are strikingly similar, and at least one order of magnitude larger than the hydrocarbon-in-water solubilities. Water possibly fits into the holes in the hydrocarbon liquid structure. This effect seems to be relatively insensitive to CH_3 groups on the ring.

V. Conclusion

We have designed, constructed and successfully operated a mutual-solubility apparatus for sparingly-soluble liquids in the region ambient to 200°C. Special care has been taken to obtain representative samples for chemical analysis using gas-liquid chromatography. Mutual solubilities and vapor pressure measurements are reported in the region 100-200 °C for binary aqueous mixtures containing benzene, toluene and m-xylene.

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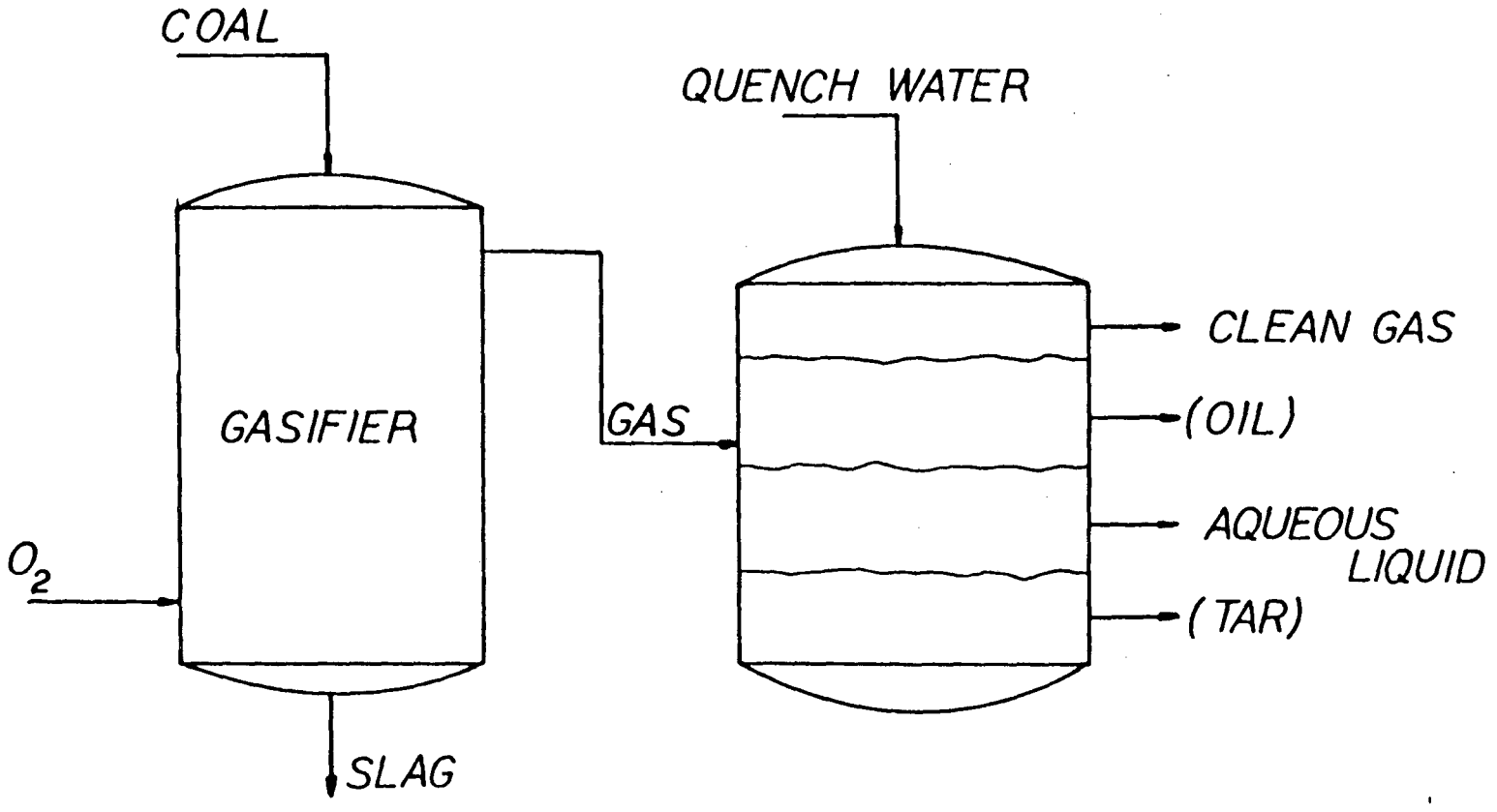
QUENCH STEP YIELDS MULTI-PHASE MIXTURE, CONTAINING 3 OR 4 PHASES.



TO DESIGN SEPARATIONS, WE NEED TO KNOW THE COMPOSITIONS OF EACH PHASE.

