Title

MUTUAL SOLUBILITIES AND VAPOR PRESSURES FOR BINARY AND TERNARY AQUEOUS SYSTEMS CONTAINING BENZENE, TOLUENE, m-XYLENE, THIOPHENE, AND PYRIDINE IN THE REGION 100-200|C

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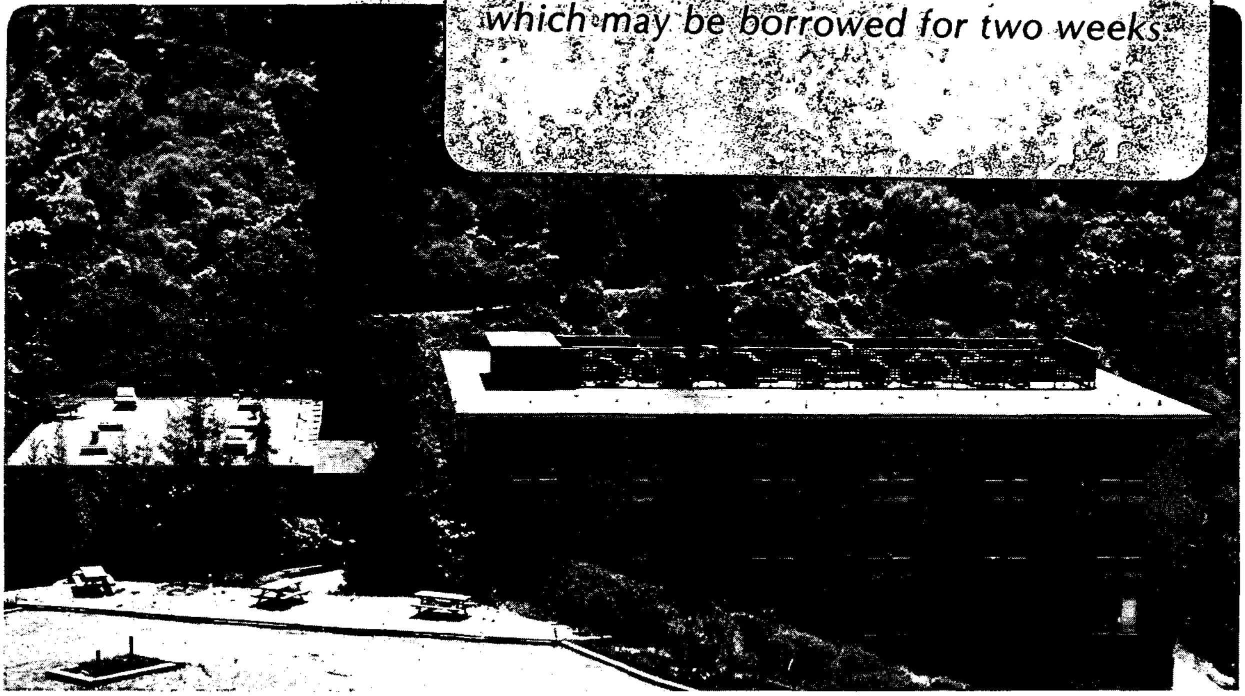

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Mutual Solubilities and Vapor Pressures for Binary and Ternary Aqueous Systems Containing Benzene, Toluene, m-Xylene, Thiophene, and Pyridine in the Region 100-200°C

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Abstract

An apparatus has been constructed for measuring mutual solubilities and vapor pressures for aqueous-organic liquid-liquid systems in the region ambient to 200°C. Both liquid phases are sampled and analyzed using gas chromatography. 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 the temperature range 100 to 200°C for binary aqueous mixtures containing benzene, toluene, m-xylene, and thiophene, and for ternary aqueous mixtures containing benzene and pyridine. The binary results are in good agreement with diverse data reported in the literature.

Introduction

Liquid-liquid mutual solubility data for aqueous systems 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.

Many petroleum reservoirs contain huge amounts of liquid water. Water injection methods for reservoir pressure maintenance add to this body of underground water. Further, each year millions of pounds of steam are injected into these reservoirs. As the oil is forced up to the surface, water is also forced up from the reservoir. The volume of water produced is often much larger than that of oil. The water produced is saturated with a variety of organic chemicals previously contained in the crude oil. This water must either be reinjected into the reservoir or treated to remove the organic contaminants.

Once the oil has been produced and transported to the refinery, further water/crude-oil contacting may take place during steam stripping. Crude oil and steam are fed to a distillation column where volatile components are removed from the crude oil. This procedure produces a large amount of high-temperature water, again contaminated with organic pollutants.

Finally, coal gasification processes often include a quench step where the hot effluent gases from the gasifier are cooled quickly by contact 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. 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 merge 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.

To design fossil fuel-water separation operations, 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. However, we cannot correlate multicomponent phase equilibria without some experimental data. Unfortunately, reliable liquid-liquid solubility data are not plentiful, especially at higher temperatures.

We present here mutual solubilities and vapor pressures for four aqueous binaries: benzene, toluene, m-xylene, and thiophene in the region 100 to 200°C. We also present data for the ternary system benzene-pyridine-water.

While a large number of investigators have reported data for aqueous, binary, mutual solubilities of benzene, toluene and m-xylene (Anderson and Prausnitz, 1983), with few exceptions, previous work has been limited to temperatures at or near ambient. While it is not simple, even at ambient temperatures, to measure (very small) mutual solubilities, such measurements become more difficult at higher temperatures where special precautions are required for sampling the equilibrated phases. Of the studies at elevated temperature, only five (Umano and Hayano,1957; Rebert and Kay,1959; Thompson and Snyder,1964; Guerrant,1964; and Tsonopoulos and Wilson,1983) present benzene-water data in the temperature range 100-200°C measured along the three-phase line. Two limited studies of the m-xylene-water system (Pryor and Jentoft,1961; and Guerrant,1964) allow comparison with some of our data. No published results are available for comparison with our toluene-water, thiophene-water, or benzene-pyridine-water data.

Phase-Equilibrium Apparatus

To measure liquid-liquid equilibria for hydrocarbon-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.

