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SOLUBILITIES OF SUBSTITUTED PHENOLS IN SUPERCRITICAL FLUID CARBON DIOXIDE

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Introduction

In recent years, there has been increased interest in supercritical fluid (SCF) technology. SCF extractions/separations are utilized in industry for various processes.
The unique feature of supercritical fluids is that the solvent power strongly depends on the fluid density, which can be adjusted by controlling the temperature and pressure.
Carbon Dioxide (CO_2) is a commonly used supercritical solvent because of its low cost and its non-toxicity. Its industrial and analytical importance lies in the convenient critical parameters (31.1°C and 73.8 bar)

Substituted phenols are an important class of compounds having widespread use (germicides, disinfectants, ingredients in fuel, etc.) There is little information in the literature regarding the solubilities of phenols in SCF CO_2. Accurate and precise solubility data for the compounds of interest is essential for the design of any SCF-based process.

In this work, the solubilities of selected substituted phenols (2,5-dimethylphenol, 2,4,6-trimethylphenol, 2,3,5-trimethyl phenol, 4-phenylphenol, 4-tert-butylphenol) in binary (single solute + SCF CO_2) and ternary (two solutes + SCF CO_2) systems were investigated.

Experimental Method

A schematic diagram of the apparatus is shown in Figure1. The apparatus was designed and built in-house (Fig 2). A microsampling technique with a dynamic flow of CO_2 was used to evaluate the solubility of the test solutes.

Procedure

An important feature of the apparatus is the use of two 6-port switching valves (Fig 3.) The first switching valve is used to direct the flow of the supercritical CO_2 either through the equilibration cell containing solute/solutes or to bypass the cell and purge the rest of the system. The second switching valve is used as a sampling valve. Switching of the sampling valve allowed for the escape of a fixed volume of the saturated SCF solution from the sample loop into a trapping solvent. Solvent is pumped through the sample loop and sampling valve to flush any precipitated solutes into the trapping solvent. The trapping solvent is then diluted to a known volume in preparation for analysis.

Chromatographic conditions

Detection	UV-265/280 nm
Separation column	Spherisorb ODS 2, 5 μ
Mobile Phase	0.01M KH_2PO_4:MeOH (40:60); 1mL/min flow rate

Solubility of the solutes is expressed as mole fraction solubility(y)

$$y = \frac{\text{number of moles of the solute}}{\text{total moles of saturated solution in sampling loop}}\ *$$

Area-concentration curves were used to determine the concentration of the collected analytes. A new calibration curve was made each time an analysis of sample solutions was conducted.

Individual solubilities were determined by taking an average of at least three replicate measurements made on separate days.

The reproducibility of the results was generally ±5% or less.

*approximated as moles of CO_2

Results and Discussion

Validation

The reliability and accuracy of our solubility measurement technique was previously established by measuring the solubility of naphthalene in CO_2.[1]The validity of the solubility data was reconfirmed by comparing the binary solubility of 2,5-dimethyl phenol with that reported by Iwai et al.[2]

Binary solubility

Binary solubilities of 2,5-dimethylphenol (2,5-DMP), 2,4,6-trimethylphenol (2,4,6-TMP), 2,3,5-trimethylphenol (2,3,5-TMP), 4-phenyl phenol (4-PP), and 4-tert-butylphenol (4-tBuP) were measured at 308 K over a range of pressures (101-280 bar).

Ternary solubility

It has been observed that in mixed solute systems the solubility of the components in SCFs may be considerably different from their respective binary solubilities.[3] Recent studies on polar multicomponent systems have indicated solubility enhancements, which could be associated with strong solute-solute interactions such as hydrogen bonding.[1,4] Solubility enhancements usually follow a pattern where solubility of one component is enhanced in proportion to the solubility of the other component in the ternary system[5] (entrainer effect).[6]

Three ternary systems 4-PP and 2,3,5-TMP; 4-PP and 2,4,6-TMP; and 2,5-DMP and 4-tBuP were investigated at 308 K over a range of pressures.

Discussion

Binary solubility

Binary solubilities of substituted phenols ranged from 10^{-5}-10^{-2} mole fraction and varied in the following order- 2,4,6-TMP > 2,5-TMP > 4-tBuP > 2,3,5-TMP > 4-PP. Binary solubilities show a regular trends of increased solubility with increased pressure (solvent density).