FIGURE 1

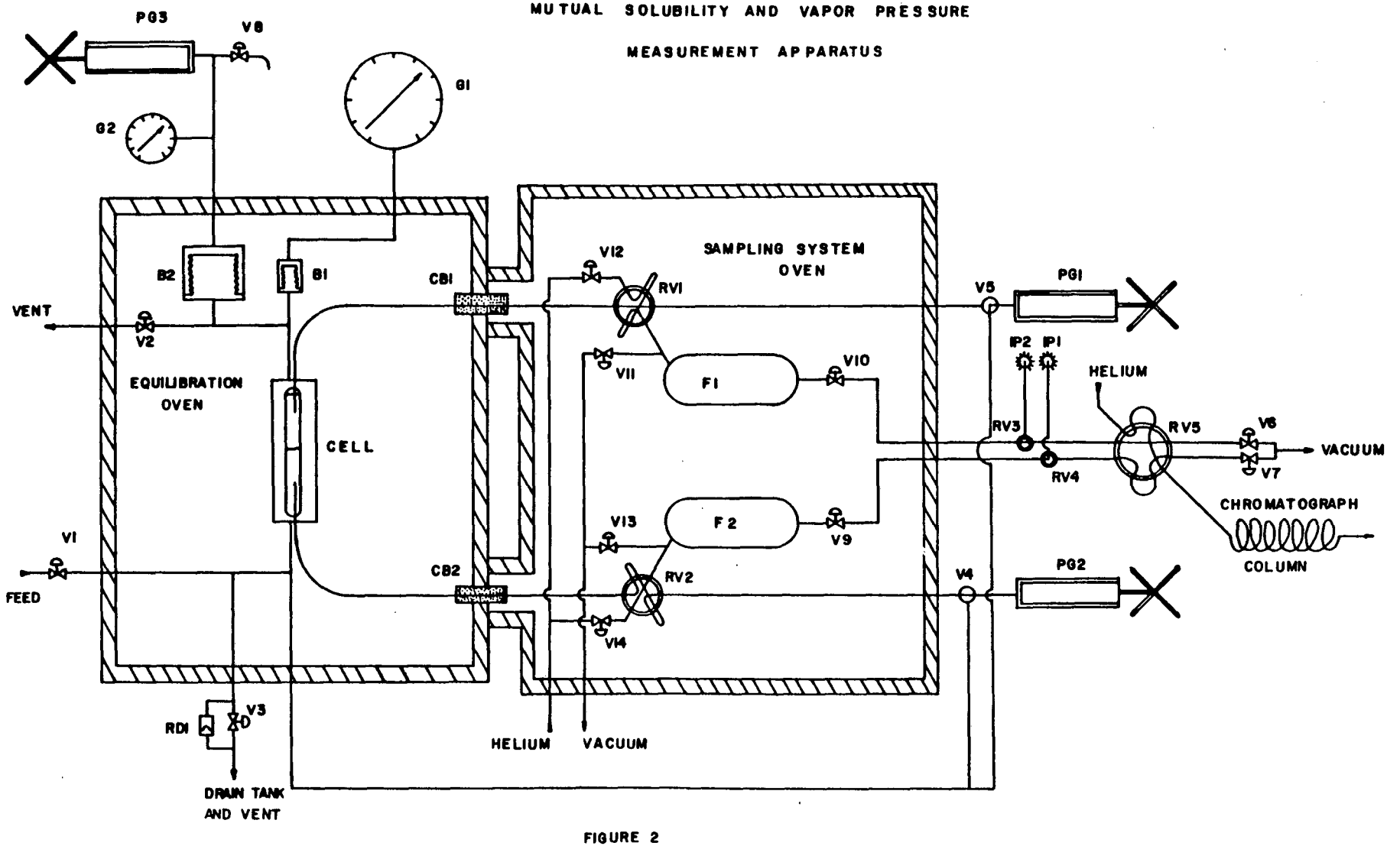

MUTUAL SOLUBILITY AND VAPOR PRESSURE
MEASUREMENT APPARATUS
PG3
V8
G1
G2
B2
B1
CB1
VENT
V2
EQUILIBRATION
OVEN
CELL
V1
FEED
CB2
RD1
V3
DRAIN TANK
AND VENT
V12
RV1
SAMPLING SYSTEM
OVEN
V11
F1
V10
V13
F2
V9
RV2
V14
HELIUM
VACUUM
V5
PG1
IP2
IP1
HELIUM
RV3
RV4
RV5
V6
V7
VACUUM
CHROMATOGRAPH
COLUMN
V4
PG2