Reliable measurement of mutual solubilities is difficult (see for example, Brady, Cunningham and Wilson,1983), particularly at elevated temperatures and pressures, because 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. Further, entrainment of small droplets of one phase in the other while sampling can lead to very large errors. 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 during sampling can lead to vapor-liquid flashing. Differential flows of one phase with respect to the other in the sample line can cause a physical separation, leading to erroneous results.

Figure 1 shows a schematic diagram of our liquid-liquid phase equilibrium apparatus. All apparatus part numbers given below refer to the labels in Figure 1.

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 as our equilibrium cell. 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.

In bellows assembly B1, a cap is welded over one end of a bellows while the other end of the bellows is welded into a body fitted with tube connectors at either end. Bellows system B1 acts as a pressure transducer for the 0-2000 psi precision pressure gauge, G1. The gauge, associated tubing, and the gauge side of bellows system B1 are filled with degassed silicon oil. The vapor pressure of the mixture in the equilibrium cell is measured using gauge G1.

Bellows assembly B2 is similar to bellows assembly B1. Bellows assembly B2 acts as a pressure transducer to gauge G2 and pressure generator PG3. The gauge-pressure generator side of B2 is filled with degassed silicon oil. The pressure generator is constructed such that by turning a handle, a piston is forced to move through a cylinder. 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.

Tubes which extend into the cell are used as sample-withdrawal 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). Two ports on each valve are connected to a sample loop. 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 valves (V12 and V14). 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 valves (V4, V5 and V6). By opening valves V11 and V13, the flash vessels can be evacuated through the vacuum line.

From the flash vessels, lines proceed through valves (V10 and V9) and rotary 3-port valves (RV3 and RV4) to the rotary 10-port gas-sampling valve (RV5) 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. 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 valves (V6 and V7). The lines leading to the gas chromatograph and to the injector ports are heat traced.

Thorough mixing of the contents of the equilibrium cell may be accomplished using the liquid pump. Fluid from the upper-liquid phase is pumped out through the sample line, through valves V5 and V6, through a 15 micron filter, through the pump, and back to the cell to bubble through the more-dense lower liquid phase. The pump was not employed for binary measurements, but decreased the required equilibration time significantly for the measurement of ternary phase equilibria.

All analyses are made using a gas chromatograph 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. Chromatograms are also recorded on a chart recorder.

Temperatures are measured at 32 locations scattered throughout the apparatus with 30 thermocouples and 2 platinum-resistance temperature detectors (RTD). Thermocouples placed on the sides of the cell show that the maximum temperature gradient across the cell is less than 2°C. The equilibrium temperature is measured 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°C of the equilibration-oven temperature.

Sampling Procedure

After loading the equilibrium cell, the temperature controllers are set at the desired temperatures. 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 degassing. Two hours are usually sufficient for phase separation following agitation of the cell contents. Complete thermal equilibration was typically accomplished overnight.

Sampling of the equilibrated cell contents is accomplished in the following manner: Ball valves V5 and V6 are 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 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 equilibrated upper liquid phase. This has removed any non-equilibrated fluid from the sample line. Rotary valve RV1 is now turned so that it is in the same position as RV2 in Figure 1. 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 repeated until each pressure generator has moved a total of 25 turns. The sample loop now contains equilibrated liquid.

Valves V11 and V10 are closed, isolating the evacuated flash vessel. The rotary 6-port valve RV1 is turned back to its initial position in Figure 1. 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.

Valves V4, V5 and V6 are now turned 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.

The contents of the flash vessels are alternately analyzed in the following manner. Valve V7 is closed, V9 is opened, and the contents of F2 flow through the previously evacuated line to fill the lower sample loop on the 10-port gas-sampling valve (RV5). Valve V9 is closed after 30 seconds, and RV5 is turned to inject the sample-loop contents into the gas-chromatograph column. Valve V7 is opened to allow evacuation of the sample lines back to V9. To sample the contents of F1, V6 is closed, V10 is opened for 30 seconds, V10 is closed, and RV5 is turned back to its initial position shown in Figure 1. Valve V6 is opened to allow evacuation of the sample line back to V10. 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.

Chromatograph Calibration

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 injector ports allow direct injection of measured amounts of hydrocarbon and water to the flash vessels. The three-way rotary valves are set such that flow occurs between the injector ports (IP1 and IP2) and the flash vessels (F1 and F2). Valve V11 is closed, isolating the evacuated 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. 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 so that flow occurs between the flash vessels and RV5. 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. For the larger compositions encountered in the ternary mixture, direct weighing of all components was used where possible; this eliminated the need for the density conversion. Mole percent may be plotted versus area percent for the lesser component to yield the desired calibration curve.

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 systems such as octane-water.

Chemicals

Benzene, toluene, m-xylene and pyridine are of spectral-grade purity obtained commercially. Thiophene is Aldrich Chemical Co. Gold Label purity (99.9+%).. Water used was purified and deionized by adsorption on activated carbon.

Results and Discussion

Tables 1-5 and Figures 2-7 present measured mutual solubilities and vapor pressures for the benzene-, toluene-, m-xylene-, thiophene-, and benzene-pyridine-water systems. Each measurement was replicated as specified in the tables. The tables report mean values. Standard deviations (s) are reported wherever the number of measurements was sufficiently large to render them significant.

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. Measured temperatures are accurate to about ±0.3°C. Pressures were measured to within ±0.1 bar.

At least five previous studies of the benzene-water system have been reported in the temperature range 100-200°C. Several studies of this system are at higher temperatures. With the exception of the work by Guerrant (1964), agreement of our results with literature values is very good.

No previous studies have been reported for the toluene-water, thiophene-water or the benzene-pyridine-water systems in this temperature range. Studies of the m-xylene-water system were made by Guerrant(1964) and Pryor and Jentoft(1961). The latter work however, reports only the solubility of m-xylene in water; it is therefore 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), they are somewhat different from those of Guerrant. In general, there is good agreement between our and previously reported vapor pressures. Due to scatter in the ternary system pressures, reported vapor pressures have been smoothed.

