

SOLUBILITY OF THIOPHENE IN SUPERCRITICAL CARBON DIOXIDE AT TEMPERATURES FROM 314 TO 363 K.

O. Elizalde-Solis, V. Serrano-Cocoletzi and L. A. Galicia-Luna*

Instituto Politécnico Nacional, ESQIE, Laboratorio de Termodinámica, Edif. Z, Secc. 6, 1^{ER} piso, UPALM Zacatenco, 07738, Lindavista, México, D. F., México.

ABSTRACT

The extractions of sulfur components from oil cuts are very important at the refining industry, in special the extraction of Thiophene and Benzothiophene from gasoline and diesel fuel.

It is important, as a first step in the development of new separation process, the knowledge of solubility behavior of Thiophene and Benzothiophene compounds in supercritical solvents. In this work a static analytic apparatus was used to determine experimental solubilities of Thiophene in supercritical carbon dioxide from 314 to 363 K.

Keywords: An apparatus for PVT data, EOS, Liquid densities

* **Corresponding Author**

INTRODUCTION

Phase equilibrium data are of great significance in the chemical and biotechnology industry, and for the development and validation of thermodynamic models. The design of separation processes in general, and supercritical fluid extraction in particular, strongly depends on accurate vapor–liquid and vapor-liquid-liquid equilibrium data.

The extractions of sulfur components from oil cuts are very important at the refining industry, in special the extraction of Thiophene and Benzothiophene from gasoline and diesel fuel. In this work are presented solubility data of Thiophene in Carbon Dioxide from 324 to 363 K.

EXPERIMENTAL METHOD AND APPARATUS

The measurements were made in an apparatus (see Fig. 1) based on the static-analytic method [1] with an equilibrium cell that can be used up to 60 MPa and 673.15 K. This apparatus, which can be used to study one, two or three phase systems, is based on the same principle as described by Galicia-Luna et al. [1]. The apparatus consists of a cell of titanium alloy (TA6V) with an internal volume of 100 cm³. A pair of symmetrical titanium holders support sapphire windows on two sides of the cell, and two caps hold one movable RolsiTM [2] sampler for temperatures up to 473 K, or three fixed samplers for higher temperatures (up to 673 K). The movable capillary sampler MCS was used in this work. The capillary goes through CT (see Fig. 1) from the sampler to the inner part of the cell. A differential screw adjusts the path of the movable stem closing the extremity of the capillary. This path controls the pressure drop at the capillary exit, and therefore the amount of sample withdrawn in a given opening time (between 0.05 and 4 s).

The transfer circuit between the MCS and the gas chromatograph (HP 5890 II) was heated using a linear resistor coupled to a West 6100 regulator. The GC used a thermal conductivity detector TCD and a 4-ft by 1/8-in-diameter column packed with Chromosorb 101. The GC carrier gas was helium at a flow rate of 30 ml/min. The measurement of pressure was done using a thermoregulated Druck model PDCR transducer that was calibrated against a Desgranges & Huot dead weight gauge (Model 5304 Class S2, +/- 0.005% F.S. precision up to 138 MPa). Temperature was measured using two platinum

probes Pt100 (Specitec, France) in thermometric wells at the top and bottom of the body of the cell, and connected to a digital indicator (Automatic Systems F250, USA, accuracy ± 0.03 K). The platinum probes were calibrated against the calibration system F300S fitted with a 25- Ω reference probe (model 162CE of ± 0.005 K certified accuracy). For measurements up to 700 K, the temperature of the equilibrium cell is kept constant using the air bath AB.

We estimate the uncertainties in our measurements to be within ± 0.03 K for temperature and $\pm 0.04\%$ pressure. Composition uncertainties were less than 1% for Thiophene with a certified puritie of 99+ %, and was supplied by the Aldrich Chemical Co. Inc. Carbon dioxide and helium, both with certified purities of 99.995%, were supplied by Air Products-Infra. These substances were used without any further purification, except for careful degassing of the Thiophene.

The measurement procedure consisted of four steps:

- 1- sensor and detector calibrations as already described;
- 2- cell loading;
- 3- setting the experimental conditions; and
- 4- performing the equilibrium measurements.

The Thiophene was introduced into the equilibrium cell, ECT, and then degassed under vacuum during which the liquid was vigorously stirred with the magnetic rod MD. After 20 minutes of degassing, valve 1 was closed, and then reopened to introduce CO₂ into the measuring cell using an Isco syringe pump (100DM) until the desired pressure was achieved. Then the magnetic stirring device, MSD, under the equilibrium cell was activated to drive the magnetic rod contained in the ECT. A computer interface periodically read the temperature at the top and bottom of the cell; both temperatures must be the same, within experimental accuracy, at equilibrium. Once the total pressure became constant, measurements were made. Typically 120 minutes was required to reach equilibrium.