FIGURE 2

ROTARY VALVE DETAIL

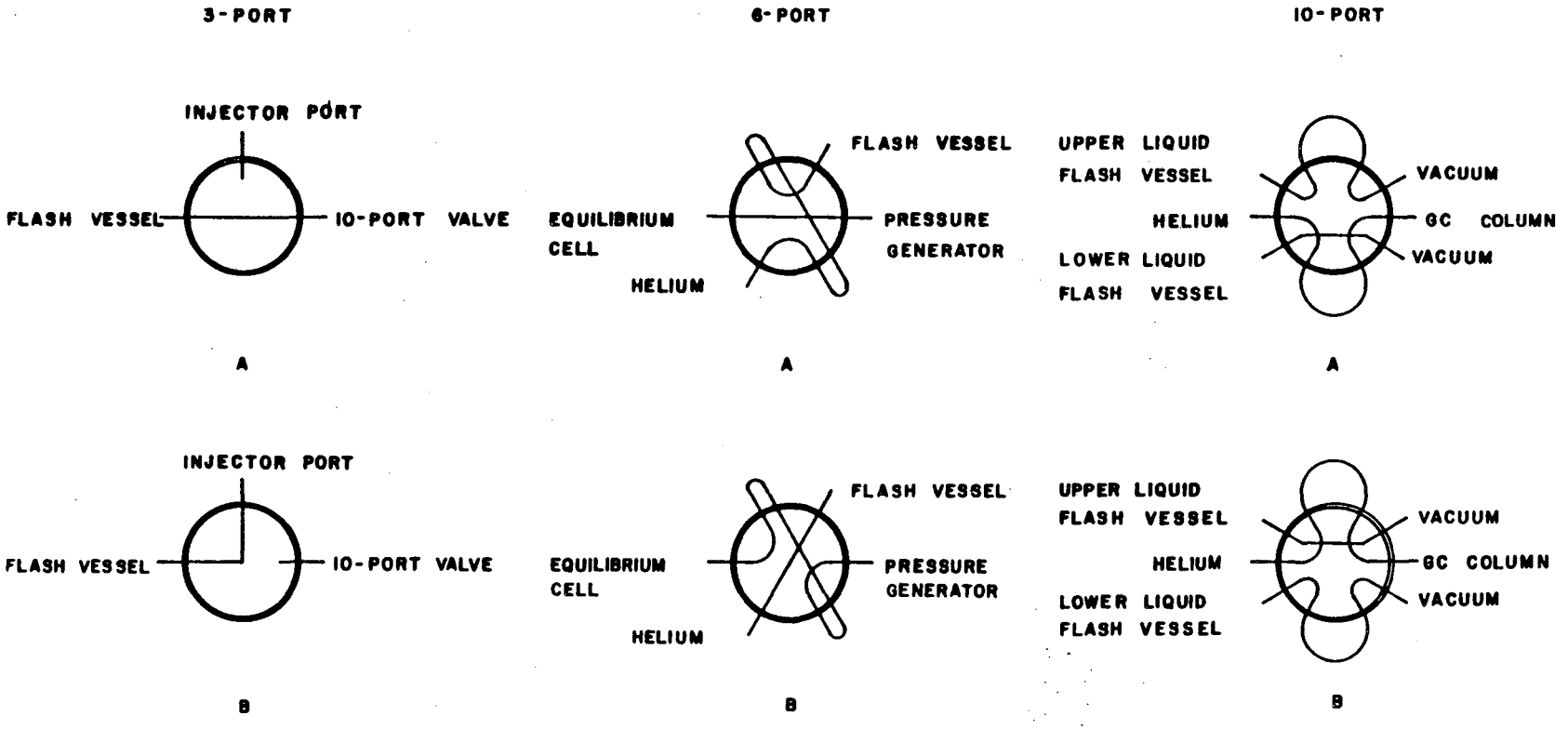
