



Solubilities of phenol in supercritical carbon dioxide from aqueous phenol solutions
by Eric Raymond Leland

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in
Chemical Engineering
Montana State University
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Abstract:

The existing techniques for treating industrial chemical wastewater could benefit from cheaper and improved processing. Recent research has focused some attention upon supercritical fluid extraction. The purpose of this research was to experimentally measure solubilities of phenol, a common wastewater pollutant, in supercritical carbon dioxide from aqueous phenol solutions. A thermodynamic model of this system was also developed.

Extraction experiments were performed with a single pass flow apparatus. Liquid carbon dioxide was fed into the extraction cell by way of a high pressure liquids pump. The charged vapor samples were bubbled through water to isolate the product phenol. A wet chemistry, direct photometric method was used for phenol analysis. Experiments were run at 40 and 60 degrees Celsius. Aqueous phenol solutions of 10,000 parts per million, ppm, 5,000 ppm, and 2,500 ppm were studied. The pressures investigated ranged from 1,100 psi to 2,800 psi.

Measured experimental phenol mole fractions in supercritical carbon dioxide ranged from 0.000060 to 0.00080. At 40 degrees Celsius the vapor phase phenol solubility increased with increasing pressure. At 60 degrees Celsius the vapor phase phenol solubility passed through minimums over pressure at lower pressures. Larger aqueous phenol solution concentrations gave larger vapor phase phenol solubilities at both temperatures. The lower temperature of 40 degrees Celsius gave larger vapor phase phenol solubilities than at 60 degrees Celsius.

The data generated by the thermodynamic model of the aqueous phenol-supercritical carbon dioxide system passed through minimums in vapor phase phenol solubilities at both 40 and 60 degrees Celsius in the pressure range of 600 to 700 psia. The model predicted general trends at both temperatures but also showed discrepancies at both temperatures. These discrepancies might have been caused by assumptions made to solve the model.

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MONTANA STATE UNIVERSITY
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APPROVAL

of a thesis submitted by

Eric Raymond Leland

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ABSTRACT

The existing techniques for treating industrial chemical wastewater could benefit from cheaper and improved processing. Recent research has focused some attention upon supercritical fluid extraction. The purpose of this research was to experimentally measure solubilities of phenol, a common wastewater pollutant, in supercritical carbon dioxide from aqueous phenol solutions. A thermodynamic model of this system was also developed.

Extraction experiments were performed with a single pass flow apparatus. Liquid carbon dioxide was fed into the extraction cell by way of a high pressure liquids pump. The charged vapor samples were bubbled through water to isolate the product phenol. A wet chemistry, direct photometric method was used for phenol analysis. Experiments were run at 40 and 60 degrees Celsius. Aqueous phenol solutions of 10,000 parts per million, ppm, 5,000 ppm, and 2,500 ppm were studied. The pressures investigated ranged from 1,100 psi to 2,800 psi.

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INTRODUCTION

Wastewater Treatment Via Supercritical Fluids

A constant and integral part of chemical process industry is the investigation and adaptation of new or existing technologies that might improve a process's economics and/or boost its overall performance. The treatment of industrial chemical wastewater is an area that could benefit from cheaper and improved processing. Supercritical fluid extraction could be a promising method for treating wastewater.

Supercritical fluid extraction involves extraction with a fluid above its critical point (critical temperature, T_c , critical pressure, P_c). The fluid's solvent power in the critical region varies greatly with small changes in temperature and pressure. Recent applications include the decaffeination of coffee, extraction of spices, and regeneration of activated carbon. Carbon dioxide is overwhelmingly the preferred solvent in most applications. Carbon dioxide has moderate critical properties ($T_c = 31$ degrees Celsius, $P_c = 1070$ psia), is environmentally safe, readily available, and relatively inexpensive.

The prospect of using supercritical fluid extraction to treat wastewater is mentioned by Bott [1, p. 229]. However, there is little published experimental data for solubilities of common wastewater pollutants in supercritical carbon dioxide as a function of pressure and temperature. Also most of the solubilities are for pure materials. In order to further assess the potential of supercritical carbon dioxide in treating wastewater there is a need to investigate aqueous waste solutions. Van Leer and Paulaitis have reported the solubilities

of a common wastewater pollutant, phenol, in supercritical carbon dioxide as a function of pressure [2, pp. 257-259]. They demonstrated that supercritical carbon dioxide is an effective solvent for phenol. Therefore, an investigation into the solubilities of aqueous phenol solutions in supercritical carbon dioxide appears worthwhile.