As shown in Figures 2-5, mutual solubilities of the pure hydrocarbons and thiophene in water differ appreciably from each other. As methyl groups are added to the aromatic ring, the solubility in water falls, probably because the larger hydrocarbon molecule cannot easily penetrate the hydrogen-bonded liquid structure of water; this effect decreases as the temperature rises. Thiophene is somewhat more soluble in water than benzene, probably because of the increased polarity of thiophene. Solubilities of water in the hydrocarbons and thiophene are strikingly similar, and at least one order of magnitude larger than hydrocarbon-in-water solubilities. It is likely that water fits more easily into "holes" in the hydrocarbon liquid structure.

Figure 7 shows our results for mutual solubilities for the ternary system water(1)-benzene(2)-pyridine(3) at 100 and 150°C. No published data are available for comparison with our data. As in the water-benzene system, water is much more soluble in the benzene-rich phase than benzene in the water-rich phase. Pyridine is also much more soluble in the benzene-rich phase than in the water-rich phase. As expected, mutual solubilities increase (at constant system composition) as temperature rises. The distribution coefficient of pyridine between the benzene-rich and water-rich phases, defined as:

$$K_3 = \frac{x_3^{(2)}}{x_3^{(1)}} ,$$

is quite large (about 15), particularly for the pyridine-dilute measurements. As pyridine is added to the system, K_3 decreases (to 1.0 at the plait point). In the limit of the system infinitely dilute in pyridine, the distribution coefficient is approximately given by:

$$K_3 = \frac{\gamma_3^{\infty(1)}}{\gamma_3^{\infty(2)}}$$

where γ^{∞} is the activity coefficient at infinite dilution. While no information is available for $\gamma_3^{\infty(1)}$ or $\gamma_3^{\infty(2)}$ at the temperatures of our measurements, values are available for both from vapor-liquid equilibria at lower temperatures. The best, thermodynamically consistent data available (Gmehling et al., 1977, 1980) show that $\gamma_3^{\infty(1)}$ is about 24 (50°C) while $\gamma_3^{\infty(2)}$ is about 1.3 (25°C); this yields a K_3 of about 18.5, in semiquantitative agreement with our data.

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, m-xylene and thiophene. Ternary liquid-liquid data are also reported for the benzene-pyridine-water system.

Acknoledgment

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References

Anderson, F.E., Prausnitz, J.M., "Mutual Solubilities and Vapor Pressures for Hydrocarbon-Water Systems", Report # LBL-17333, Materials and Molecular Research Division, Lawrence Berkeley Laboratory, University of California, Berkeley, CA 94720.a

Brady,C.J.,Cunningham,J.,Wilson,G.,"Water-Hydrocarbon Liquid-Liquid- Vapor Equilibrium Measurements to 530 F", Gas Processors Association Research Report 62, Gas Processors Association, 1812 First Place, Tulsa, OK.(1983).

Gmehling, J., Onken, U., "Vapor-Liquid Equilibrium Data Collection: Aqueous-Organic Systems", DECHEMA Chemistry Data Series, Volume 1, Part 1 (1977) pages 463-475.

Gmehling, J., Onken, U., Arlt, W., "Vapor-Liquid Equilibrium Data Collection: Aromatic Hydrocarbons", DECHEMA Chemistry Data Series, Volume 1, Part 7 (1980) pages 208-221.

Guerrant,R.,"Hydrocarbon-Water Solubilities at High Temperatures Under Vapor-Liquid-Liquid Equilibrium Conditions", M.S.Thesis, The Pennsylvania State University(1964).

Pryor,W.,Jentoft,R., "Solubility of m- and p-Xylene in Water and Aqueous Ammonia from 0° to 300°C", J.Chem.Eng.Data,6,36(1961).

Rebert,C.,Kay,W., "The Phase Behavior and Solubility Relations of the Benzene-Water System", AIChE J.,5(3),285(1959).

Thompson,W.,Snyder,R., "Mutual Solubilities of Benzene and Water", J.Chem.Eng.Data,9,516(1964).

Tsonopoulos, C., Wilson, G., "High-Temperature Mutual Solubilities of Hydrocarbons and Water", AIChE J.,29(6),990(1983).

Umano, S., Hayano, I., "Solubility of Water and Sodium Chloride Solutions in Benzene", Kogyo Kagaku Zasshi,60,1436(1957).

Figure Captions

1. Mutual Solubility and Vapor Pressure Apparatus

2. Mutual Solubilities of Benzene and Water at the Three-Phase Pressure

3. Mutual Solubilities of Toluene and Water at the Three-Phase Pressure

4. Mutual Solubilities of m-Xylene and Water at the Three-Phase Pressure

5. Mutual Solubilities of Thiophene and Water at the Three-Phase Pressure

6. Vapor Pressures of Aqueous Binary Mixtures

7. Mutual Solubilities for the Benzene-Pyridine-Water System at 100° and 150°C and the Three-Phase Pressure

Table 1

Water (1) - Benzene (2) Mutual Solubilities

Number of Measurements	T (^{o}C)	S_T	P (bar)	$10^2 x_1$	$10^4 S_1$	$10^4 x_2$	$10^5 S_2$
7	101.0	-	2.87	2.135	4.5	10.2	3.5
7	124.8	-	5.77	3.658	6.8	14.0	4.7
6	147.7	.14	10.53	6.081	3.4	21.7	4.2
7	149.8	-	10.73	6.513	7.4	22.8	4.0
7	174.8	.48	19.01	10.58	19.	34.9	1.4
7	175.4	.17	18.59	10.53	16.	34.0	5.5
3	200.2	.55	30.45	17.92	6.0	56.4	35.
4	203.8	.14	32.18	18.86	7.3	60.7	9.2

T = Temperature

P = Three-Phase Pressure

x_i = Solubility of Component i in Conjugate Liquid Phase in Mole Fraction (Mean)

S_i = Standard Deviation of Measurements

Table 2

Water (1) - Toluene (2) Mutual Solubilities

Number of Measurements	T (°C)	s_T	P (bar)	$10^2 x_1$	$10^4 s_1$	$10^4 x_2$	$10^5 s_2$
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.