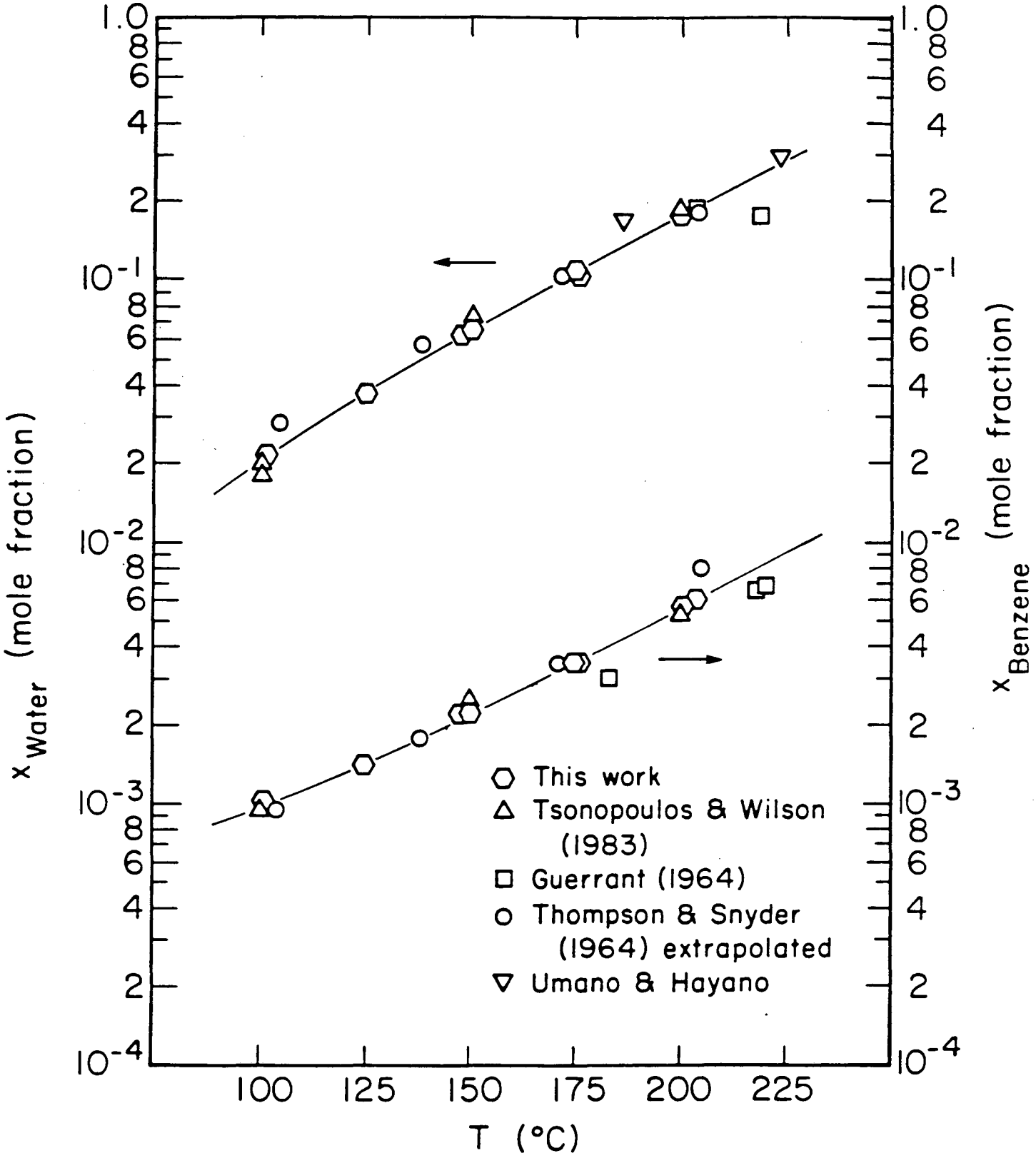
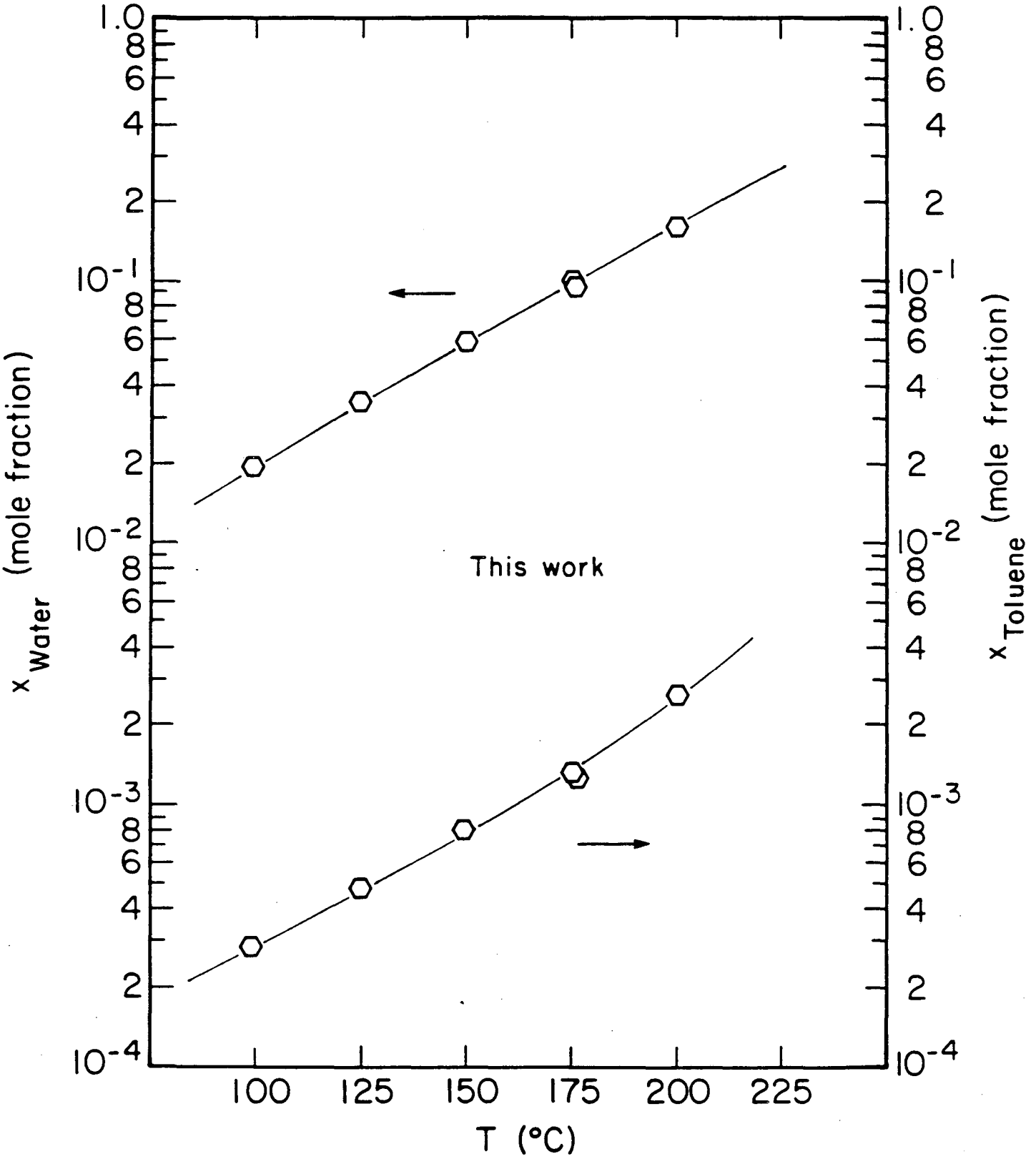