Ternary solubility

The ternary systems of 2,3,5-TMP/4-PP and 2,4,6-TMP/4-PP conform to the entrainer effect, with 4-PP showing enhancements up to 21% and 233%, respectively, while no enhancement occurred with the two other solutes. The ternary system of 2,5-DMP/4-tBuP exhibited an unusual behavior where the solutes had more than 1000% solubility enhancement while the individual solubilities decreased with increased pressure. This degree of solubility enhancement is very uncommon in mixed solid systems.There could be a possible shift in the LCEP of this mixture from the critical point of pure SCF CO_2. This ternary system is still under investigation.

Technical difficulties

The micrometering valve, which serves as a pressure reducer, was heated to minimize solute plugging. Though the heated valve worked effectively for most of our solutes, in cases of extremely high solubility plugging problems were frequent, which led to poor reproducibility in our solubility measurements.

Phase Behavior

The phase behavior of organic solids in CO_2 can be quite complex. Pure solids may undergo depression in melting point under the influence of high pressure CO_2,[7] which could be more significant in mixed solute systems[8]. In order to ensure that only solid-fluid equilibrium conditions exist, we visually check the lower critical end point (LCEP)[9] and the possible depression in the melting point of solutes in SCF CO_2. The LCEP of solute systems is usually very close to the critical point of pure SCF, which is characterized by critical opalescence.

Experimental section

The SFT Phase Monitor (Supercritical Fluid Technologies, Inc.) consists of a variable-volume view cell equipped with quartz windows, a movable piston, a mixer, a variable focus video camera, and a monitor (Fig 4.)

To check for melting, the solute was placed in the view cell and the system was pressurized slowly at 308 K to the maximum pressure used in this work.

No depression in the melting point was observed in any of the systems investigated. The LCEP determinations of the solute systems are in progress.