Table 3

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

Number of Measurements	T (°C)	S_T	P (bar)	$10^2 x_1$	$10^4 S_1$	$10^4 x_2$	$10^5 S_2$
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

Table 4

Water (1) - Thiophene (2) Mutual Solubilities

Number of Measurements	T (^{o}C)	S_T	P (bar)	$10^2 x_1$	$10^4 S_1$	$10^4 x_2$	$10^5 S_2$
5	125.2	.10	5.46	4.011	4.3	25.6	6.0
6	150.0	.30	10.05	7.428	10.	39.5	10.
5	175.1	.10	17.91	12.66	5.1	61.6	7.2
5	200.1	.11	29.21	19.73	8.9	99.3	28.

Table 5

Water(1) - Benzene(2) - Pyridine(3) Mutual Solubilities

Number of Measurements	T (^{o}C)	P (bar)	$x_1^{(1)}$	$x_2^{(1)}$	$x_3^{(1)}$	$x_1^{(2)}$	$x_2^{(2)}$	$x_3^{(2)}$
1	100.3	2.22	.9343	.0048	.0609	.4150	.2162	.3688
3	100.1	2.22	.9432	.0038	.0530	.3766	.2499	.3735
2	100.0	2.22	.9493	.0035	.0472	.3493	.2808	.3699
2	100.0	2.23	.9608	.0029	.0363	.2833	.3437	.3730
2	100.0	2.24	.9695	.0021	.0284	.2194	.4267	.3539
4	100.2	2.25	.9741	.0020	.0239	.1788	.4920	.3292
2	150.0	8.10	.8686	.0231	.1083	.6433	.1032	.2535
2	150.1	8.15	.9164	.0116	.0720	.5537	.1559	.2904
3	150.2	8.22	.9277	.0096	.0627	.4943	.1943	.3114
4	150.0	8.28	.9345	.0082	.0573	.4740	.2136	.3124
2	150.0	8.36	.9411	.0079	.0510	.4560	.2277	.3163
3	150.2	8.55	.9536	.0055	.0409	.3759	.3053	.3188
3	150.1	9.16	.9743	.0035	.0222	.2351	.4920	.2729
3	150.1	9.50	.9816	.0030	.0154	.1830	.5867	.2303

