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Measurement of Solubility for Disperse Dyestuffs in SC-CO_2 by Using *in situ* Apparatus

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OBJECTIVES

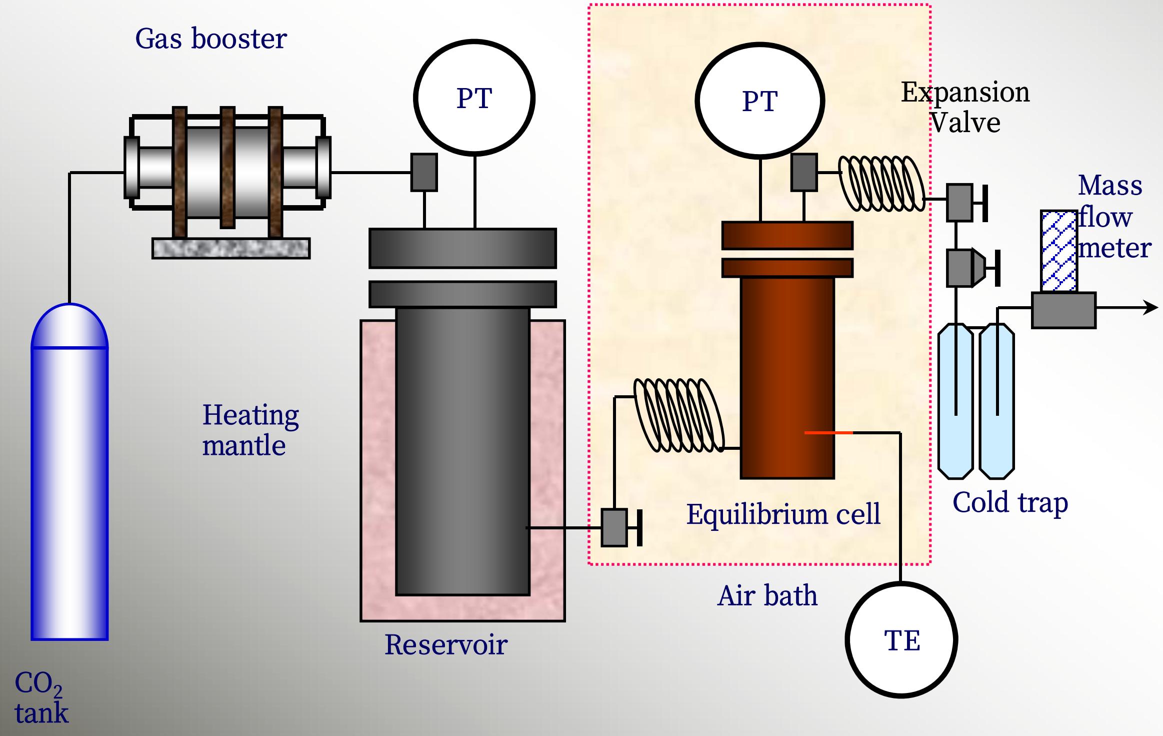
- Development of experimental apparatus and technique for measuring of solubility in supercritical carbon dioxide
- Measurement and correlation of solubility for dyestuffs in supercritical carbon dioxide
- Criteria of optimum conditions for SFD

BACKGROUND

▶ Classification of the experimental technique

- **Dynamic method**
  - *Continuous flow method*
  - *Circulated batch method*
- **Static method**