Research Objectives

The primary objective of this research was to measure experimental vapor-liquid equilibrium data for the aqueous phenol-supercritical carbon dioxide system. Experimental apparatus and procedures were developed to create a reproducible system. A thermodynamic model of the above mentioned system was developed to predict vapor and liquid phase compositions at equilibrium.

Supercritical Fluids

Pure fluids are generally thought of as liquids and gases. This is true for most fluids up to a specific point called the critical point, here the two phases become indistinguishable. The critical point has the coordinates of critical temperature and critical pressure. Above the critical temperature it is not possible to liquefy the fluid at any pressure. The critical pressure is the pressure required to liquefy the fluid at its critical temperature. A discussion of the critical region of pure fluids and a physical description of a fluid at its critical point is provided by Smith and Van Ness [3, pp. 57-60].

Extraction With Supercritical Fluids

The inherent physical properties of supercritical fluids are very attractive from the standpoint of a separation technique. The following description of these properties is given by Bott [1, p. 229]. In its supercritical state the dense fluid is very mobile. The fluid has a density of up to one-third or more compared to the liquid state, while its viscosity can be as low as one-fifth or less depending on pressure and temperature. This results in fluid solubilities approaching those of the liquid phase yet the fluid can penetrate faster and deeper into a solid matrix of natural substances or could progress faster through a densely packed fixed bed or column.

Extraction via supercritical fluids is characterized by the following features which are provided by Wilke [4, p. 701]: (1) relatively involatile materials can be dissolved by supercritical fluids, sometimes even selectively, (2) phenomena of distillation and extraction are simultaneously involved, i.e. enhancement of vapor pressure and phase separation both play a role, (3) the properties of the supercritical fluid such as density can be varied within wide limits by means of pressure and temperature, and (4) separation of the dissolved substances can be accomplished either by a reduction of pressure (at constant temperature) or by raising temperature (at constant pressure). Two additional features are given by Bott [1, p. 229]: (1) the lower operating temperatures involved allow for the successful extraction of heat sensitive compounds, and (2) the use of supercritical carbon dioxide leaves no harmful residues.

Supercritical fluid extraction is a relatively high pressure process. High pressure processes are recognized as high cost operations due to expensive equipment and energy demands to maintain plant pressure. These costs may be prohibitive to supercritical fluid extraction unless there is some type of energy recovery and/or a process enjoys key advantages from using supercritical fluid extraction. There is very little published information on the costs of supercritical fluid extraction. An article by Peter and Brunner discussed data on the costs of separation of non-volatile substances [5, pp. 746-750].

Supercritical Fluid Applications

Chemical process industries have begun to exploit the uses of supercritical fluids. An article by Kohn and Savage reviews promising applications of supercritical fluids, but it is without references [6, pp. 41-43].

Supercritical carbon dioxide has demonstrated an affinity towards some natural product constituents such as caffeine in coffee and extracts of spices. An article by Zosel gives a description of the decaffeination of coffee via supercritical carbon dioxide [7, pp. 707-709]. Hubert and Vitzhum provide an introduction to the methods of supercritical carbon dioxide extraction of hops, spices, and tobacco in their article [8, pp. 710-715].

Supercritical carbon dioxide is also being used to regenerate activated carbon [9].

The uses of supercritical fluids are finding applications in the fuels industry. Kerr-McGee has commercialized a process that extracts asphaltenes and residues from distillation residue in oil refineries using supercritical aliphatic hydrocarbons [6, pp. 41-42]. Britain's National Coal Board Research Establishment is using supercritical toluene to extract light hydrocarbons from coal leaving behind a charred residue [6, pp. 42-43].

High Pressure Experimental Methods

There are two general approaches to measuring high pressure vapor-liquid equilibrium. These are flow systems and static systems. An article by Young describes these systems in general and also presents specific experimental systems that have been used [10, pp. 83-104].

