A High Pressure Fiber-Optic Reactor with Charged-Coupled Device Array Ultraviolet-Visible Spectrometer for Monitoring Chemical Processing in $SCCO_2$

LEE KWANG JAE

Thermodynamics and Green Processing Laboratory,
Dept. of Chem. Eng., Sogang Univ.

Objective

(1) A fiber-optic based reactor connected directly to a CCD array ultraviolet(UV) - visible spectrometer for *in situ* determination of reaction rates in supercritical carbon dioxide

(2) To measure the solubility in a supercritical dyeing process directly

(3) To measure dissolution rates

(4) To obtain a absorbance data from samples

Equipment type for measurement of solubility

(1) A Flow Type Method – Dymamic method
- the simplest experimental method
- being the clogging of the expansion valve due to dry ice formation
- dye particle precipitation
- becomes an obstacle to the correct solubility evaluation especially at high solute concentration

(2) A Batch Type Method – Static method
- hard to collect samples
- need to measure a volume accurately

(3) A Online Spectroscopic Method By Using Optical Fibers
- easy to measure an absorbance
- in situ observation of the phase equilibrium by VIS-spectroscopy

Theory

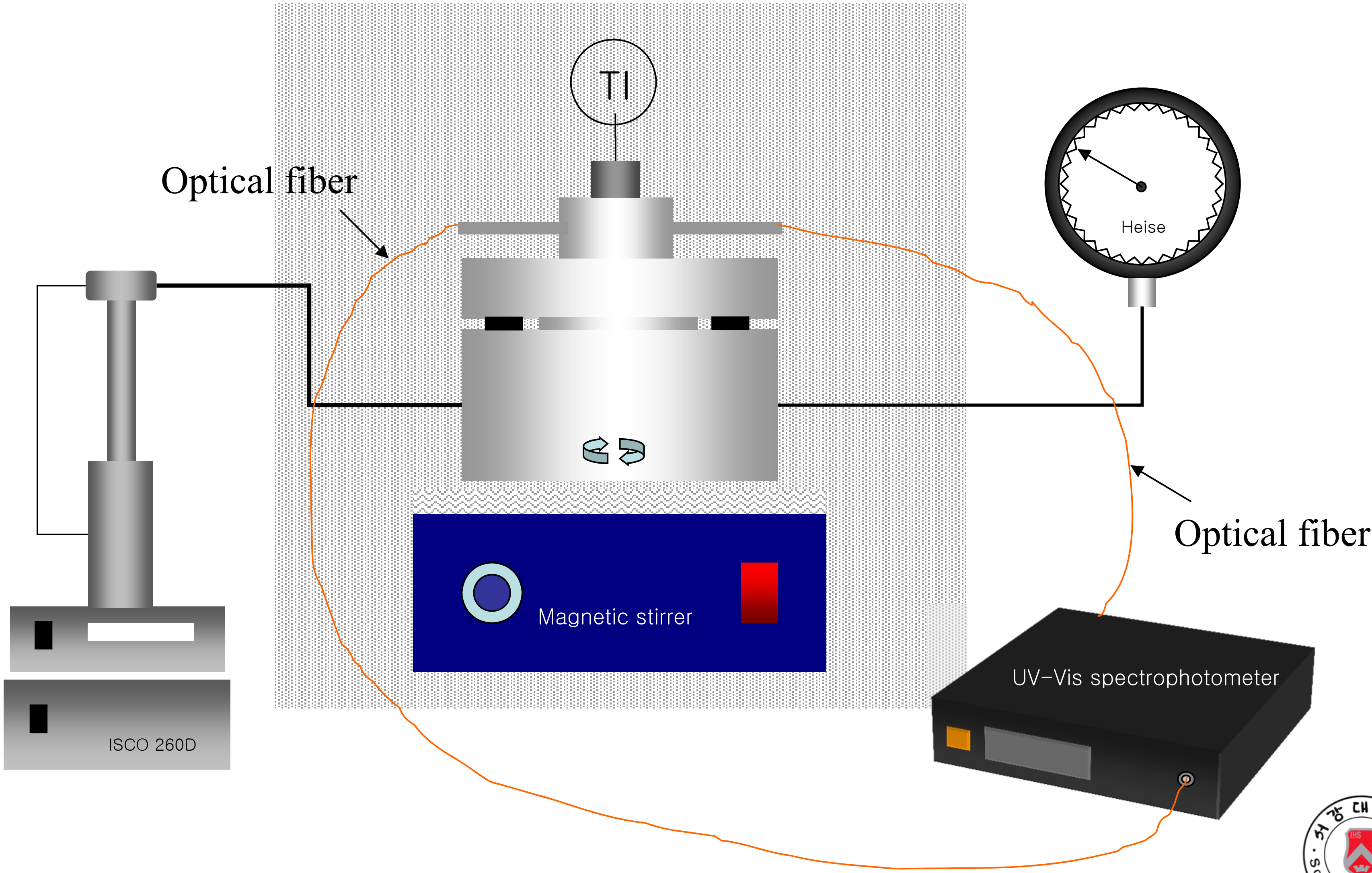
(1) Beer-Lambert's Law

$$A = \varepsilon l\ C$$

where, A = absorbance of sample
l = path length
C = concentration of sample
ε = optical density

(2) Hexane was used as the solvent for calibration because it has a polarity similar to that of CO_2 and has been shown to exhibit similar extinction coefficient and negligible shifts in the position of absorption maxima

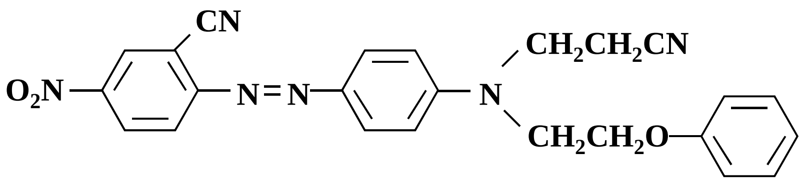
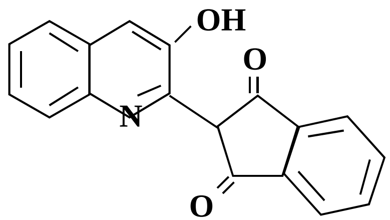
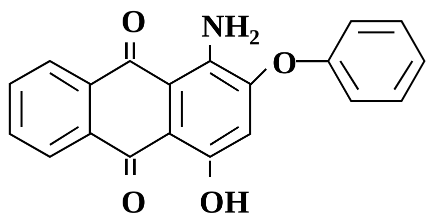
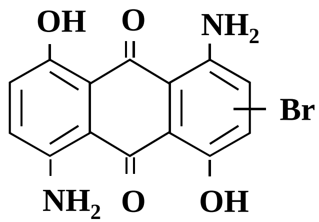
Experimental Apparatus



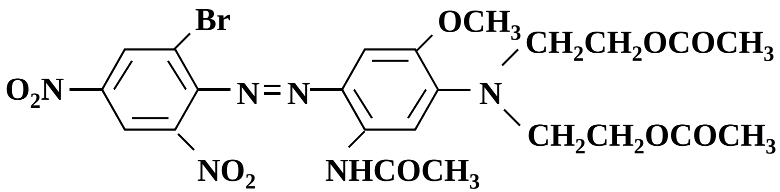
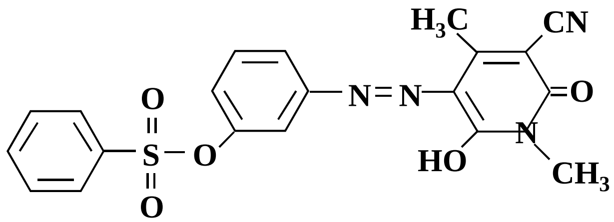
Specification of equipment

Parts	Specification
Optical Fiber	Ocean Optics, ID 600μm
PEEK tube	VICTREX, USA
UV-VIS Spectroscopy	Ocean Optics, USA with Xenon lamp
Pressure gauge	CMM-43776, HEISE, USA
High Pressure Reactor	house made
Syringe Pump	260D, ISCO, USA