● Dynamic method - continuous flow method



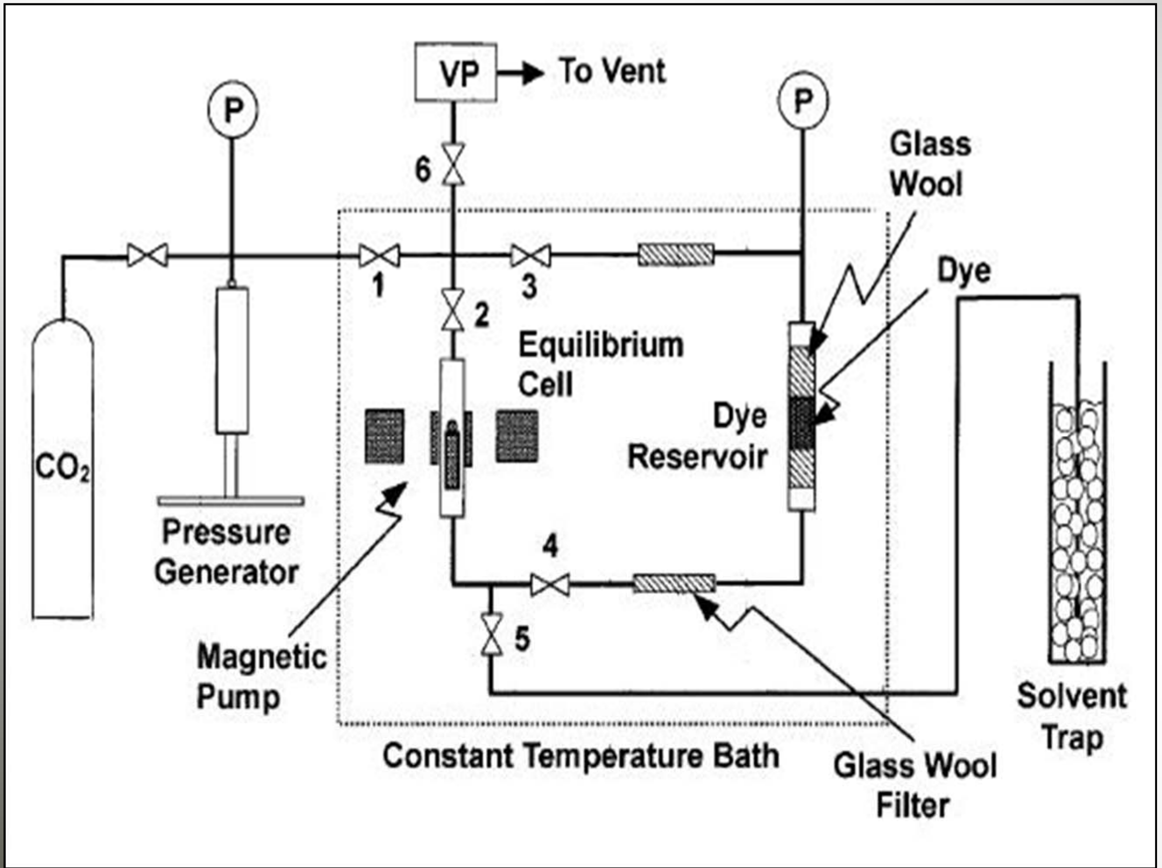
Advantage

- to be surely the simplest experimental technique
- easy to operate
- small leakage available

Disadvantage

- a complete equilibrium cannot be achieved
- clogging of expansion valve
  1) dry ice formation
  2) dye particle precipitation