Isothermal phase envelopes were traced out by consecutive increments of pressure..

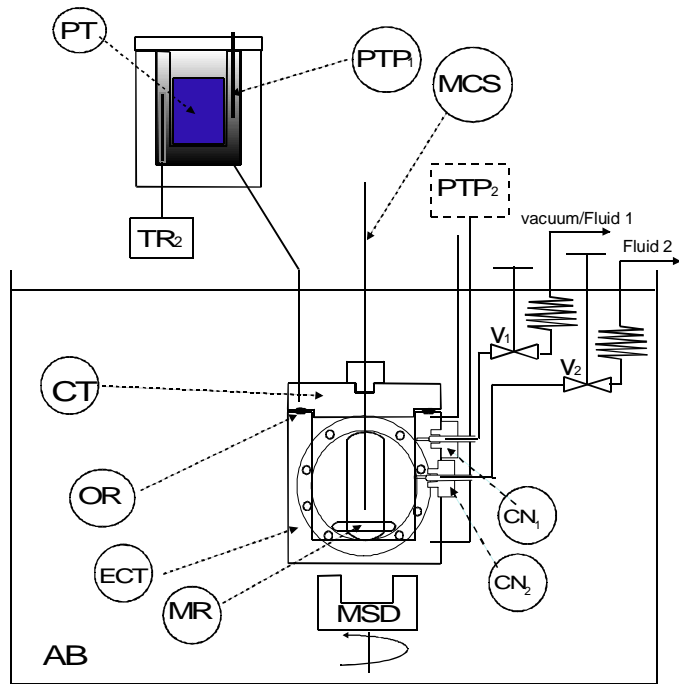
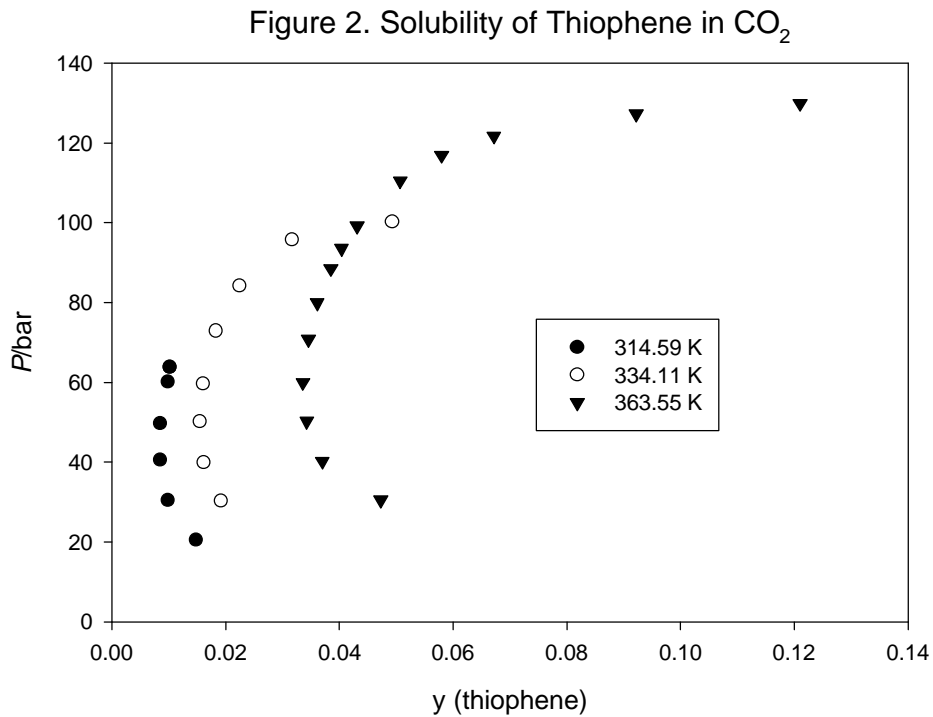


Figure 1. Flow diagram of the equilibrium cell: AB air bath; CT titanium cap; Cni connecting nuts; ECT titanium equilibrium cell; MCS movable capillary sampler; MR magnetic rod; MSD magnetic stirring device; OR O-ring; PT pressure transducer; PTPi platinum temperature probe; TRi thermal regulator I, and Vi :shut-off valve i.

EXPERIMENTAL RESULTS

Solubility data for the CO₂+Thiophene systems were obtained in this work at 314.59, 334.11 and 363.55 K. The results are plotted in Figure 2, where they show that the solubility of Thiophene increase with the temperature and pressure.



CONCLUSIONS

In this work a static-analytic apparatus was used to obtain the solubility of Thiophene in CO₂+ethanol mixtures at temperatures from 313 to 363 K

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