Flow Methods

There are two types of flow systems, the single pass system, and the vapor recirculation system. In the single pass system a sample of pure gas at a specified pressure is passed through a liquid at a specified temperature. In a given length of time the liquid and vapor are essentially in equilibrium, which in a well designed system is less than fifteen minutes [10, p. 83]. When equilibrium is reached samples of vapor and liquid are withdrawn for analysis.

The vapor recirculating method starts with liquid and vapor in a vessel at a specified temperature and pressure. Vapor is withdrawn and recirculated through the liquid, this vapor-liquid contact allows for a rapid approach to equilibrium. When equilibrium is reached samples of vapor and liquid are withdrawn for analysis.

The single pass method suffers from two major disadvantages with respect to the vapor recirculation method. First, it is difficult to establish whether equilibrium has been reached in one pass or not. The second disadvantage involves the pressurizing of the vessel containing liquid. All of the vapor used to pressurize the vessel contacts the liquid below the specified pressure. To insure that the vapor sample withdrawn is representative of the operating pressure, the vessel must either have enough vapor passed through it to "clear" out the initial vapor or the vessel's contents must be mixed at operating conditions.

Static Methods

There are several types of equipment systems for measuring static high pressure equilibrium. A typical method consists of placing a two-phase mixture in a sealed vessel at a specified temperature and pressure. Then the vessel's contents are mixed and when equilibrium is reached vapor and liquid samples are withdrawn for analysis. There is one major disadvantage to static methods. The pressure is usually not held constant while samples are being withdrawn, which can lead to considerable error.

EXPERIMENTAL

Experimental Design

The experimental work was performed in three stages. The first stage was the development of a working and reliable extraction apparatus. Next a series of experiments were performed to develop a practical experimental procedure with reproducible results. These experiments also gave the investigator a feel for the apparatus. The last stage was the gathering of useful data. The first set of data was at 40 degrees Celsius. Here, phenol solution concentrations of 10,000 ppm, 5,000 ppm, and 2,500 ppm were investigated over the pressure range of 1,100 psig to 2,800 psig. The second set of data was at 60 degrees Celsius. Phenol solution concentrations of 10,000 ppm and 2,500 ppm were investigated over the same pressure range as at 40 degrees Celsius.

Experimental Apparatus

A schematic of the experimental apparatus appears in Figure 1. The apparatus used was a single pass flow system. An inverted carbon dioxide gas cylinder was used to feed liquid carbon dioxide to the liquids pump. A Milroy Model HBD-1-30R high-pressure liquid pump was used to pressurize the extraction cell and to deliver carbon dioxide to the extraction cell at constant pressures. The pump was charged with ambient temperature carbon dioxide by a carbon dioxide gas cylinder which was inverted to deliver liquid solvent. The pump's liquid end was always packed in ice to keep the carbon dioxide liquid in the pumping chamber and thus insuring consistent flow by preventing a vapor