References

1. Ravipaty, S.; Chesney, D. J.
   Presented at the Pittsburgh Conference, New Orleans, LA, March 2001; paper 1753P.

2. Iwai, Y.; Yamamoto, H.; Tanaka, Y.; Arai, Y.
   J. Chem. Eng. Data **1990**, *35*, 174-176.

3. Kurnik, R.T.; Reid, R.C.
   Fluid Phase Equilib. **1982**, *8*, 93

4. Lucien, F. P.; Foster, N. R.
   J. Chem. Eng. Data **1998**, *43*, 726-731.

5. Dobbs, J. M.; Johnston, K.P.
   Ind. Eng. Chem. Res. **1987**, *26*, 1476.

6. Lucien, F. P.; Foster, N. R.
   J. Supercrit. Fluids **2000**, *17*, 111.

7. McHugh, M. A.; Yogan, T. J.
   J. Chem. Eng. Data **1984**, *29*, 112-115.

8. Zhang, D.; Adachi, Y.; Lu, B. C. Y.
   Proc. Int. Symp. Supercrit. Fluids **1988**, *1*, 19.

9. McHugh, M.A.; and Krukonis, V. J.
   Butterworths: Boston, 1986; Chapter 3.

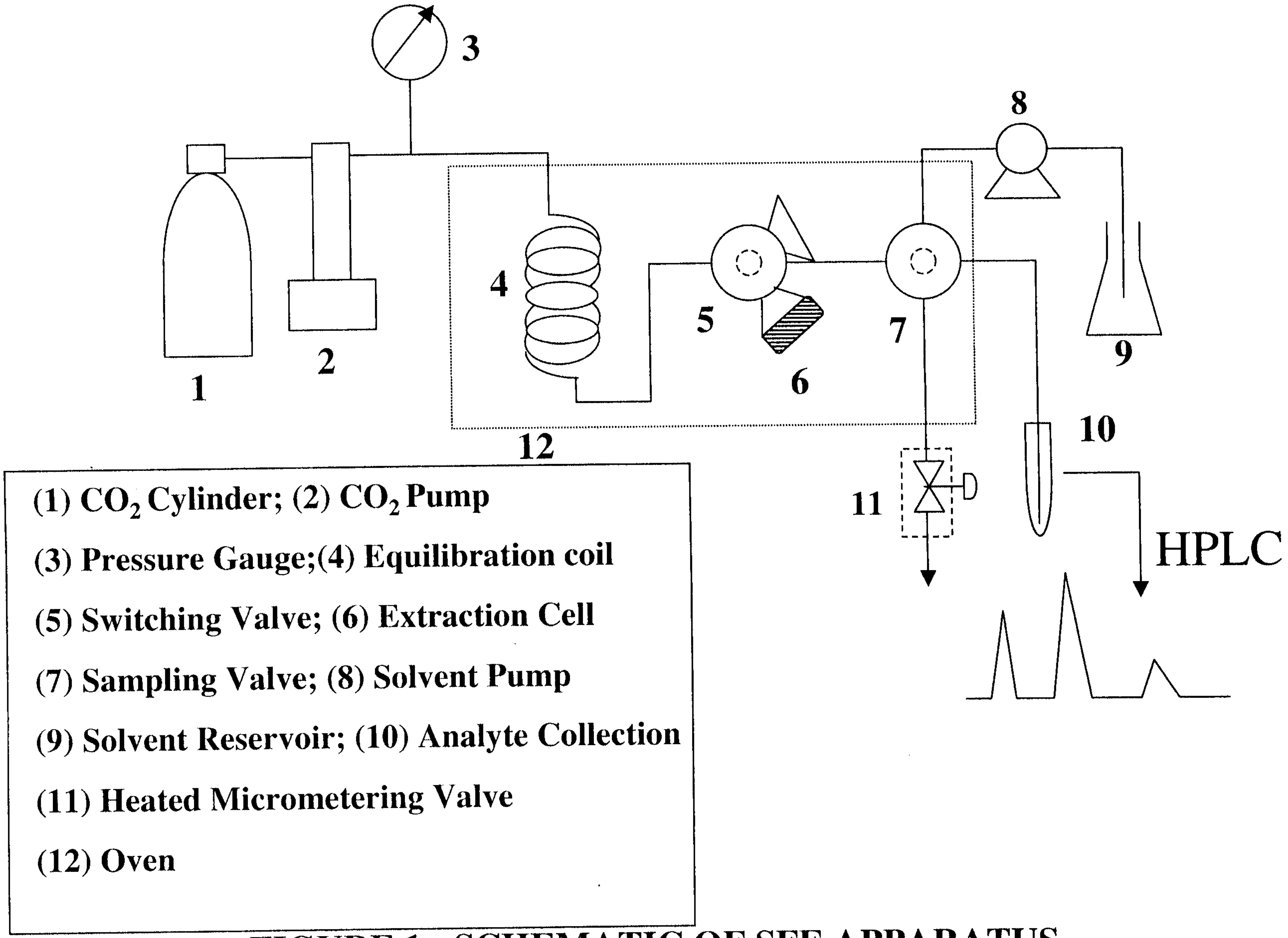


FIGURE 1: SCHEMATIC OF SFE APPARATUS

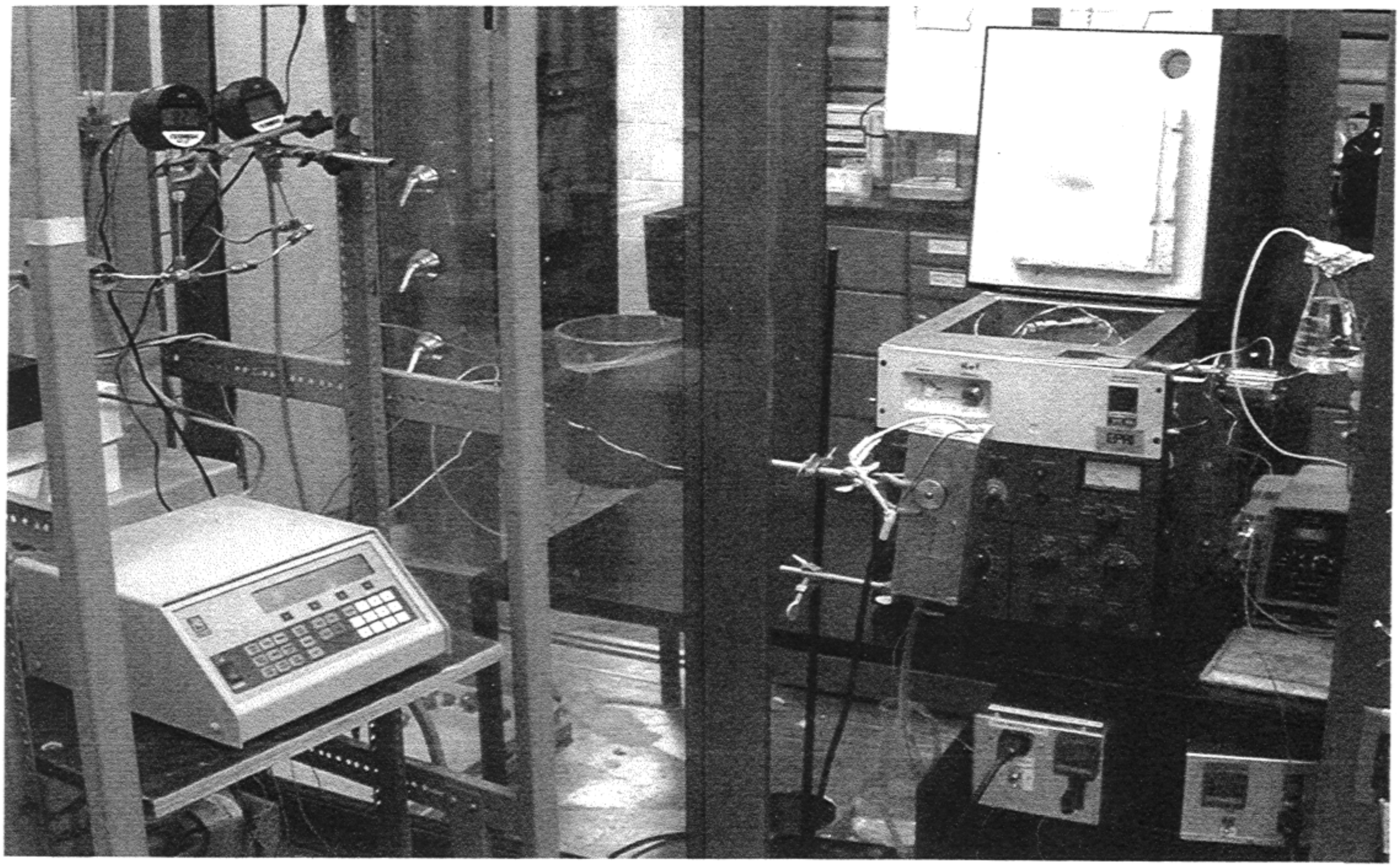


FIGURE 2: SFE APPARATUS

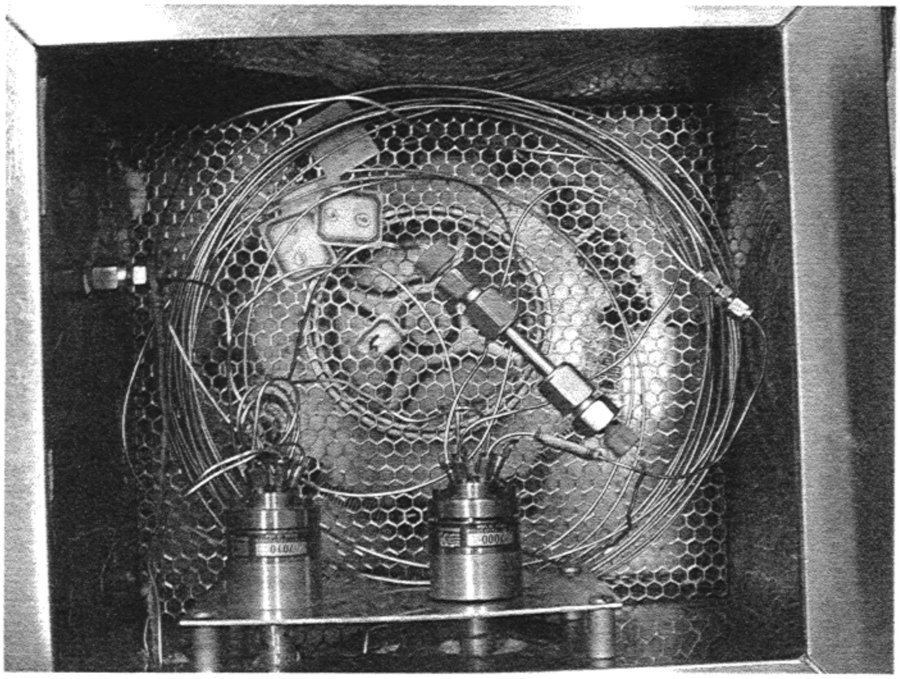
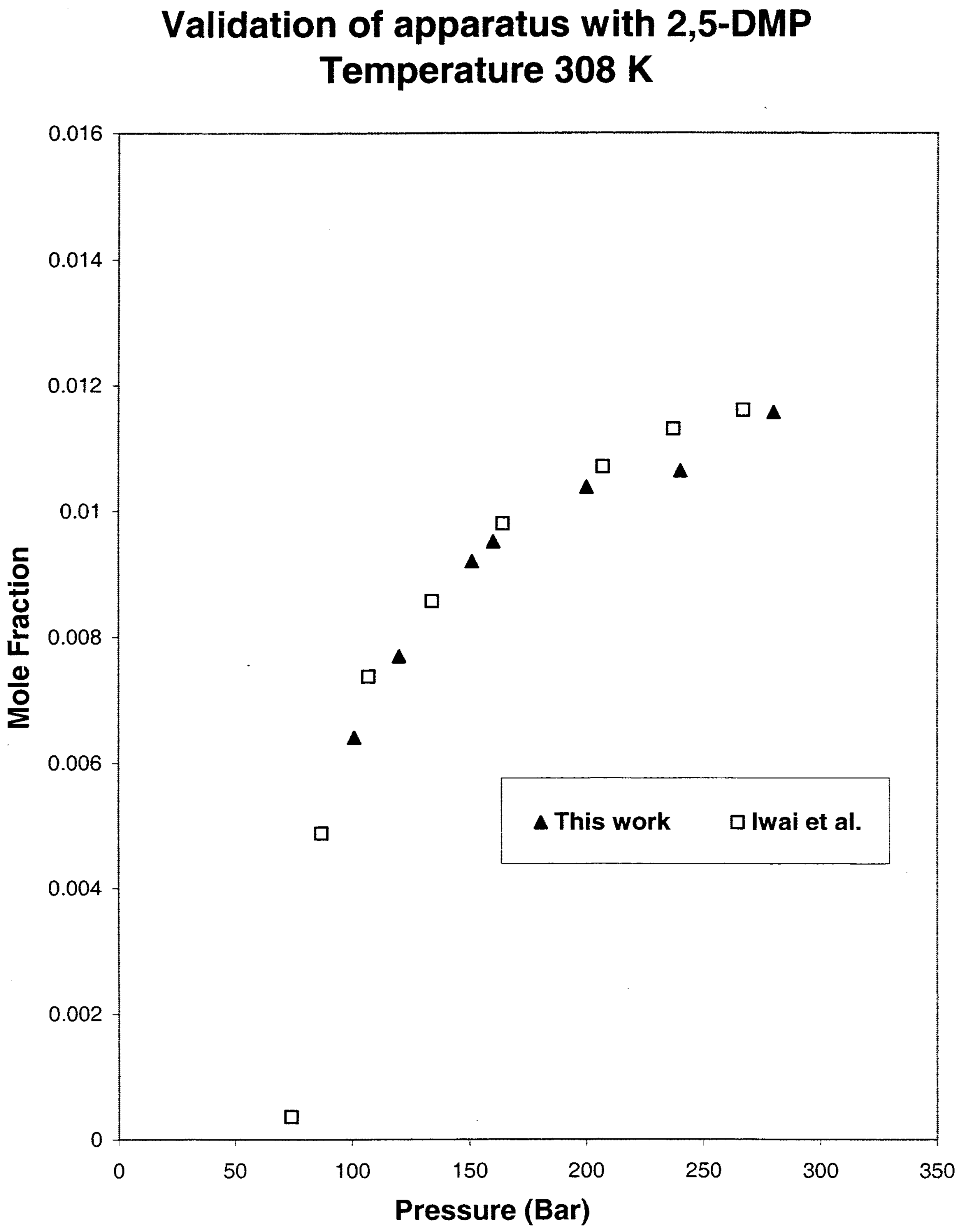
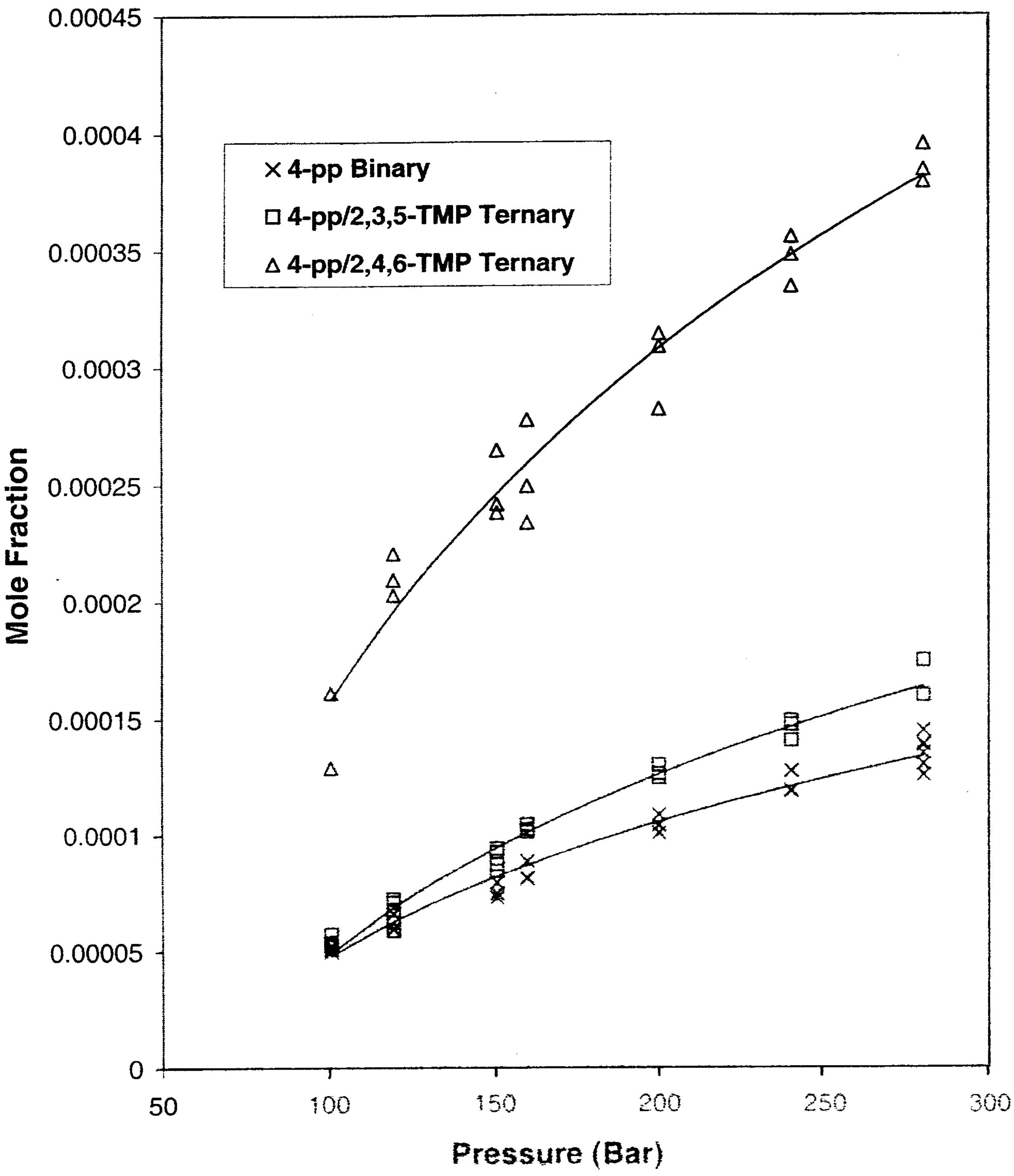