FIGURE 3



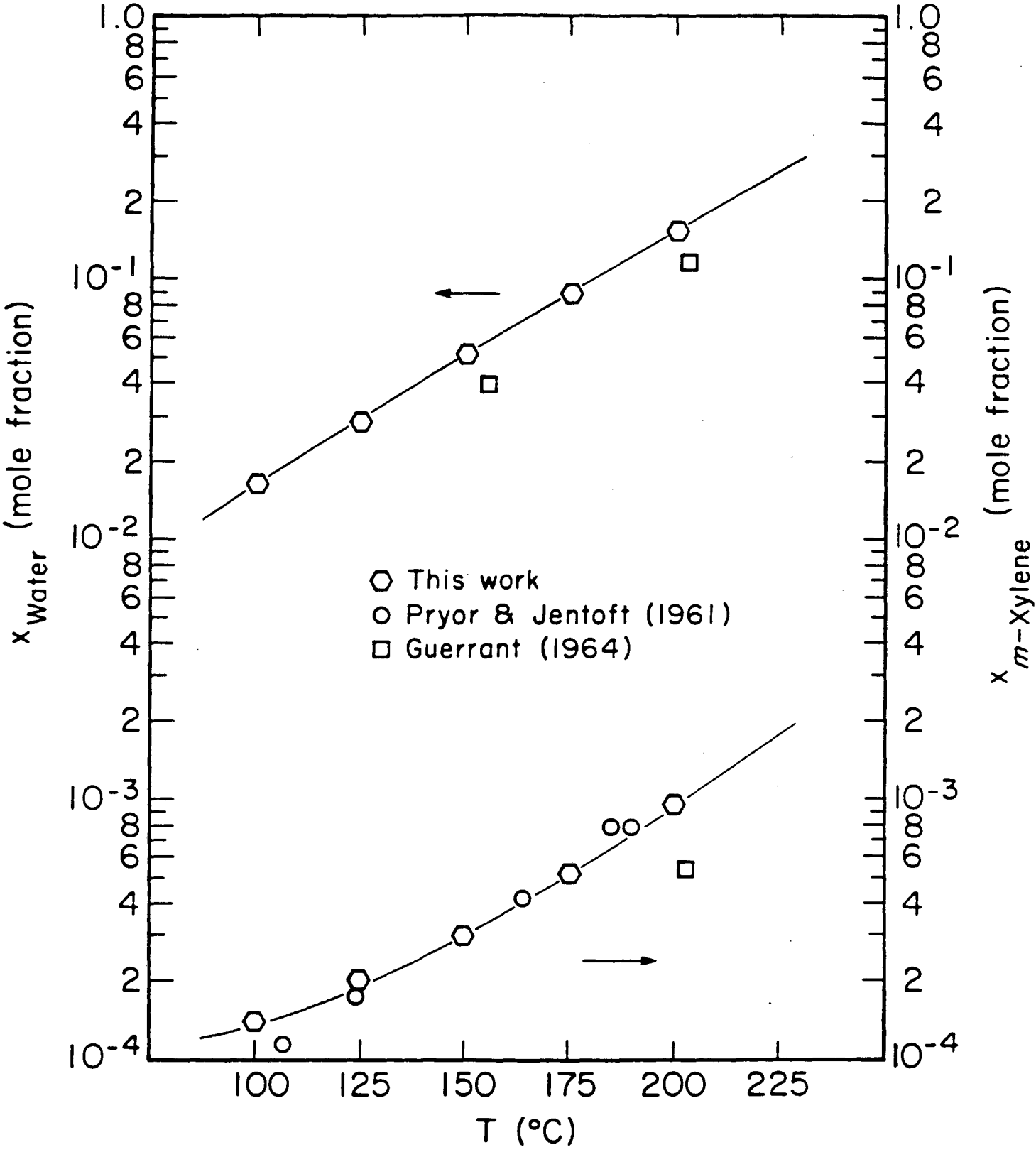
MUTUAL SOLUBILITIES OF BENZENE AND WATER AT THE THREE-PHASE PRESSURE

FIGURE 4



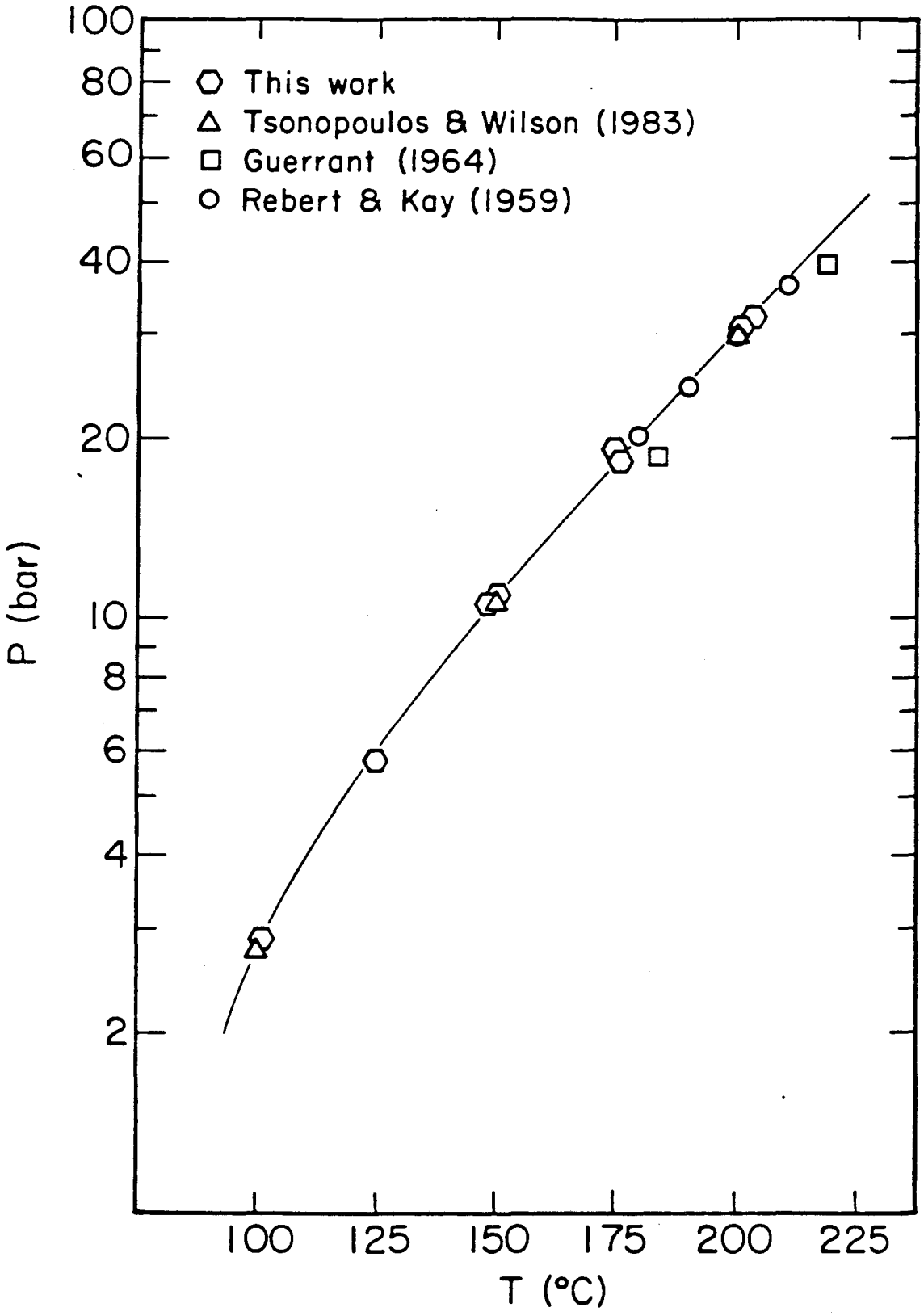
MUTUAL SOLUBILITIES OF TOLUENE AND WATER AT THE THREE-PHASE PRESSURE

FIGURE 5



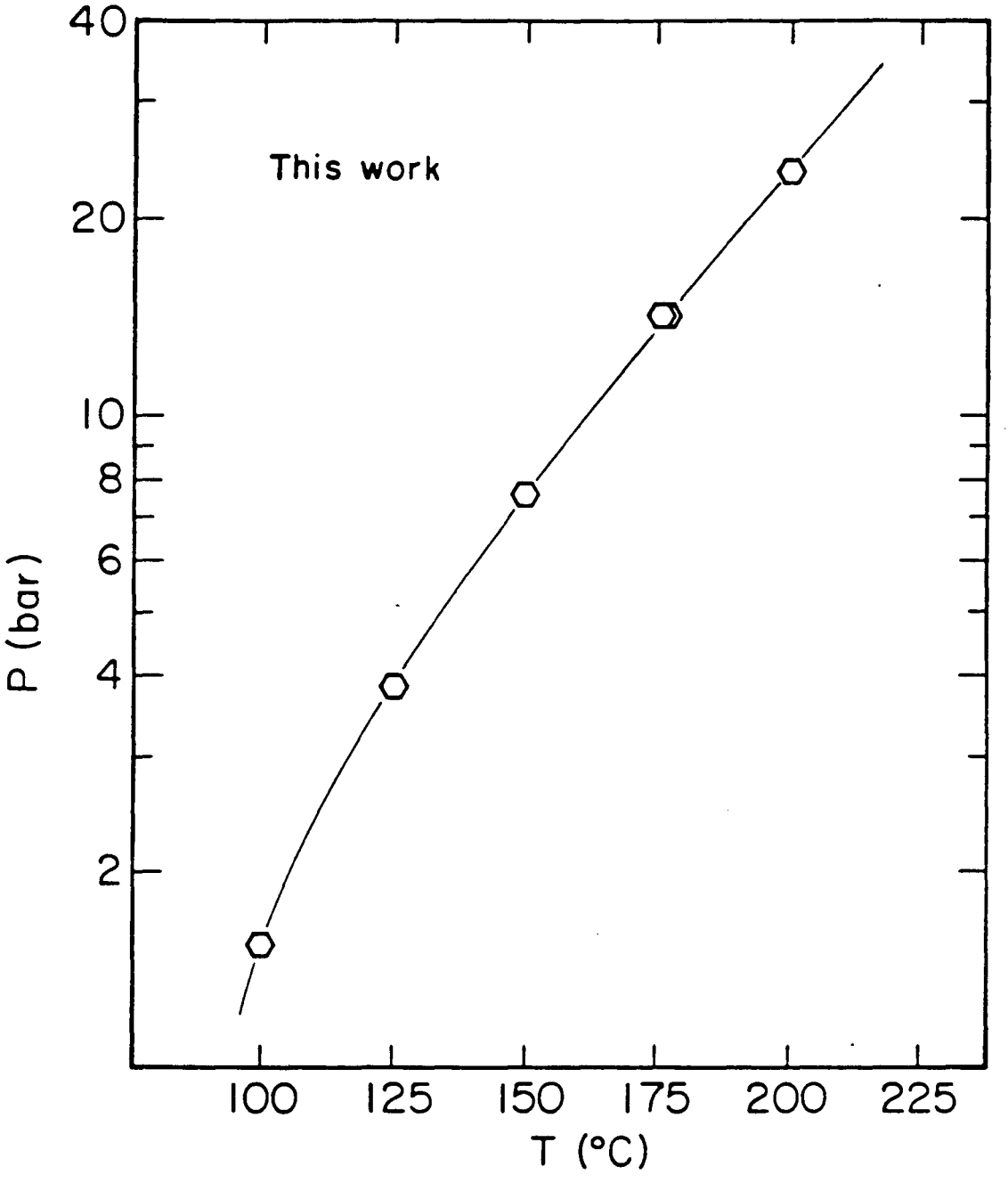
MUTUAL SOLUBILITIES OF *m*-XYLENE AND WATER AT THE THREE-PHASE PRESSURE

FIGURE 6



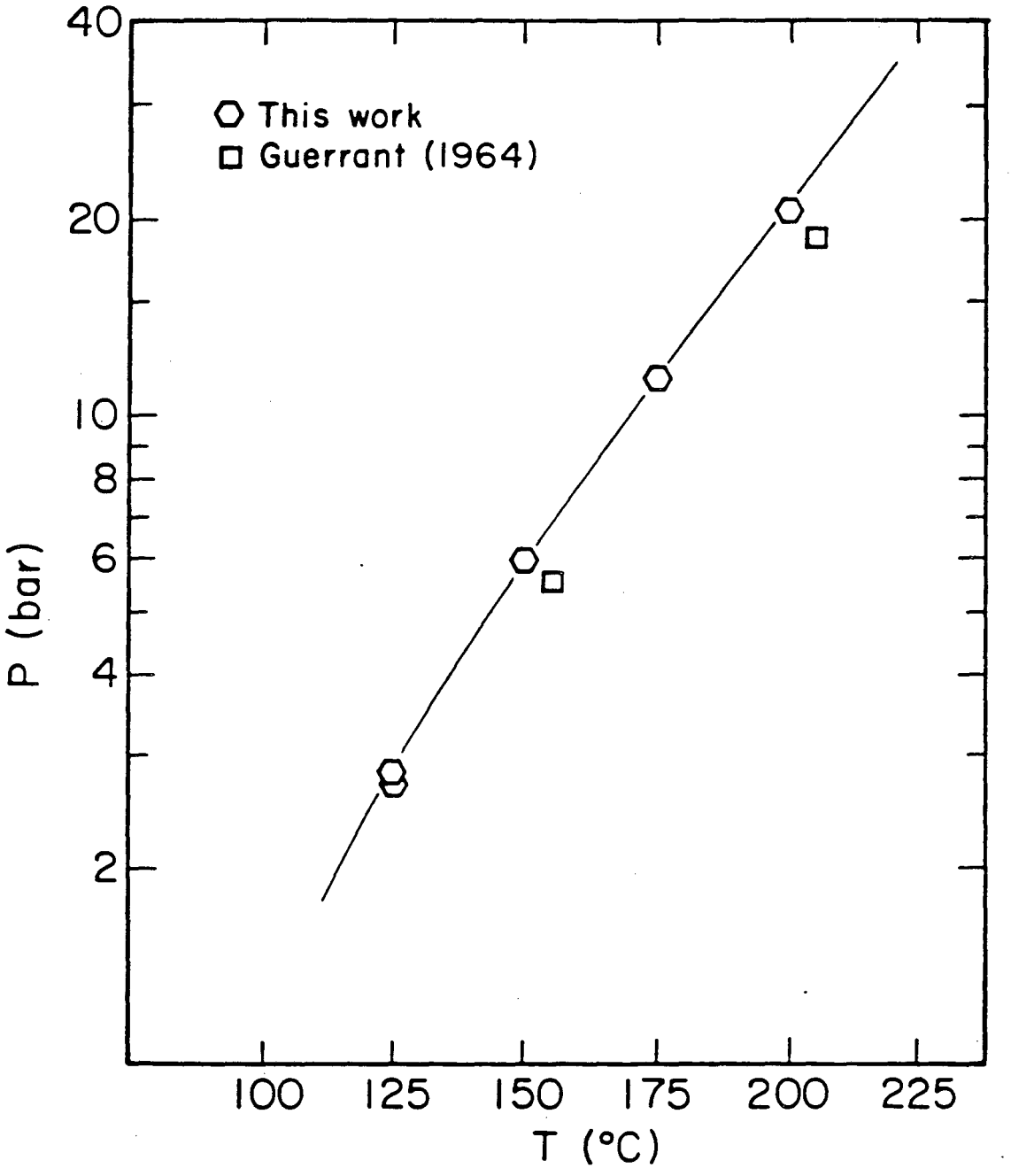
VAPOR PRESSURES OF BENZENE-WATER MIXTURES

FIGURE 7



VAPOR PRESSURES OF TOLUENE-WATER MIXTURES

FIGURE 8