Properties of materials

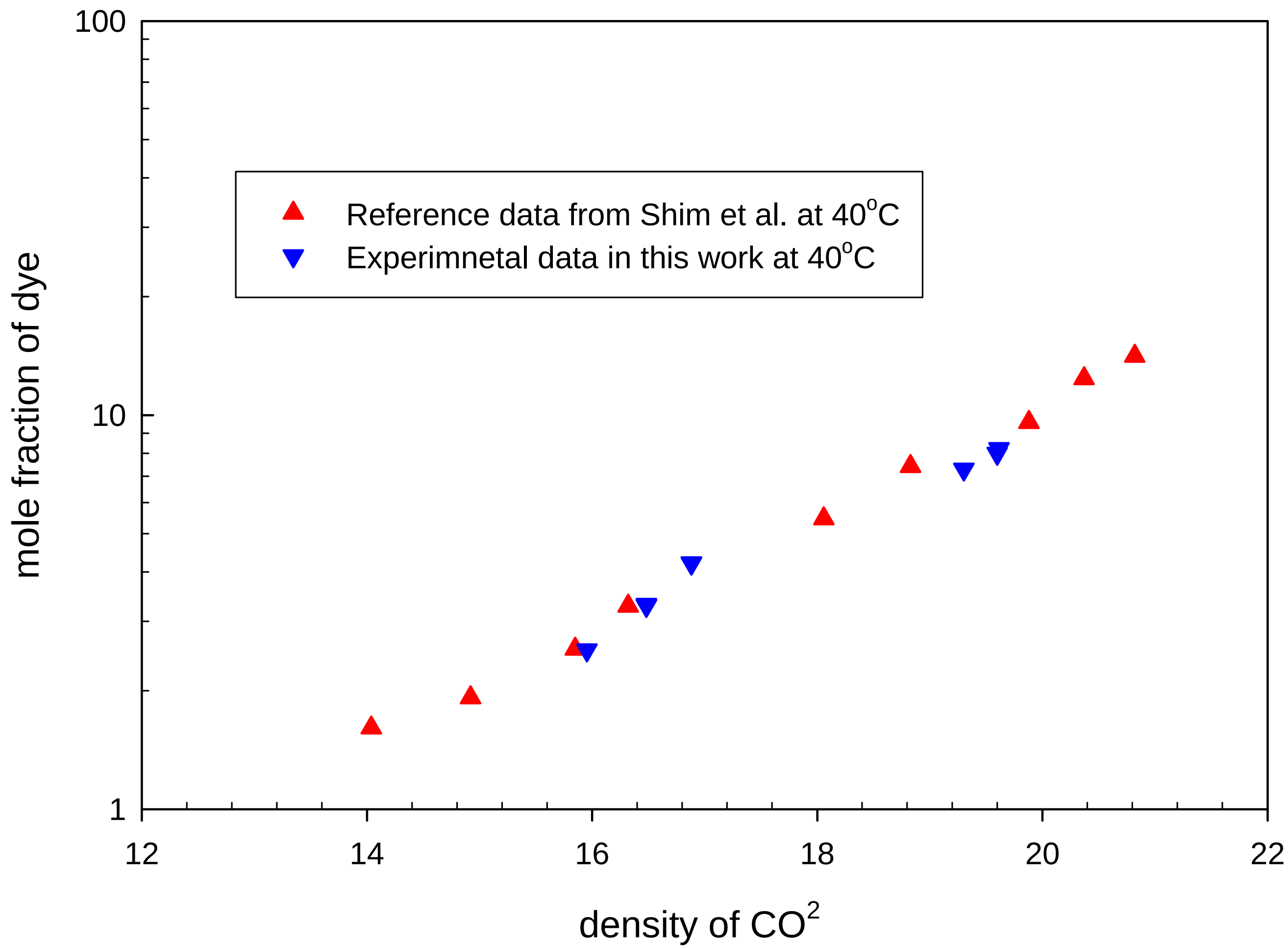
Type	Dyestuff	Formula	Mw
S	C.I. Disperse Red 360 (S type, mono-azoic)		440.45
E	C.I. Disperse Yellow 54 (E type, quinoline)		289.28
	C.I. Disperse Red 60 (E type, anthraquinone)		331.32
	C.I. Disperse Blue 56 (E type, anthraquinone)		365.18