FIGURE:3
INTERIOR OF THE OVEN SHOWING THE SWITCHING VALVES, EQUILIBRATION COIL AND THE CELL

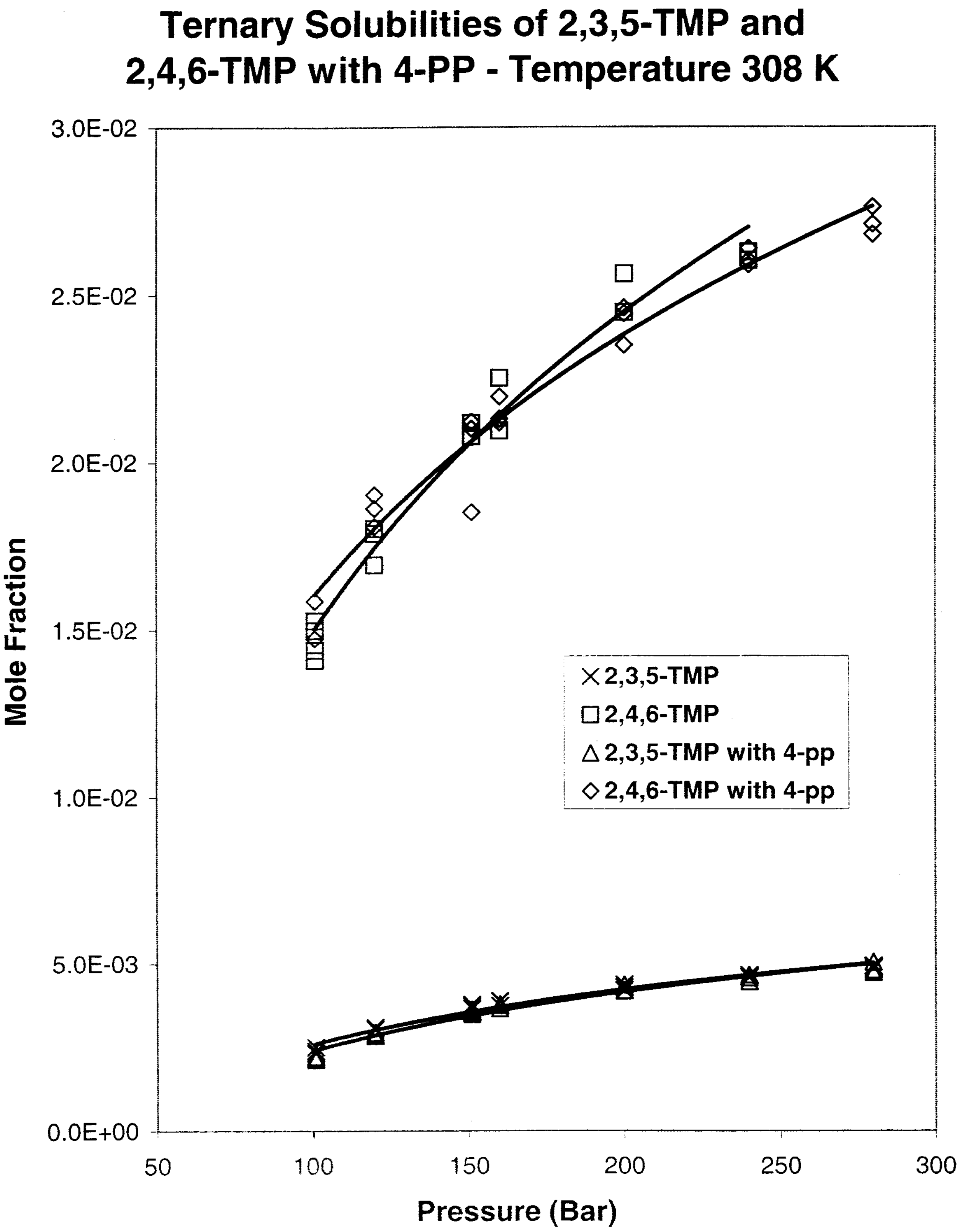
Phase Behavior

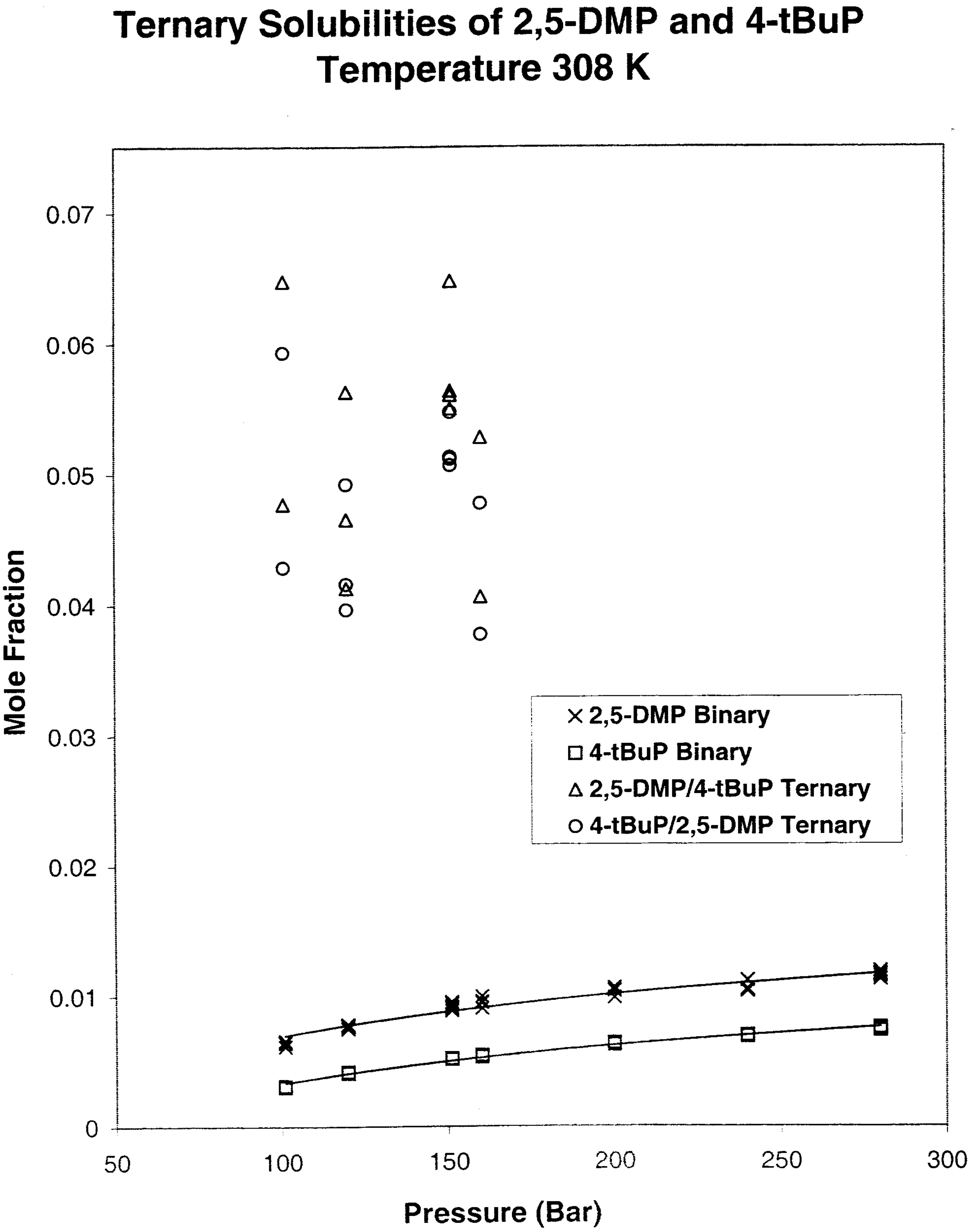
FIGURE 4: HIGH PRESSURE VIEW CELL


Validation of apparatus with 2,5-DMP
Temperature 308 K
Mole Fraction
0.016
0.014
0.012
0.01
0.008
0.006
0.004
0.002
0
Pressure (Bar)
0
50
100
150
200
250
300
350
▲ This work
□ Iwai et al.



Ternary Solubilities of 4-PP with 2,3,5-TMP and 2,4,6-TMP, Temperature 308 K


Ternary Solubilities of 2,3,5-TMP and 2,4,6-TMP with 4-PP - Temperature 308 K
Mole Fraction
3.0E-02
2.5E-02
2.0E-02
1.5E-02
1.0E-02
5.0E-03
0.0E+00
50
100
150
200
250
300
Pressure (Bar)
× 2,3,5-TMP
□ 2,4,6-TMP
△ 2,3,5-TMP with 4-pp
◇ 2,4,6-TMP with 4-pp



Ternary Solubilities of 2,5-DMP and 4-tBuP
Temperature 308 K

Table I: Binary Solubilities of Substituted Phenols at 308 K (Mole Fraction)

Pressure (Bar)	4-PP 10^5y	2,3,5-TMP 10^3y	4-tBuP 10^3y	2,4,6-TMP 10^2y	2,5-DMP 10^3y
101	5.139	2.413	3.090	1.469	6.403
120	6.334	3.092	4.145	1.761	7.697
151	7.547	3.713	5.188	2.091	9.199