● Dynamic method - circulated batch method



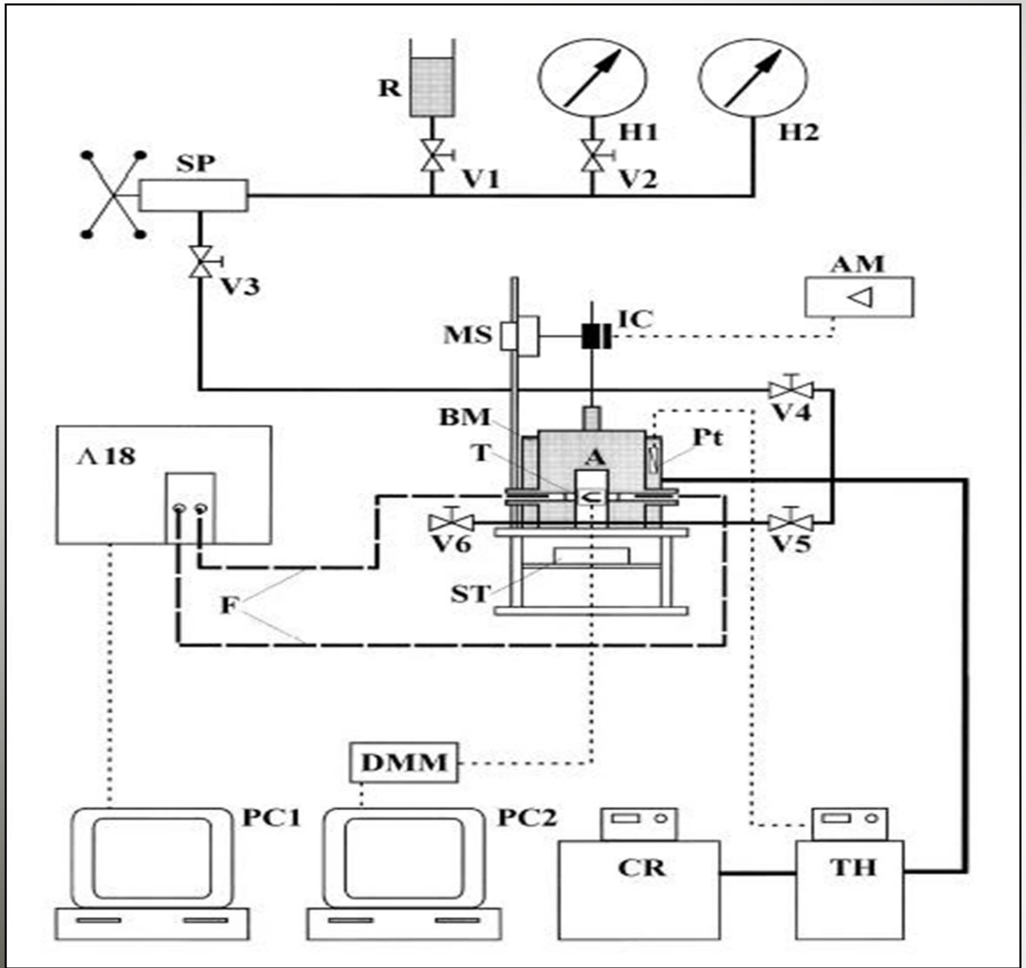
Advantage

- a complete equilibrium state can be achieved
- no clogging

Disadvantage

- the results are strongly influenced by a small leakage from the cell

● Static method



Advantage

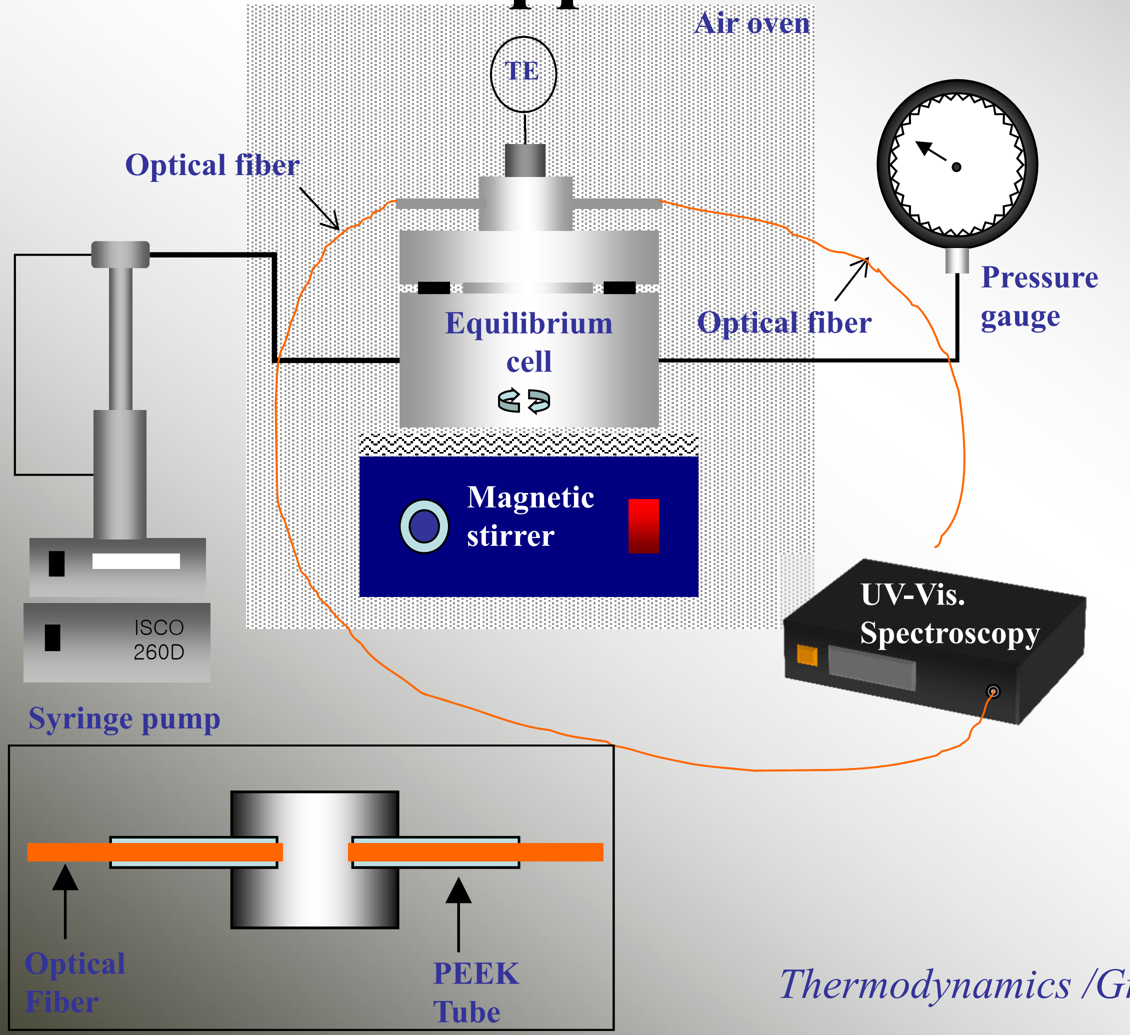
- easy to make equilibrium state
- no clogging
- a small leakage available

Disadvantage

- fixed path length
  - cannot measure the high solubility of solution
- high cost