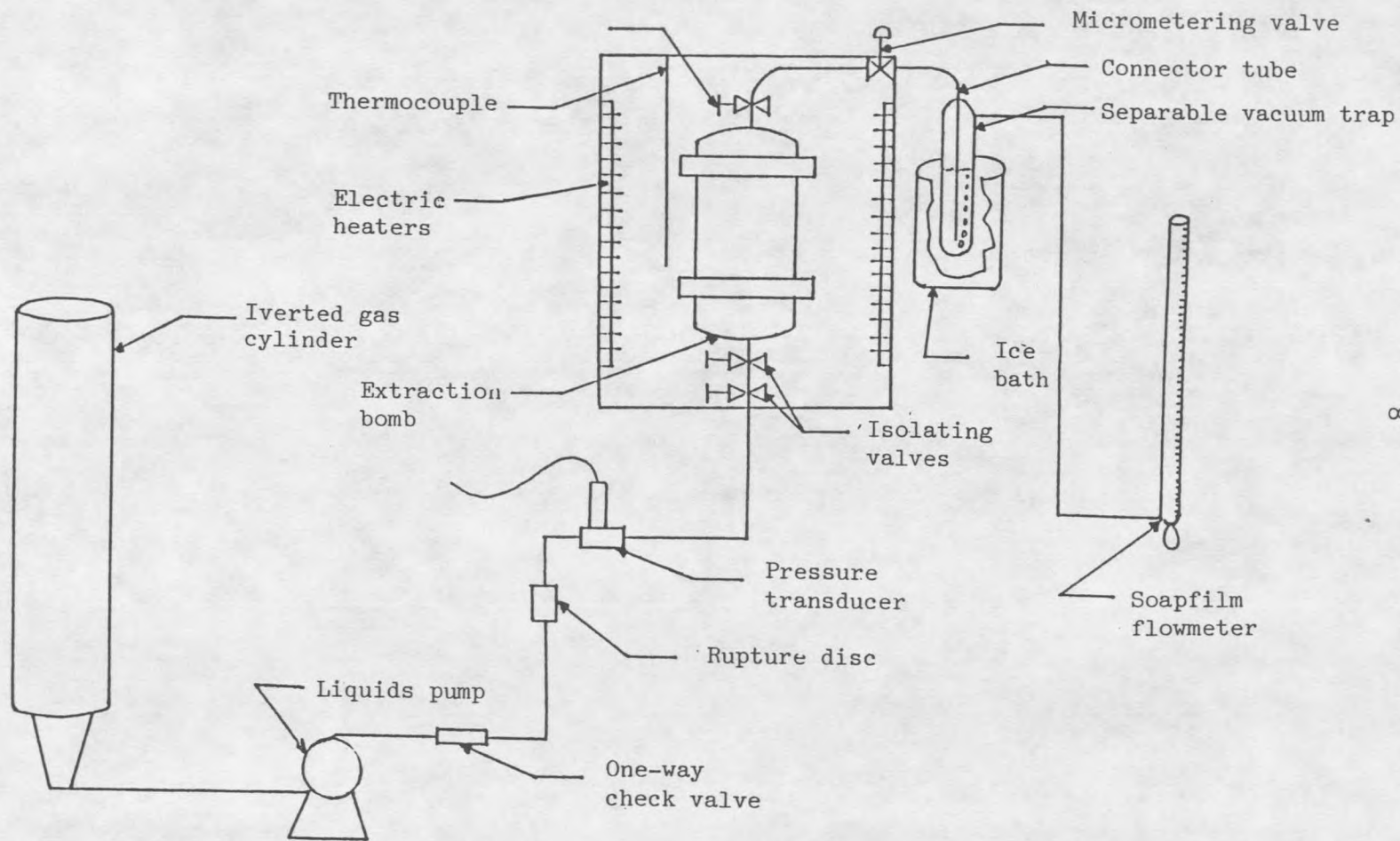


Figure 1. Schematic of phenol extraction apparatus

lock. Pumping liquid carbon dioxide yielded consistent flow and stable system pressures. The pump was protected by a rupture disc and a one-way check valve located beyond the pump and before the extraction cell.

The extraction cell was a one-liter monel bomb rated at 3,500 psi suspended in an electrically heated oven. Eighty percent of the bomb's volume was packed with 0.64 centimeter ceramic Berl saddles. This left a two hundred milliliter empty space and roughly a height of six centimeters for vapor-liquid disengagement. Oven temperature was controlled by electrical heaters controlled by a Powerstat type 3PN1168 variable auto transformer. There was a network of valves around the bomb which allowed for the isolation and removal of the bomb while under pressure.

A Whitey Model number SS-22RS4 micrometering valve was used to control pressure and collect samples for analysis. This valve flashed the saturated vapor to atmospheric pressure. Then the flashed vapor bubbled through a separable vacuum trap containing seventy-five milliliters of deionized water that was held at 0 degrees Celsius by means of an ice bath. Then the "clean" vapor was routed through a one hundred milliliter soap film flowmeter and then to the atmosphere. Initially an attempt was made to collect phenol samples in a dry trap held at 0 degrees Celsius by an ice bath. This failed to produce any detectable traces of phenol in the trap. Therefore, the alternative method of using deionized water in the trap was employed, and was satisfactory. The failure of the first attempt might have been caused by the small size of the condensed phenol particles which may have been carried through the trap by the effluent vapor flow.