Properties of materials

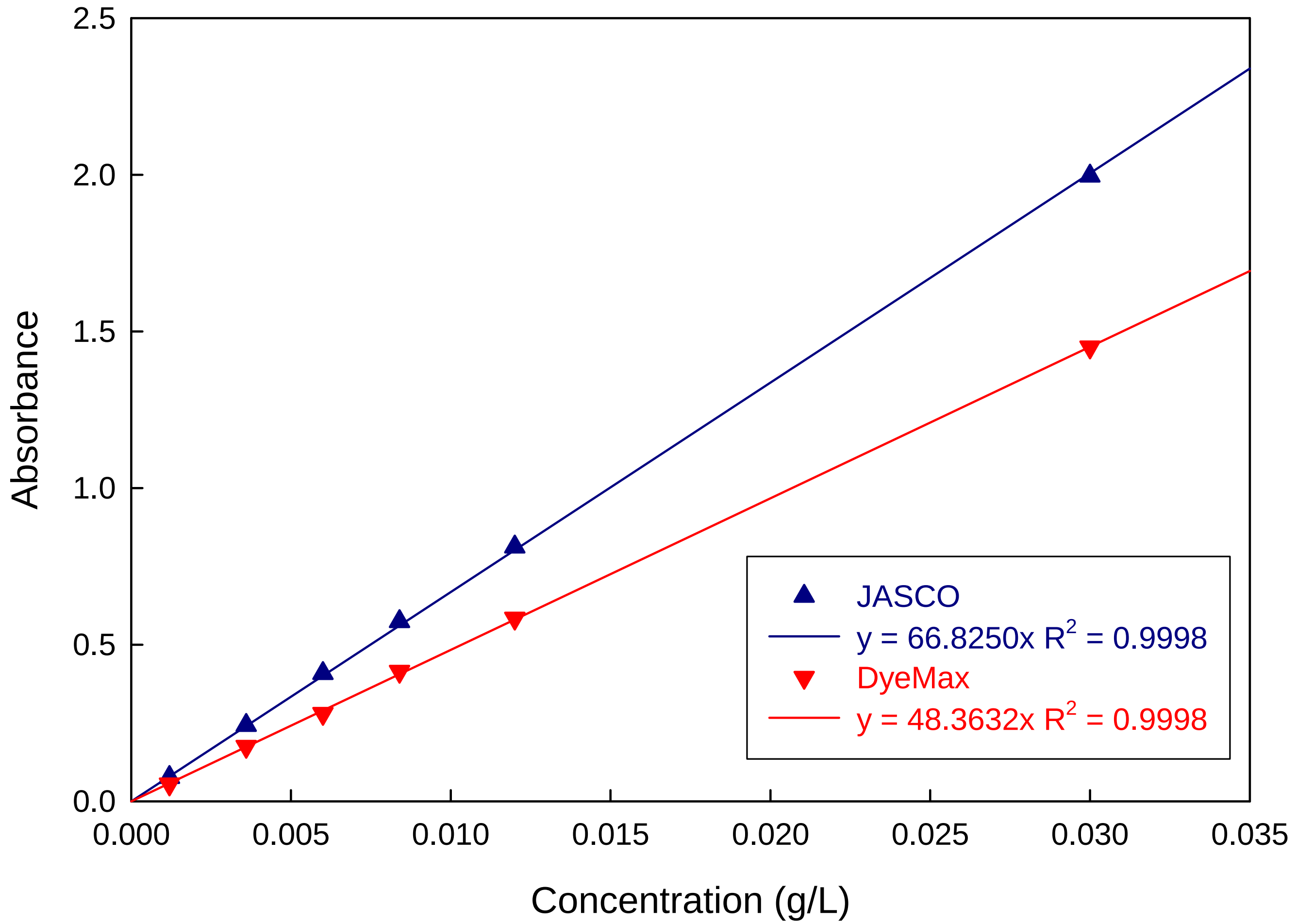
Type	Dyestuff	Formula	Mw
S	C.I. Disperse Blue 79.1 (mono-azoic)		530
	C.I. Disperse Yellow 114 (mono-azoin)		424.43

Materials	**Tc (K)**	**Pc (bar)**	**Specification**	**Mw**
Hexane	507.5	30.1	99.5%, HPLC grade, Adlich, USA	86.18
CO_2	304.1	73.8	99.9%, Daewoo gas, Korea	44.01