EXPERIMENTAL

▶ House made apparatus used in this work



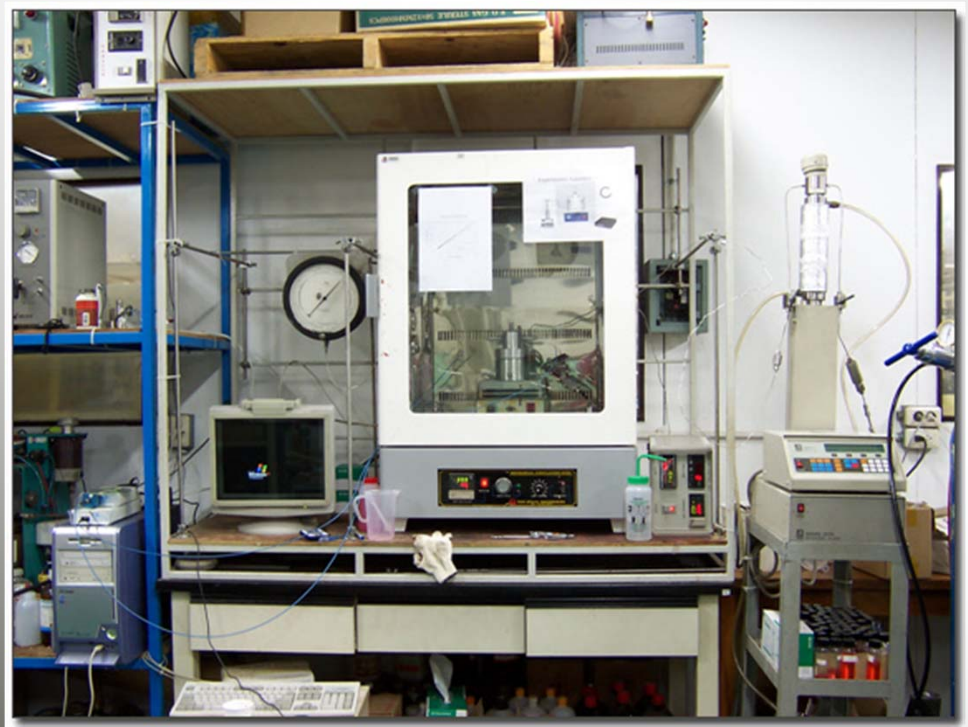
Advantage

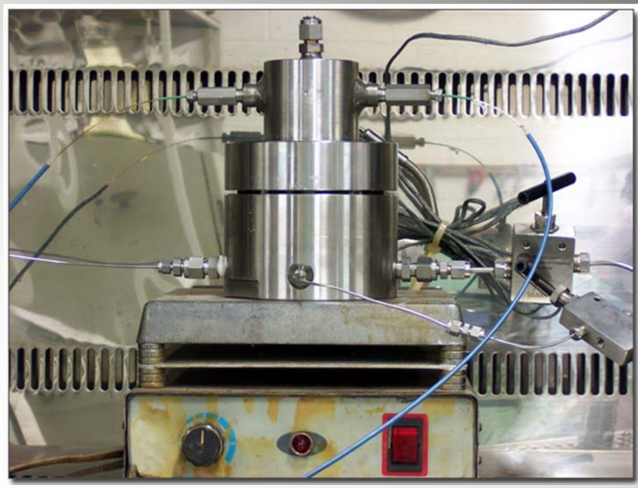
- can measure the solubility with *in situ* UV-Visible spectroscopy
- a complete equilibrium state can be achieved
- no clogging
- flexible path length
  - enable to measure over a concentration range of several orders of magnitude
- low cost

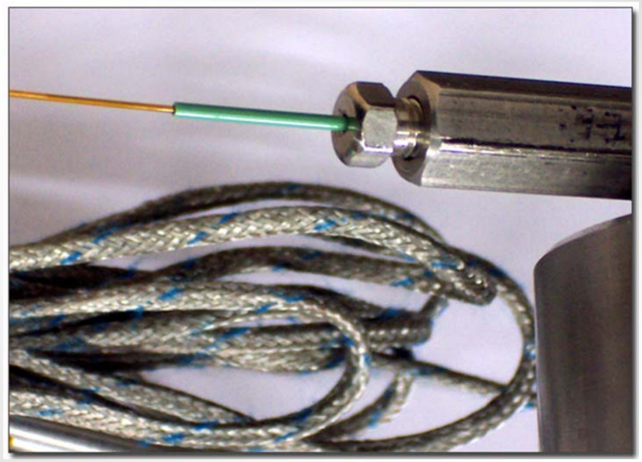
Disadvantage

- need solvent for calibration

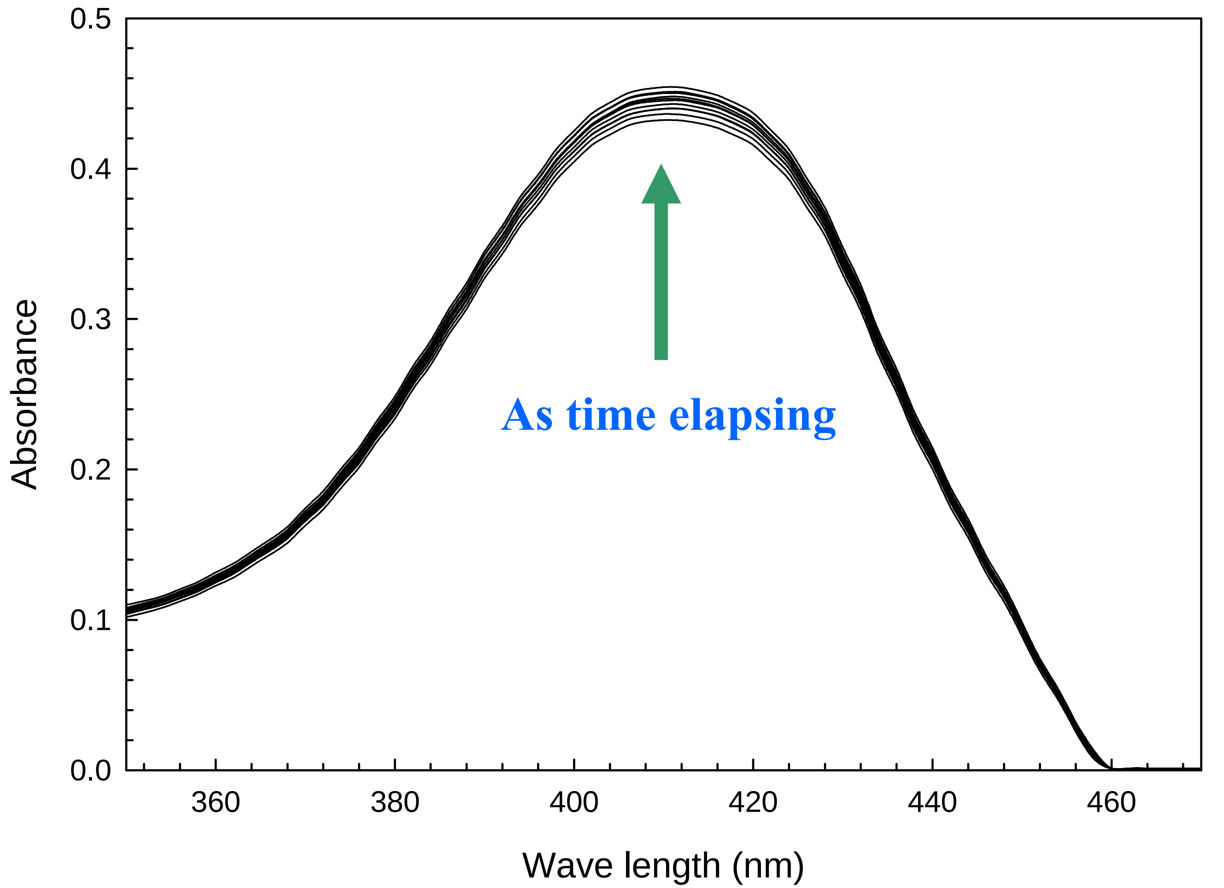
▶ *in situ* Solubility measurement system