P = Smoothed Pressure

x_i = Mole Fraction of Component i

Superscripts : 1 = Aqueous Phase

2 = Hydrocarbon Phase

MUTUAL SOLUBILITY AND VAPOR PRESSURE MEASUREMENT APPARATUS

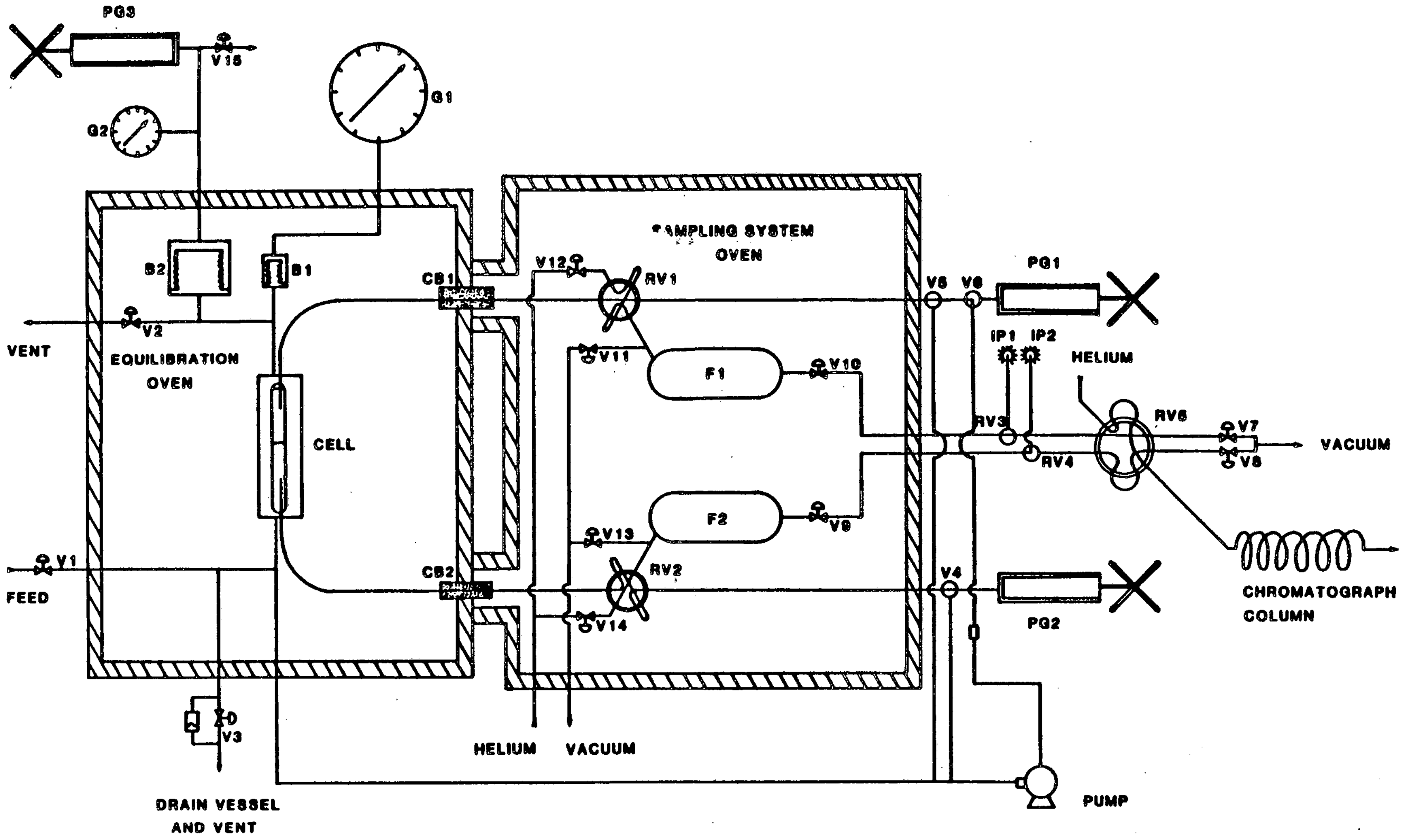
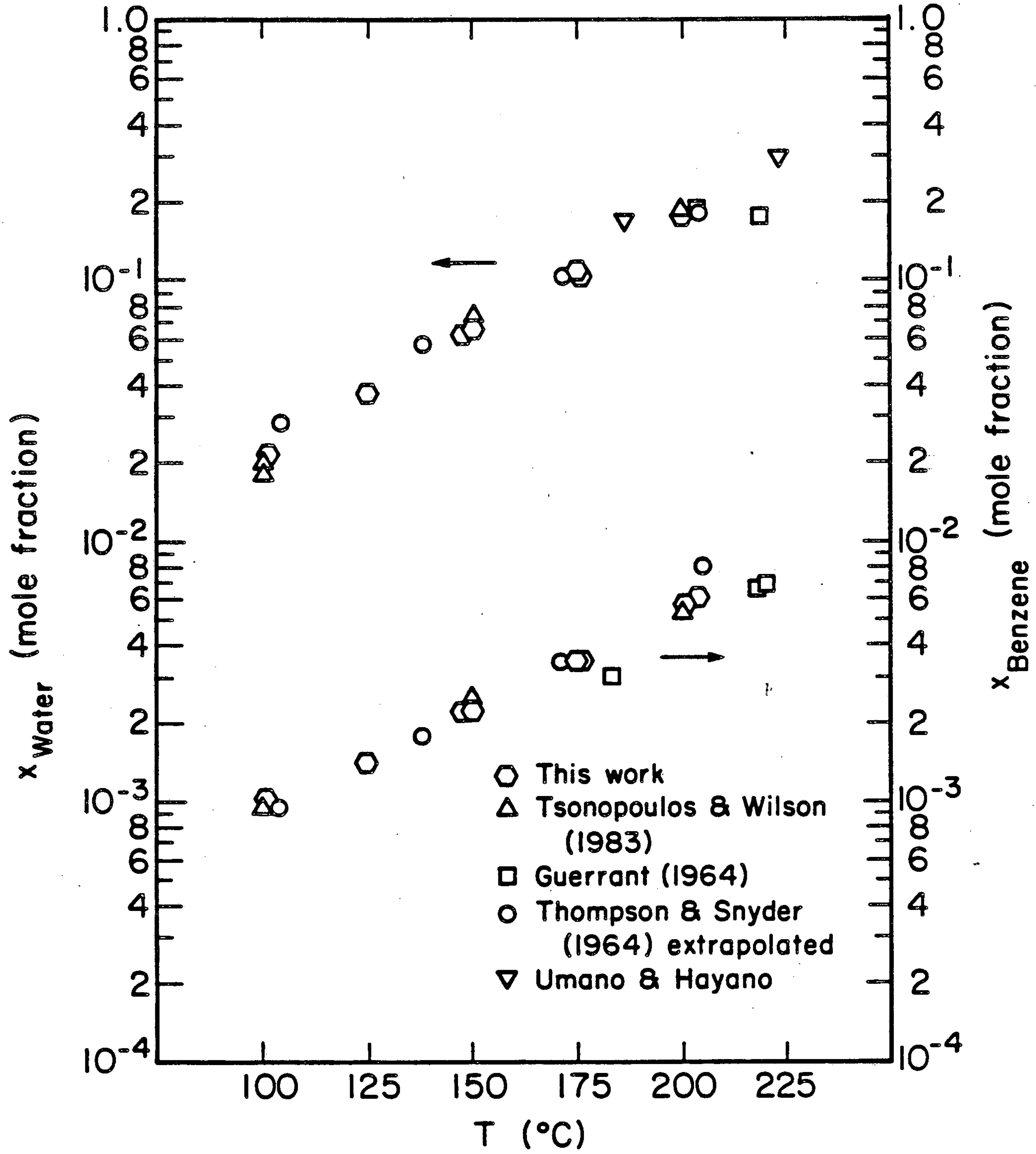
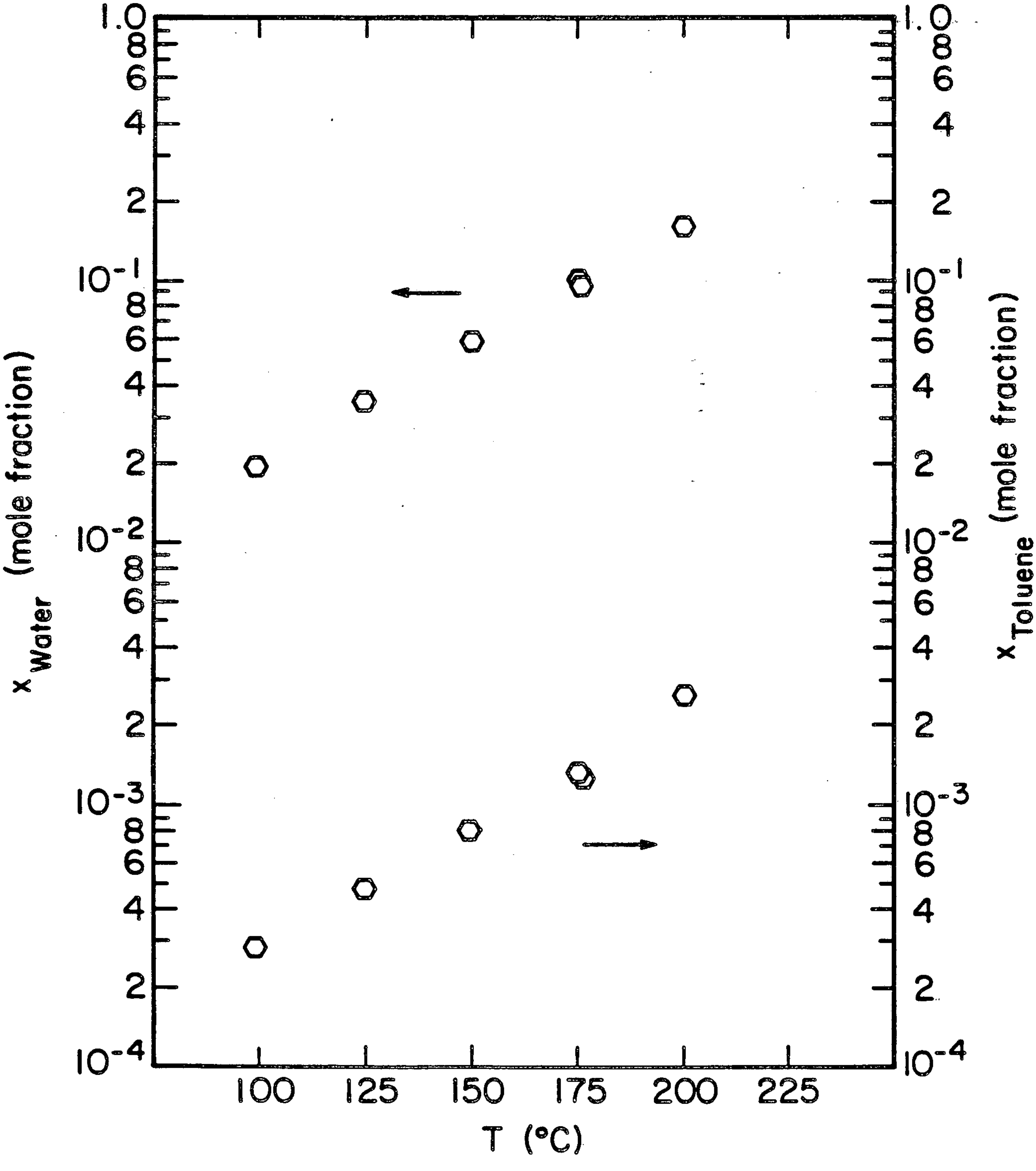