System pressures were monitored by an Autoclave Engineers Model DPS0081 pressure sensor and an Autoclave Engineers Model DPT418 pressure transducer. The pressure transducer was located before the extraction cell by roughly 1.5 meters of tubing. A calculation of pressure drop over this distance due to frictional flow was made and was negligible. Oven temperature was monitored by a Cole Palmer Model 8530 thermometer and a thermocouple in the oven.

Phenol analysis used the following equipment; an Orion 901 ionalyzer used as a pH meter; a Bausch and Lomb Spectronic 20 spectrophotometer; a magnetic stirrer; and a mass balance.

Experimental Procedure

Preparation for an experimental run began the evening before. The bomb was charged with fresh solution if necessary. Phenol solutions were prepared from reagent grade phenol and deionized water. The bomb needed to be recharged if the next run required a different phenol solution concentration. Charging the bomb with fresh solution involved gravimetrically filling the bomb with roughly six hundred milliliters of the desired solution, which filled the bomb to the level of its packing. Next the bomb was clamped into the oven which had been preheated to the run temperature. Then the bomb was connected to the system's tubing and pressurized with saturated carbon dioxide at room temperature, roughly 900 psi. The bomb was then sealed from the system and heated up to the run temperature overnight.

The experimental run began the next morning. First the pump was used to bring the system up to the operating pressure and then

maintained at this pressure for 15 minutes. Next the bomb was isolated from the system and removed from the oven for mixing. This mixing insured intimate vapor-liquid contact at operating pressure. When the bomb reached operating pressure, virtually all of the carbon dioxide in the bomb, roughly 200 milliliters, had been bubbled through the liquid at sub-operating pressure. This included the pressurizing of the bomb with saturated carbon dioxide at room temperature and the pumped carbon dioxide that brought the bomb up to operating pressure. All of this carbon dioxide remained in the bomb since the outlet of the bomb was closed to flow. Therefore, the vapor and liquid in the bomb needed to be re-contacted at operating conditions. Upon reaching operating pressure and after a 15 minute wait, the bomb was isolated and removed from the oven and shaken vigorously for roughly one minute. Then the bomb was clamped back into the oven and opened up to the system. The bomb's drop in pressure during removal from the oven ranged from less than 10 psi up to 50 psi. The larger pressure drops were associated with higher operating pressures and all pressure drops were corrected within 5 minutes. These pressure drops were probably due to the slight cooling of the bomb upon oven removal. When the bomb pressure had been restored it was maintained for one hour.

After the one hour period a sample of vapor was ready to be withdrawn. The micrometering valve was opened to deliver a desirable flow, which ranged from 50 milliliters per minute to 200 milliliters per minute. The phenol in the vapor sample was condensed out of the vapor in the separable vacuum trap, and was also deposited in the micrometering valve and on the connecting tube. The vapor flowrate was

measured with the soap film flowmeter and a stop watch. The amount of carbon dioxide from each run ranged from around 4,500 milliliters to 6,000 milliliters at ambient conditions. Ambient pressure was recorded along with effluent vapor temperature. During the run and the hour period before sample collection pressure was always held to ± 10 psi and usually held to ± 5 psi. Also during this time oven temperature was held to ± 1 degree Celsius. During the experimental run the phenol solution was depleted somewhat. The amount of solution depletion was small due to the relatively large amount of liquid solution and the small solubilities of phenol in the vapor phase. The phenol solution concentration was always within 95% of the stated concentration.

When the sample had been taken, the micrometering valve was isolated from the system. Then the valve, connecting tube, and separable vacuum trap were removed as a unit, and then taken to the lab for phenol recovery. Only these components were used in phenol recovery because they were the only components that were exposed to the phenol in the vapor sample collected during the run. Here all the components were thoroughly washed with 175 milliliters of deionized water and all of the washings plus the contents of the trap were placed in a tightly-sealed, labeled, and tared sample bottle. Then the sample bottle was weighed and stored for later phenol analysis. Also after each run, the 0.16 centimeter O.D. stainless steel tubing that ran from the bomb to the micrometering valve was washed out with deionized water. This insured that the next run would not be influenced by phenol that might have been left in the tubing from the previous run.