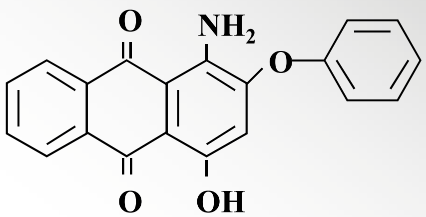
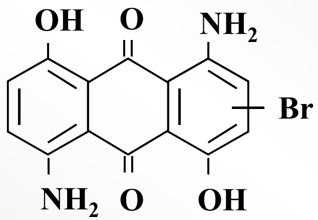
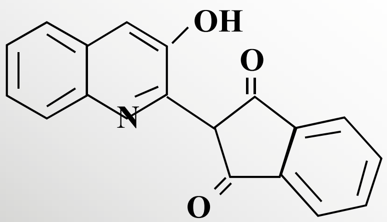


▶ The UV-Visible spectra of DY114

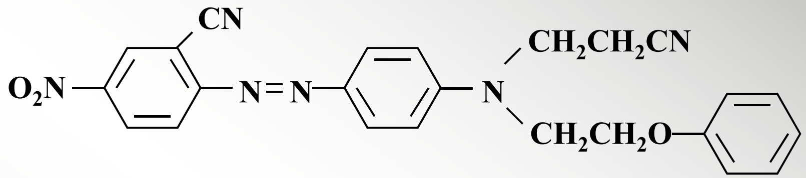
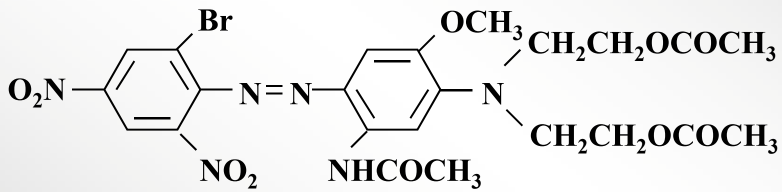
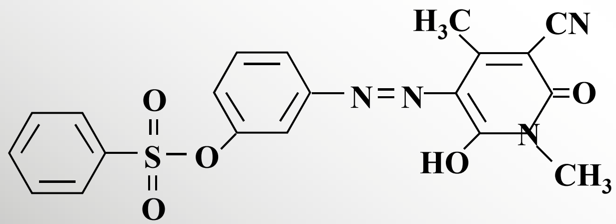


▶ Materials

● Dyestuffs used in this work (E-type)

Type	Dyestuff	Formula	Tm	Mw
	C.I. Disperse Red 60 (anthraquinone)		187 ℃	331.32
E type (mild)	C.I. Disperse Blue 56 (anthraquinone)		199 ℃	365.18
	C.I. Disperse Yellow 54 (quinoline)		270 ℃	289.28

● Dyestuffs used in this work (S-type)

Type	Dyestuff	Formula	Tm	Mw
	C.I. Disperse Red 360 (mono-azoic)		146 ℃	424.43
S type (thick)	C.I. Disperse Blue 79.1 (mono-azoic)		146 ℃	530
	C.I. Disperse Yellow 114 (mono-azoic)		205 ℃	424.43

● Solvents used in this work

Solvent	Formula	Mw	ρ	T_C (K)	P_C (MPa)	T_b (K)	Dipm. (debye)
Acetone	CH_3COCH_3	58.08	0.792	508.2	4.71	329.65	2.9
Benzene	C_6H_6	78.11	0.879	562.16	4.88	353.25	0.0
Ethanol	CH_3CH_2OH	46.07	0.789	513.92	6.12	351.55	1.7
n-Hexane	$CH_3(CH_2)_4CH_3$	86.17	0.659	507.6	3.04	342.15	0.0
Carbon dioxide	CO_2	44.01	0.713*	304.19	7.38	-	0.0

THEORY

▶ Beer-Lambert's Law

$$A = \varepsilon l\, C$$

A = absorbance of sample, l = path length
C = concentration of sample, ε = molar extinction coefficient

▶ Calibration Solvent

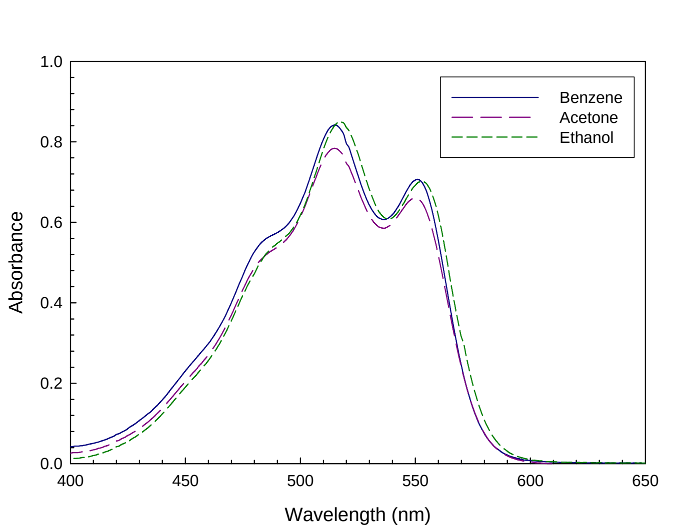
Hexane : reference solvent

- *polarity and extinction coefficient are similar to* CO_2
- *negligible shifts in the position of absorption maxima*