160	8.356	3.812	5.386	2.173	9.514
200	10.43	4.274	6.293	2.506	10.38
240	12.19	4.605	6.930	2.615	10.63
280	13.57	4.882	7.441		11.57

Table II: Ternary Solubilities and S.E.* of Substituted Phenols at 308 K (Mole Fraction)

Pressure (Bar)	4-pp w 2,3,5-TMP		4-pp w 2,4,6-TMP		2,3,5-TMP w 4-pp	
	10^5y	S.E.	10^4y	S.E.	10^3y	S.E.
101	5.466	6.4%	1.452	183%	2.196	-9.0%
120	6.634	4.7%	2.111	233%	2.883	-6.8%
151	8.948	18.6%	2.484	229%	3.551	-4.4%
160	10.27	22.9%	2.539	204%	3.726	-2.3%
200	12.70	21.8%	3.018	189%	4.238	-0.8%
240	14.58	19.6%	3.464	184%	4.555	-1.1%
280	16.44	21.1%	3.866	185%	4.855	-0.6%
Average S.E.		16.4%		201%		-3.6%

Pressure (Bar)	2,4,6-TMP w 4-pp		2,5-DMP w 4-tBuP		4-tBuP w 2,5-DMP	
	10^2y	S.E.	10^2y	S.E.	10^2y	S.E.
101	1.530	4.2%	5.624	4343.4%	5.108	1553%
120	1.858	5.5%	5.348	3808.6%	4.792	1056%
151	2.024	-3.2%	5.804	3964.2%	5.196	902%
160	2.149	-1.1%	4.672	2769.2%	4.275	694%
200	2.419	-3.5%				
240	2.611	-0.2%				
280	2.718					
Average S.E.		0.3%		3721.4%		1051%

*S.E. is Solubility Enhancement defined by [(Ternary Solubility - Binary Solubility)/Binary Solubility]