Figure 1



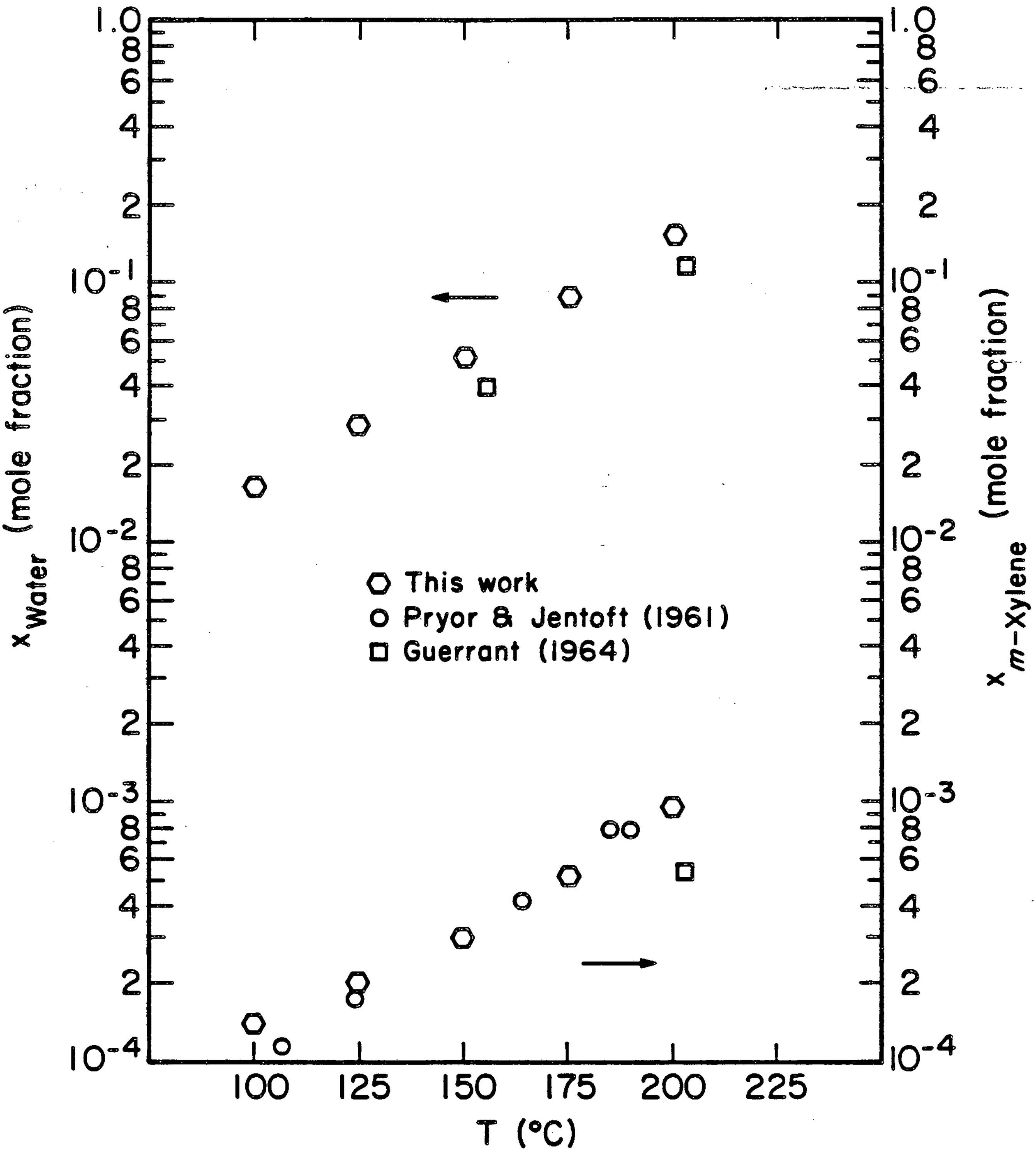
MUTUAL SOLUBILITIES OF BENZENE AND WATER AT THE THREE-PHASE PRESSURE

Figure 2



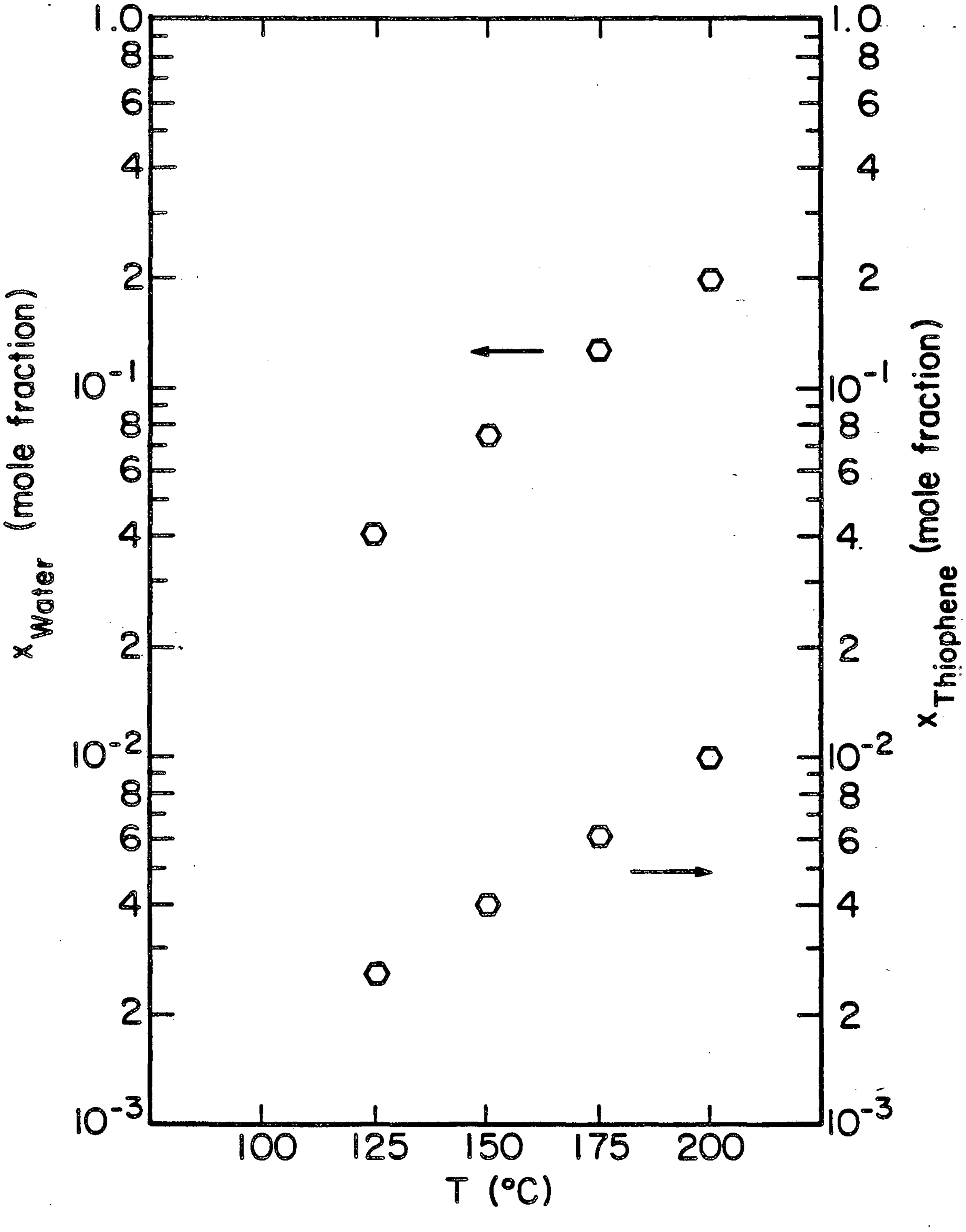
MUTUAL SOLUBILITIES OF TOLUENE AND WATER AT THE THREE-PHASE PRESSURE

Figure 3



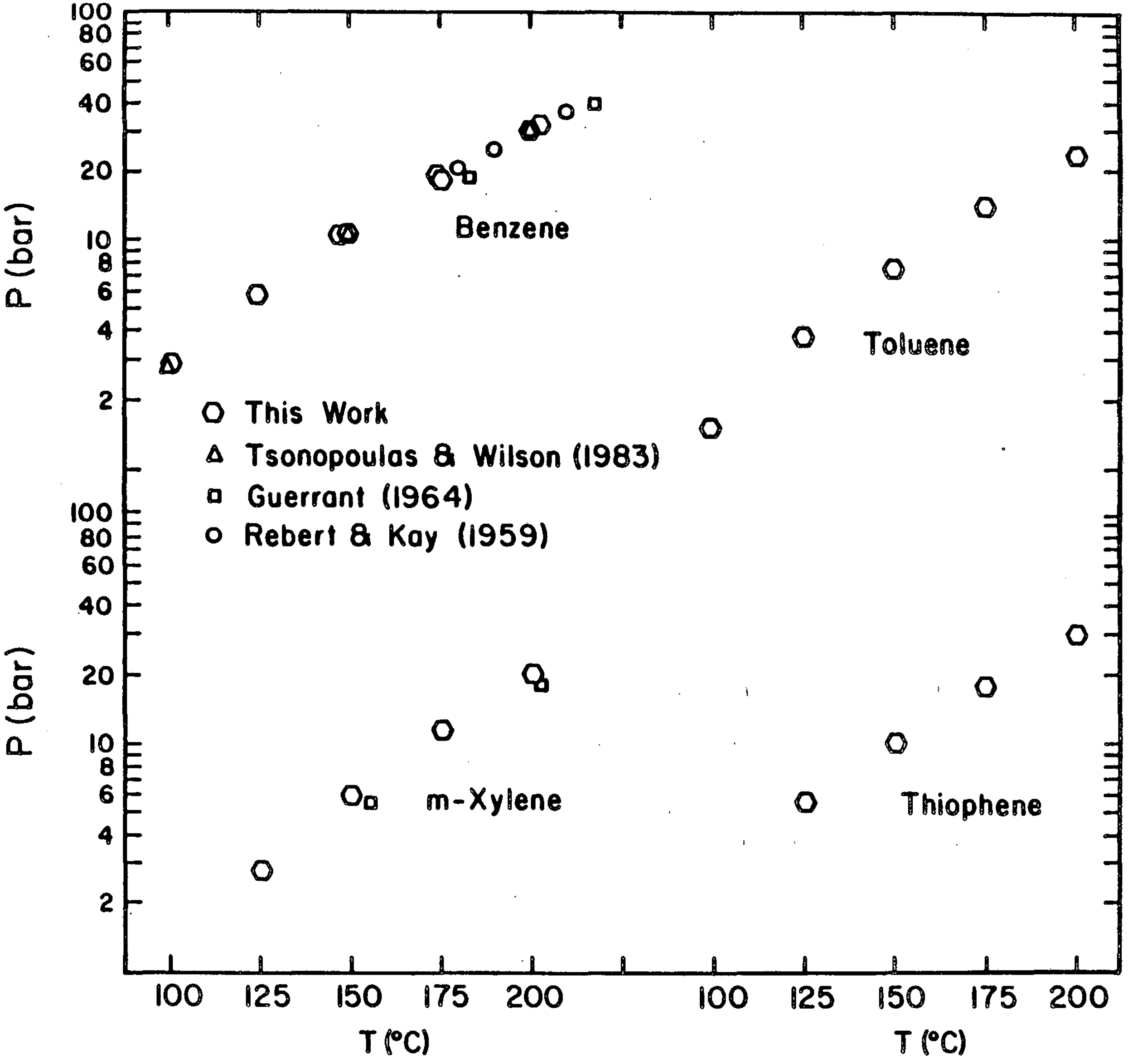
MUTUAL SOLUBILITIES OF *m*-XYLENE AND WATER AT THE THREE-PHASE PRESSURE