Phenol Analysis

The phenol analysis was a direct photometric method. The actual wet chemistry is presented in Standard Methods For the Examination of Water and Wastewater [11, pp. 510-513]. A series of phenol standards was prepared and analyzed by the above procedure. From this a calibration curve was constructed, which plotted absorbance versus phenol concentration (appendix C). The absorbance readings of unknowns were compared against the calibration curve and phenol concentrations were read directly off the curve. Phenol analyses were performed on three known prepared solutions and repeated on a couple of experimental samples in order to evaluate the accuracy of the phenol analysis. All analyses were within 5% error.

The calculation of phenol mole fraction in the vapor samples was accomplished by individually calculating the amounts of carbon dioxide and phenol. The amount of phenol was calculated from knowing the phenol concentration of the collected water sample and its mass. The amount of carbon dioxide was calculated from the ideal gas law. Ambient temperature and pressure were known along with sample volume.

Reagents

All chemicals used were reagent grade except carbon dioxide. The carbon dioxide was welding grade and was 99.9% pure. The water used was deionized.

RESULTS AND DISCUSSION

General Observations

Phenol solubilities were measured at a constant temperature and at a constant phenol solution concentration over a range of pressures. As previously mentioned the depletion of phenol during a run changed the aqueous phenol concentration less than 5%. Also as mentioned before phenol analysis by the direct photometric method produced results with less than 5% error.

The critical properties of the supercritical phase mixture (T_c , P_c) were assumed to be identical to those of pure carbon dioxide ($T_c = 31$ degrees Celsius, $P_c = 1070$ psia) and unaffected by the presence of phenol and water since they were in such small concentrations.

Experimental Solubilities

The primary objective of this research was to measure experimental solubility data for phenol in supercritical carbon dioxide from aqueous phenol solutions. The parameters studied during these vapor-liquid equilibrium runs were temperature, pressure, and phenol solution concentration. Solution concentrations were reported in parts per million, ppm, which was a weight ratio (e.g. 10,000 ppm was 1 weight % phenol).

The reported phenol solubilities were for temperatures of 40 degrees Celsius and 60 degrees Celsius, and were mole fraction phenol in the vapor phase. Each experimental run was duplicated and the difference between replicates averaged 17%.

Data at 40 Degrees Celsius

The phenol solubilities for 40 degrees Celsius are listed in Table 1. This data includes the values for each experimental replicate and the average. For this temperature the following three phenol solution concentrations were investigated: 10,000 ppm; 5,000 ppm; and 2,500 ppm. The pressure range investigated for each of these solution concentrations was 1,100 psig to 2,800 psig. The average values for each duplicated experiment are plotted in Figure 2.

The effect of pressure upon vapor phase phenol solubility was consistent among the three phenol solution concentrations. The vapor phase phenol solubility increased significantly in the pressure range of 1,100 psig to 2,000 psig. Beyond 2,000 psig the vapor phase phenol solubility leveled off indicating a much weaker function of pressure. Figure 2 also shows that increased phenol solution concentration gave larger vapor phase phenol solubilities.

The effect of pressure on vapor phase phenol solubility was similar to its effect on supercritical carbon dioxide density (Figure 3).

The density increased rapidly with increased pressure in the same pressure range as did vapor phase phenol solubility. Also the density started tapering off at roughly the same pressure as did the vapor phase phenol solubility. It was apparent that increased density in the vapor phase resulted in increased solute solubility in the vapor phase.

Table 1. Mole Fraction Phenol in Supercritical Carbon Dioxide at 40 degrees Celsius

10,000 ppm				5,000 ppm				2,500 ppm			
Press	Mole Fraction Phenol			Press	Mole Fraction Phenol			Press	Mole Fraction Phenol		
(Psig)	Exp. 1	Exp. 2	Ave.	(Psig)	Exp. 1	Exp. 2	Ave.	(Psig)	Exp. 1	Exp. 2	Ave.
1100	0.000095	0.00013	0.00011	1100	0.00012	0.000086	0.00010	1100	0.000069	0.000071	0.000070
1200	0.00026	0.00022	0.00024	1200	0.00020	0.00019	0.00020	1200	0.000048	0.000068	0.000058
1400	0.00034	0.00032	0.00033	1400	0.00016	0.00022	0.00019	1400	0.000096	0.00011	0.00010
1800	0.00051	0.00087	0.00069	1700	0.00025	0.00034	0.00030	1700	0.00013	0.00015	0.00014
2600	0.00080	0.00083	0.00082	2000	0.00057	0.00039	0.00048	2000	0.00018	0.00019	0.00019
				2800	0.00060	0.00041	0.00051	2800	0.00019	0.00027	0.00023