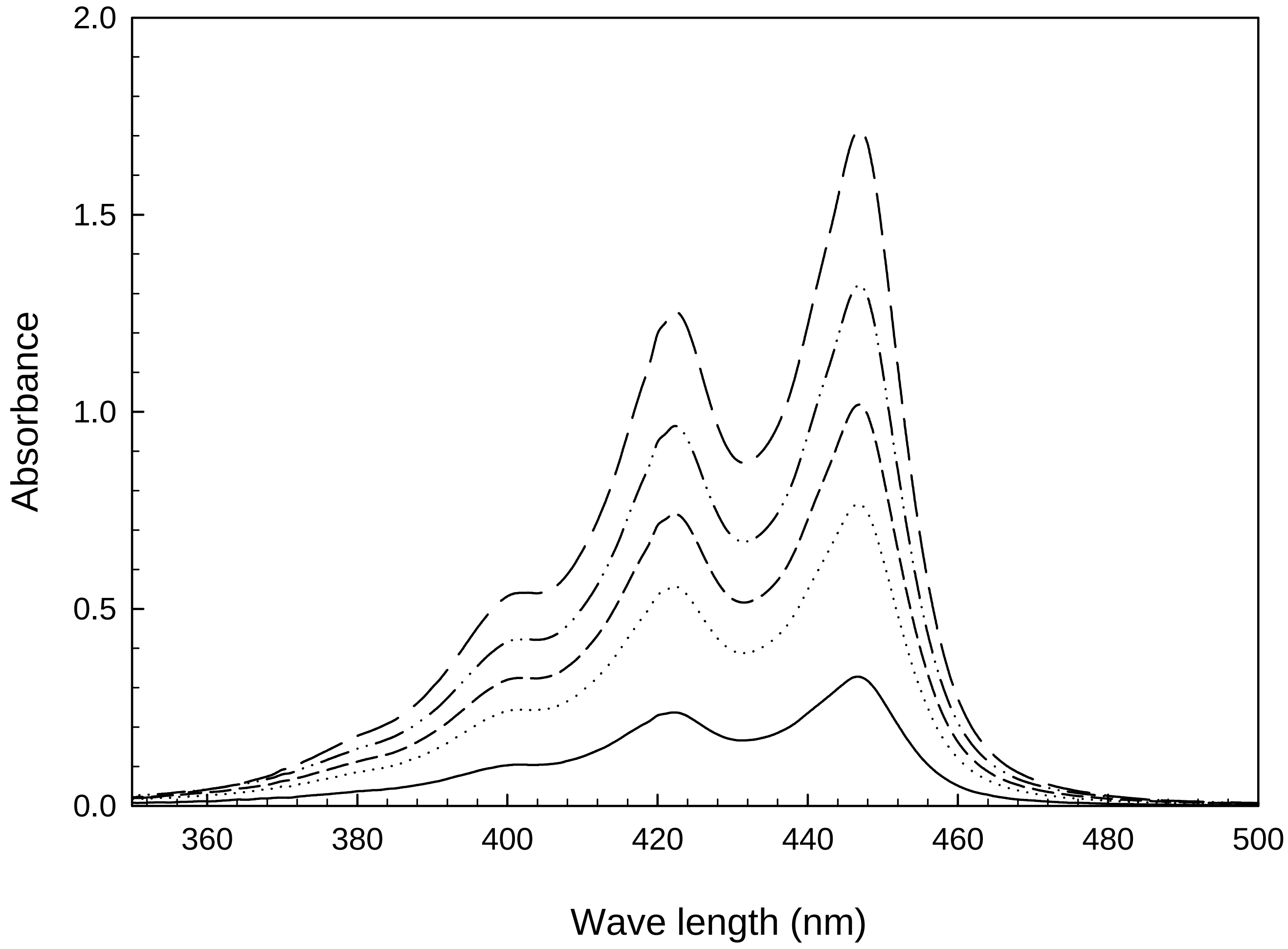
Comparison of data for DR 60



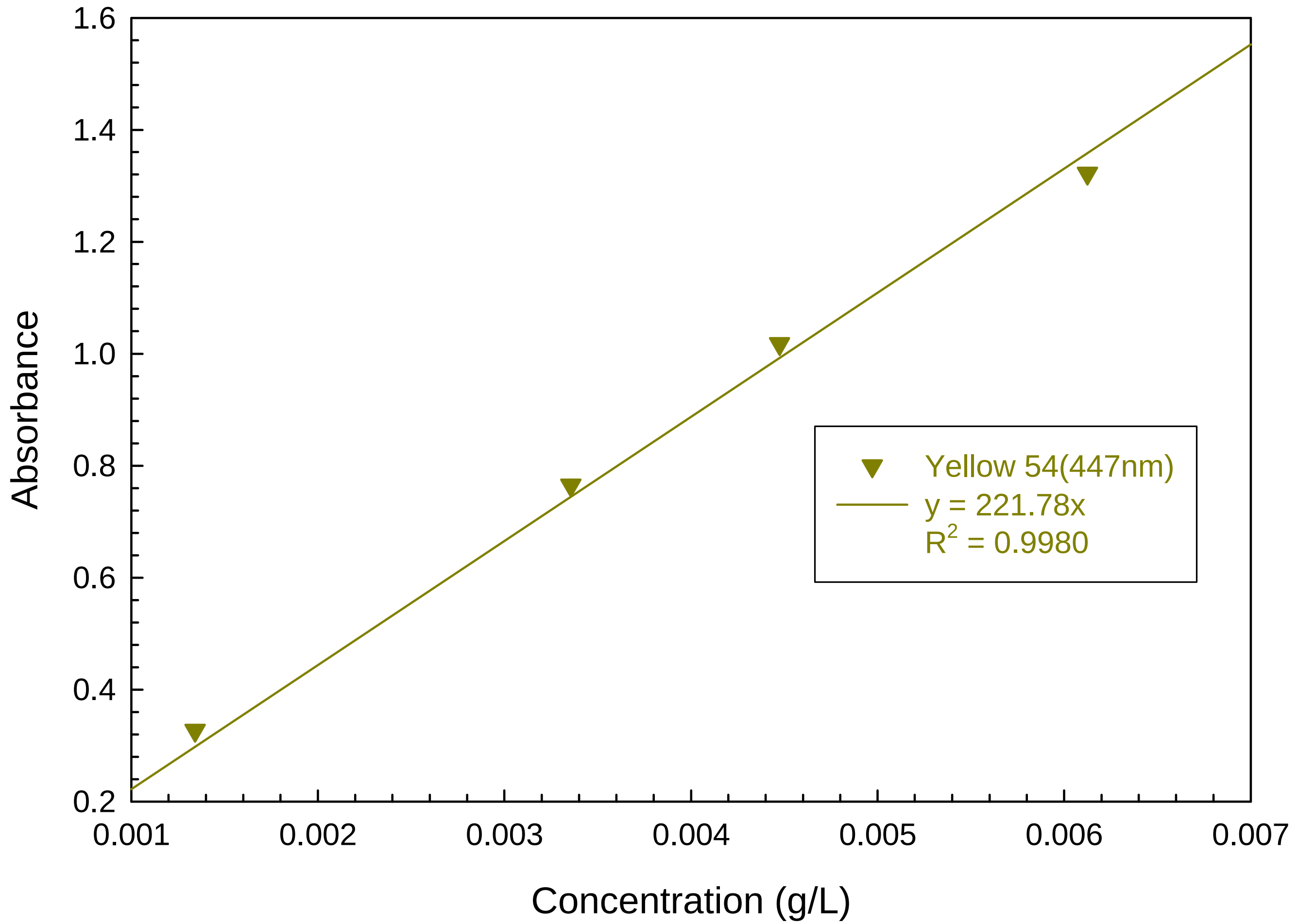
Determination of a path length



Absorbance curves for DY 54

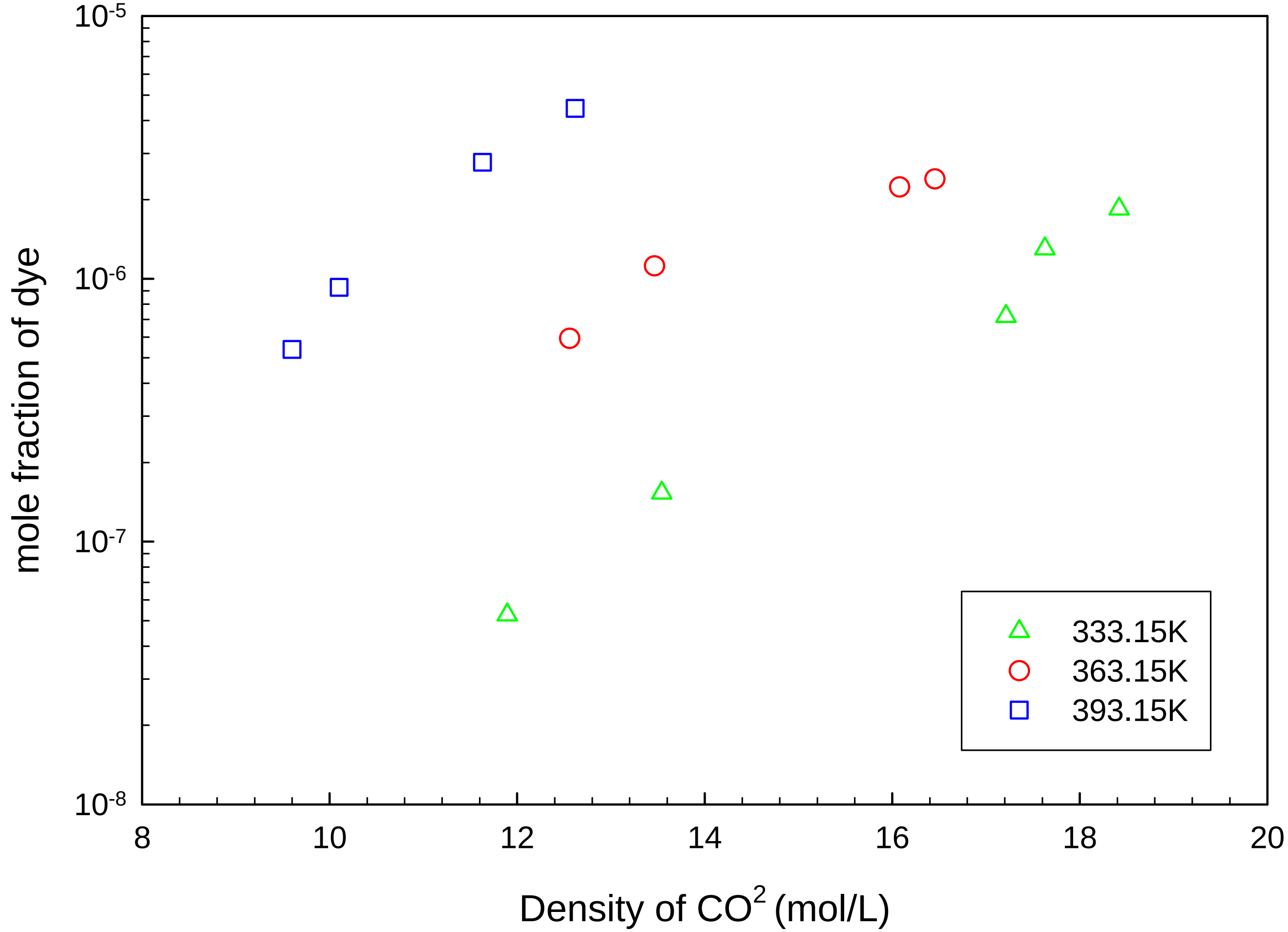


Determination of optical density for DY 54



Result

The Solubility data for DY 54 in $SCCO_2$



Conclusion and future works

(1) We can be obtained the solubility data of dye stuffs in $SCCO_2$ by using a *in situ* UV-VIS spectroscopy with optical fiber.

(2) The path length of the optical fiber in the reactor can be changed to suit the experimental needs. For example, the path length can be increased for measuring compounds with low solubilities.

(1) The obtained data will be correlated with empirical equation and MF-NLF equation of state.

(2) We will measure and correlate the solubility of various disperse dyestuffs in $SCCO_2$.