Figure 4



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

Figure 5



Vapor Pressures of Aqueous Binary Mixtures

Figure 6

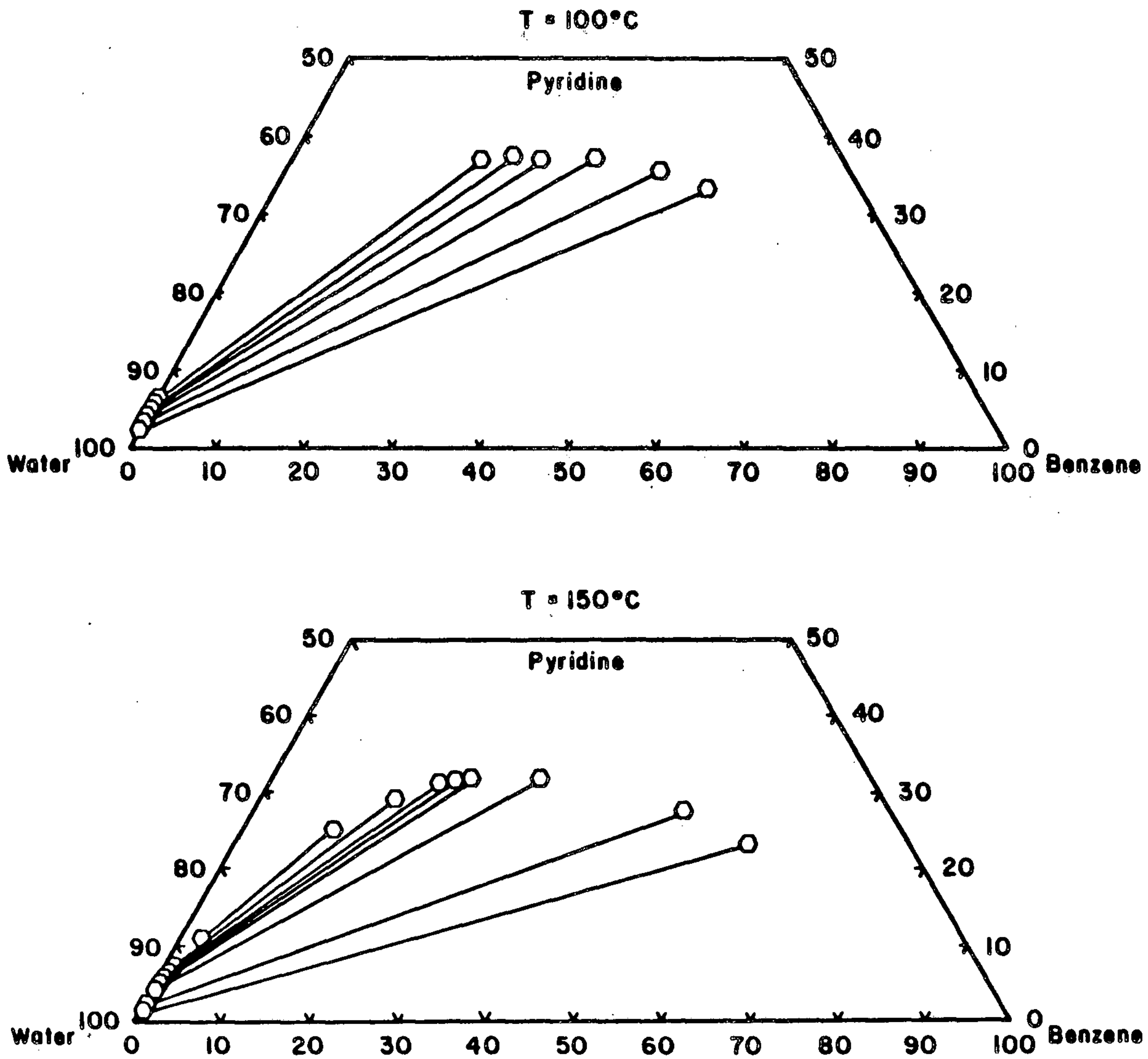


Figure 7

Mutual Solubilities for the Benzene-Pyridine-Water System at 100°C and 150°C and the Three-Phase Pressure

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