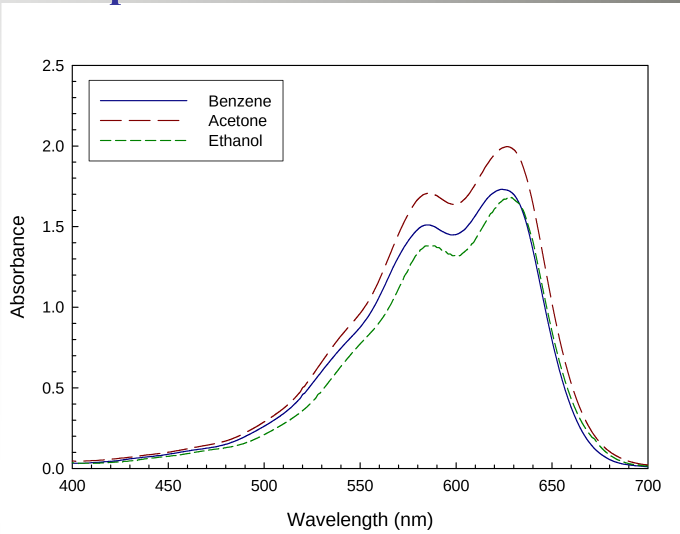
RESULTS

▶ **UV-Visible spectra of E-type dyestuffs in organic solvents**

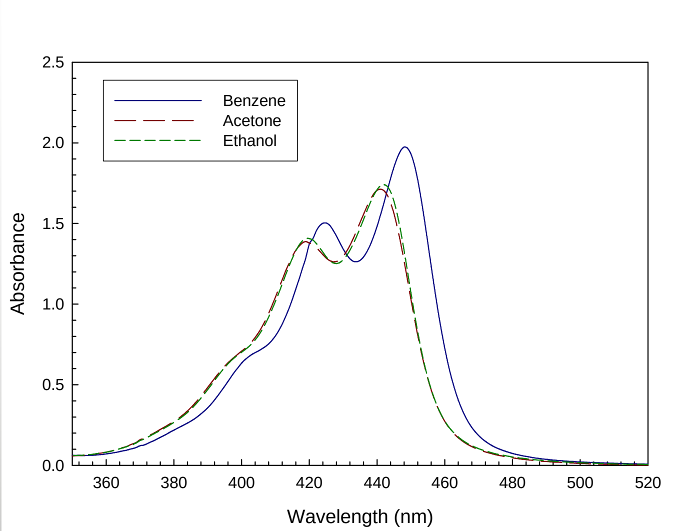
C. I. Disperse Red 60



C. I. Disperse Blue 56

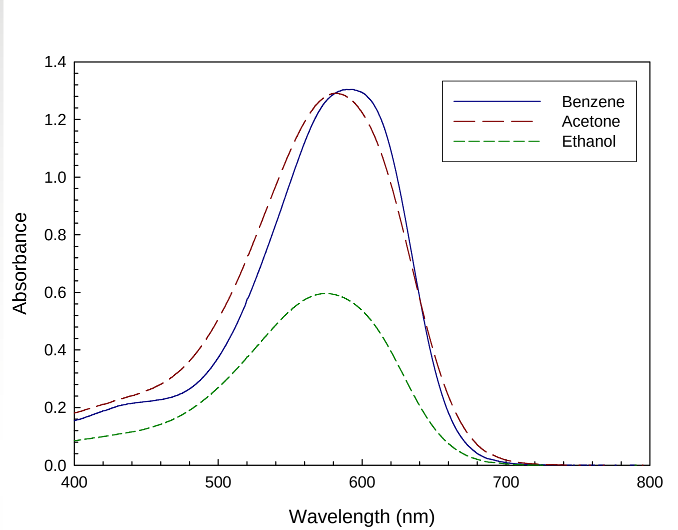


C. I. Disperse Yellow 54

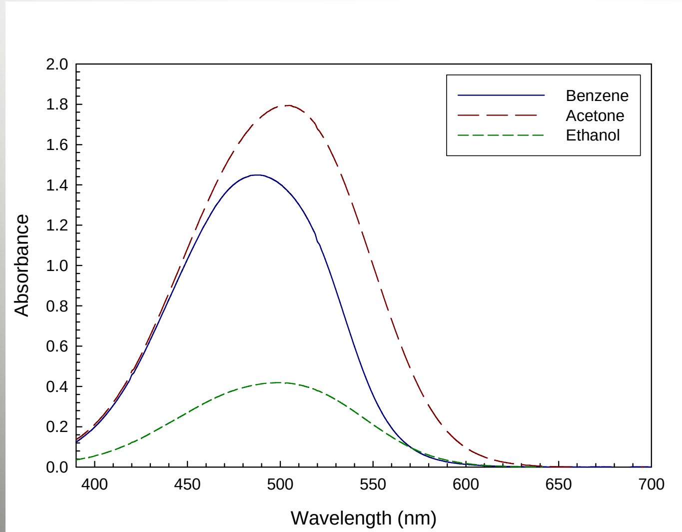