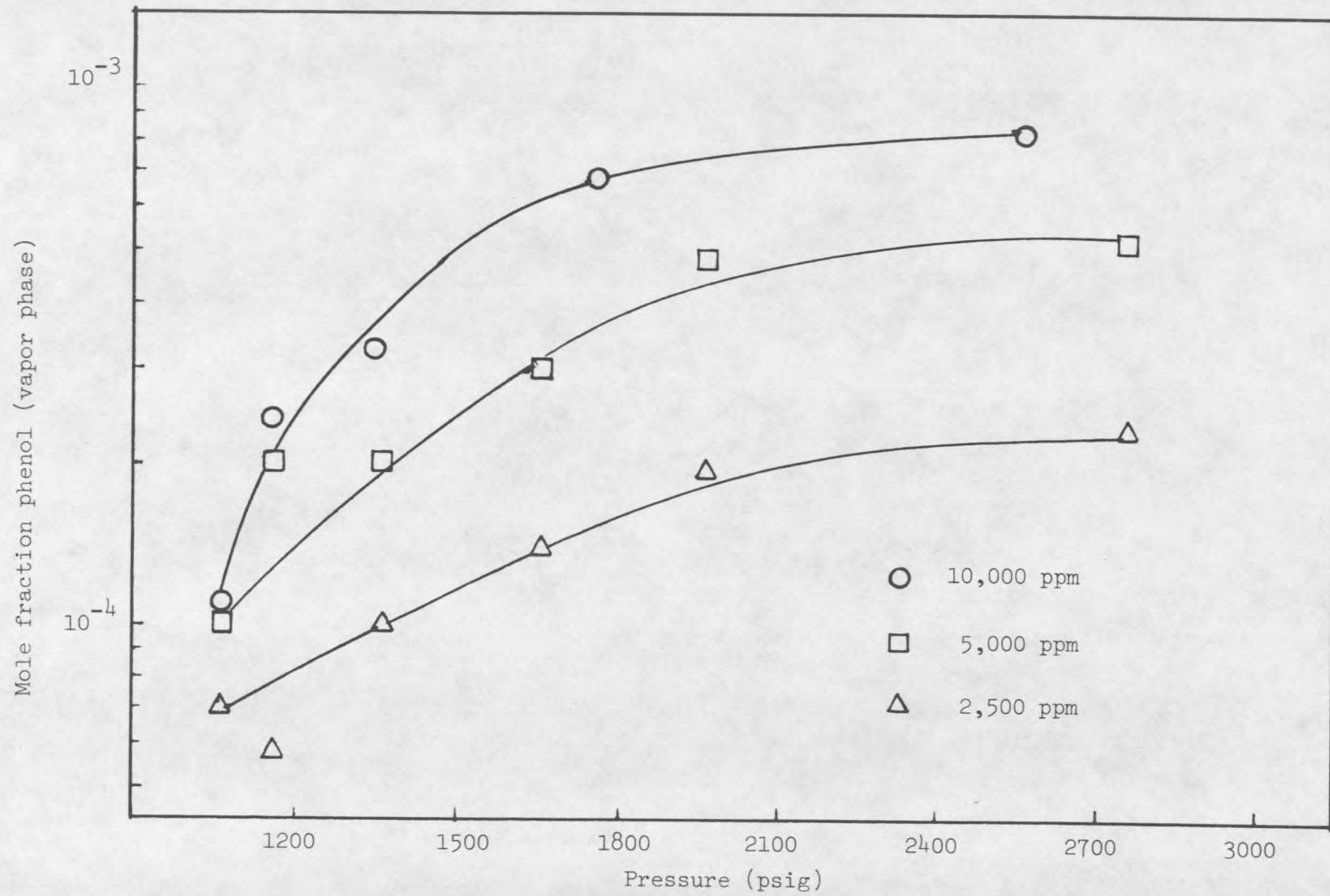


Figure 2. Experimental vapor phase phenol solubilities in supercritical carbon dioxide at 40 degrees Celsius