VAPOR PRESSURES OF *m*-XYLENE-WATER MIXTURES

FIGURE 9

TABLE 1

Water (1) - Benzene (2) Mutual Solubilities

# Measurements	T (^{o}C)	S_T	P (bar)	$x_1 X\ 10^2$	$S_1 X\ 10^4$	$x_2 X\ 10^3$	$S_2 X\ 10^5$
7	101.0	-	2.87	2.135	4.5	1.02	3.5
7	124.8	-	5.77	3.658	6.8	1.40	4.7
6	147.7	.14	10.53	6.081	3.4	2.17	4.2
7	149.8	-	10.73	6.513	7.4	2.28	4.0
7	174.8	.48	19.01	10.58	19.	3.49	1.4
7	175.4	.17	18.59	10.53	16.	3.40	5.5
3	200.2	.55	30.45	17.92	6.0	5.64	35.
4	203.8	.14	32.18	18.86	7.3	6.07	9.2

T = Temperature
P = Three-Phase Pressure
x = Solubility in Mole Fraction (Mean)
S = Standard Deviation of Measurements

TABLE 2

Water (1) - Toluene (2) Mutual Solubilities

# Measurements	T (^{o}C)	S_T	P (bar)	$x_1 X\ 10^2$	$S_1 X\ 10^4$	$x_2 X\ 10^4$	$S_2 X\ 10^5$
7	99.4	.36	1.53	1.923	3.5	2.86	1.7
5	124.8	.05	3.84	3.411	4.4	4.63	1.5
5	149.4	.11	7.53	5.789	8.0	7.94	3.0
5	175.2	.07	14.25	9.826	7.5	13.0	2.3
10	175.3	.05	14.04	9.525	17.	12.3	2.7
6	200.4	.13	23.63	15.92	16.	25.9	11.

T = Temperature
P = Three-Phase Pressure
x = Solubility in Mole Fraction (Mean)
S = Standard Deviation of Measurements

TABLE 3

Water (1) - m-Xylene (2) Mutual Solubilities

# Measurements	T (^{o}C)	S_T	P (bar)	$x_1 X\ 10^2$	$S_1 X\ 10^4$	$x_2 X\ 10^4$	$S_2 X\ 10^5$
9	100.4	.43	-	1.647	5.1	1.38	1.5
5	125.0	.09	2.81	2.785	2.7	2.04	1.4
7	125.1	.15	2.74	2.857	7.7	2.00	1.6
6	150.0	.11	5.98	5.131	5.2	2.98	1.5
6	175.2	.10	11.42	8.840	6.5	5.17	1.7
5	200.2	.25	20.04	15.10	9.2	9.64	6.2

T = Temperature
P = Three-Phase Pressure
x = Solubility in Mole Fraction (Mean)
S = Standard Deviation of Measurements

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