▶ UV-Visible spectra of S-type dyestuffs in organic solvents

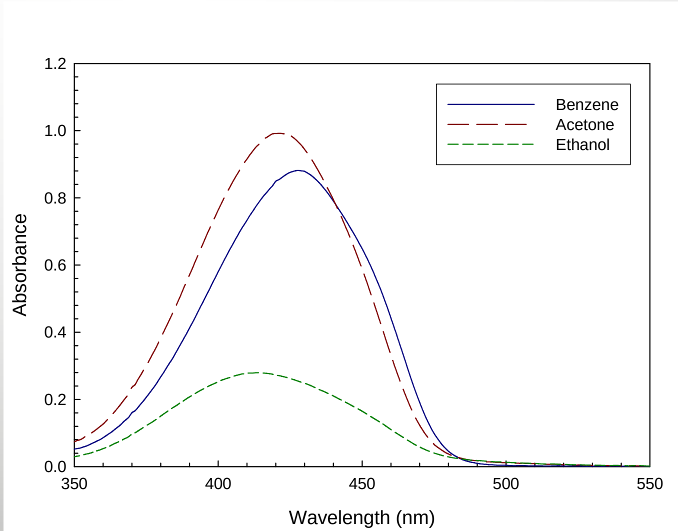
C. I. Disperse Blue 79.1



C. I. Disperse Red 360

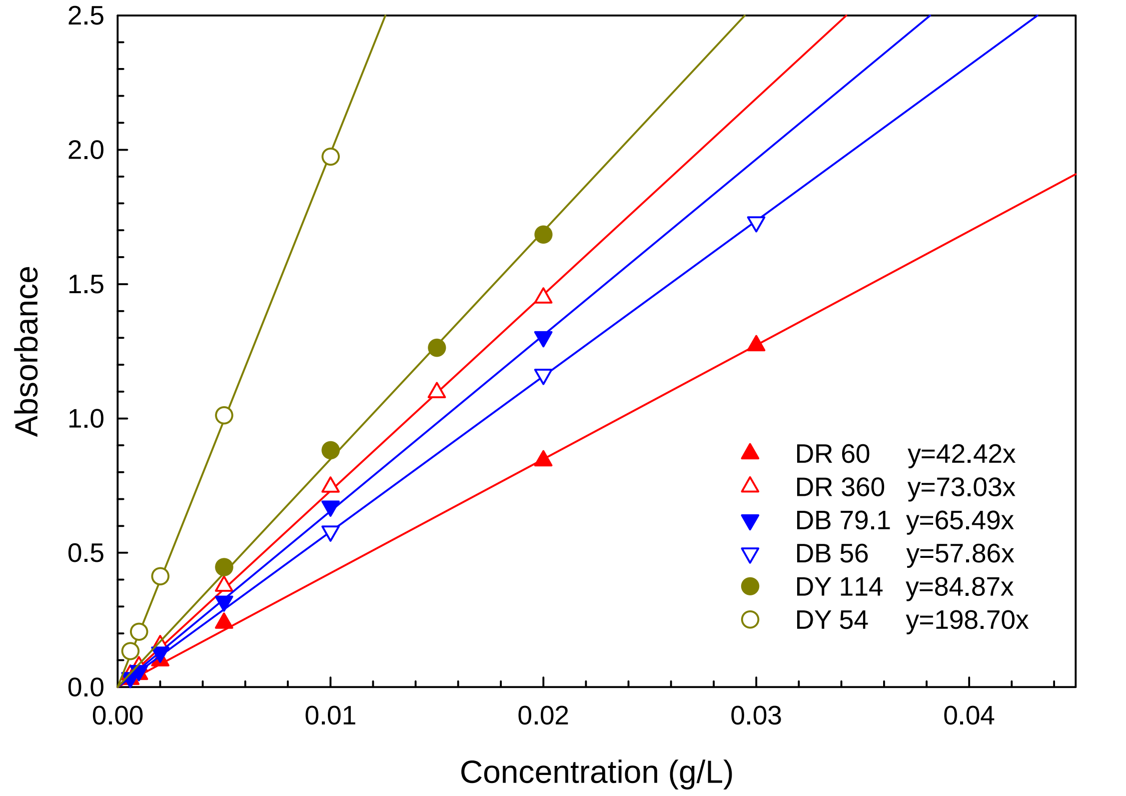


C. I. Disperse Yellow 114



▶ Determination of ε for dye-acetone system

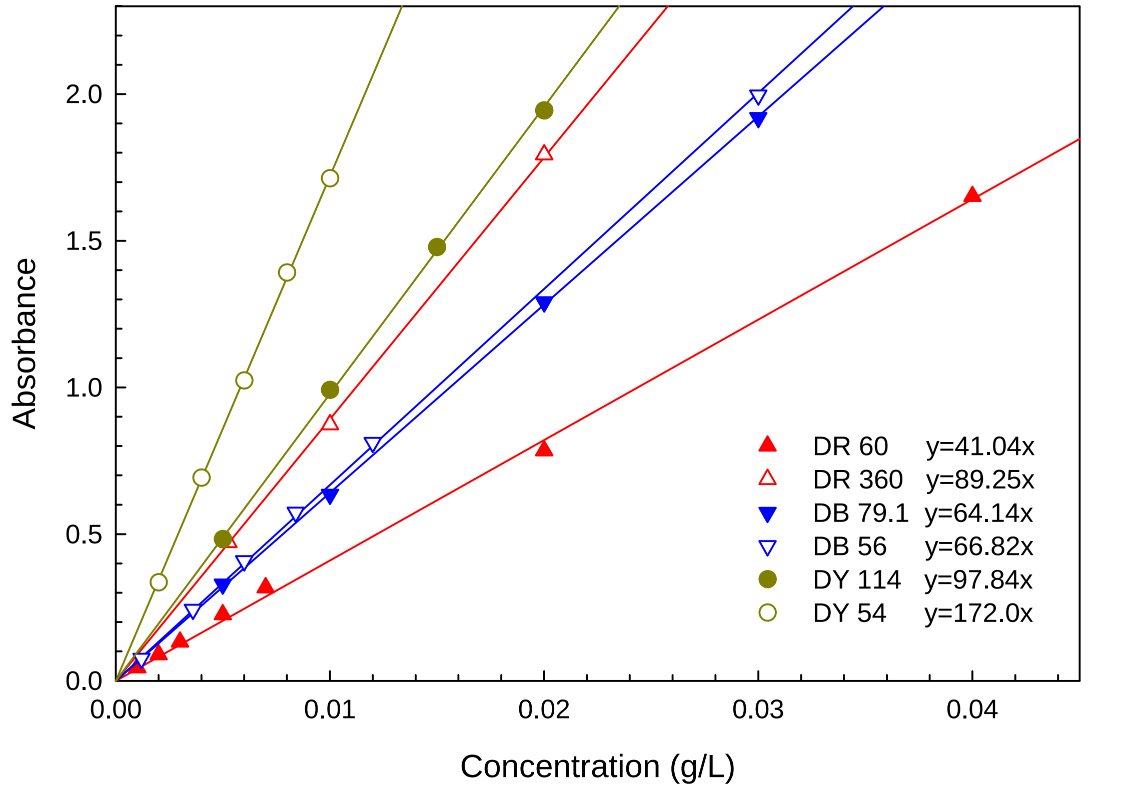
- *ε = slope of calibration curve / 10 mm*