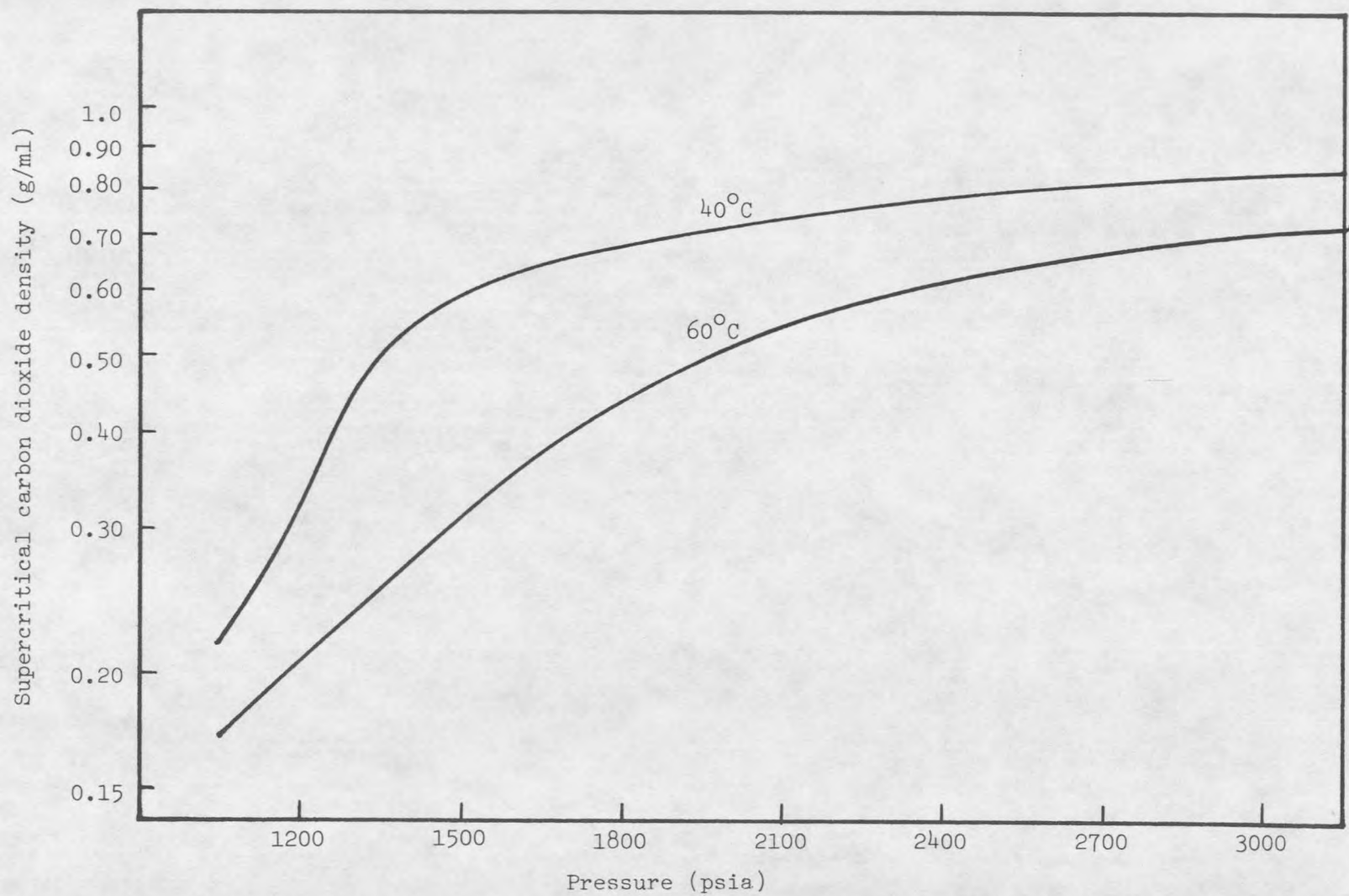


Figure 3. Supercritical carbon dioxide density as a function of pressure at 40 and 60 degrees Celsius