by using conventional UV-Visible spectroscopy

▶ Determination of ε for dye-benzene system

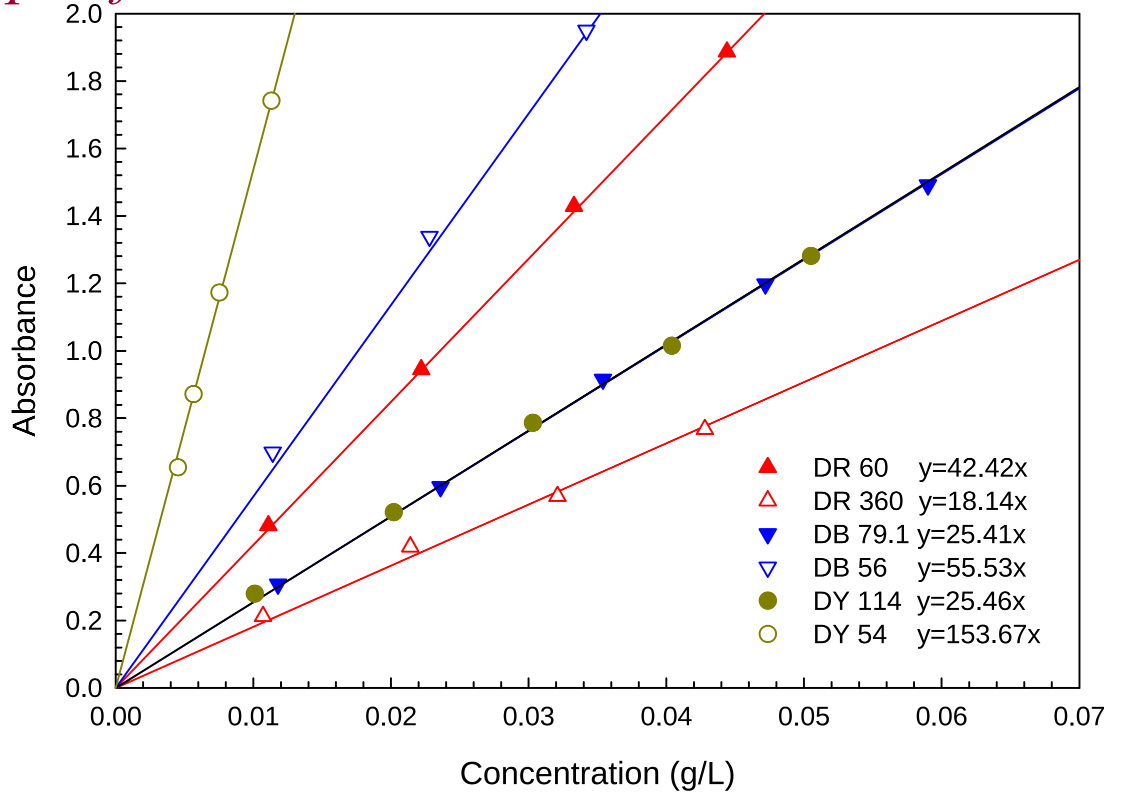
● *ε = slope of calibration curve / 10 mm*



by using conventional UV-Visible spectroscopy

▶ Determination of ε for dye-ethanol system

- *ε = slope of calibration curve / 10 mm*



by using conventional UV-Visible spectroscopy

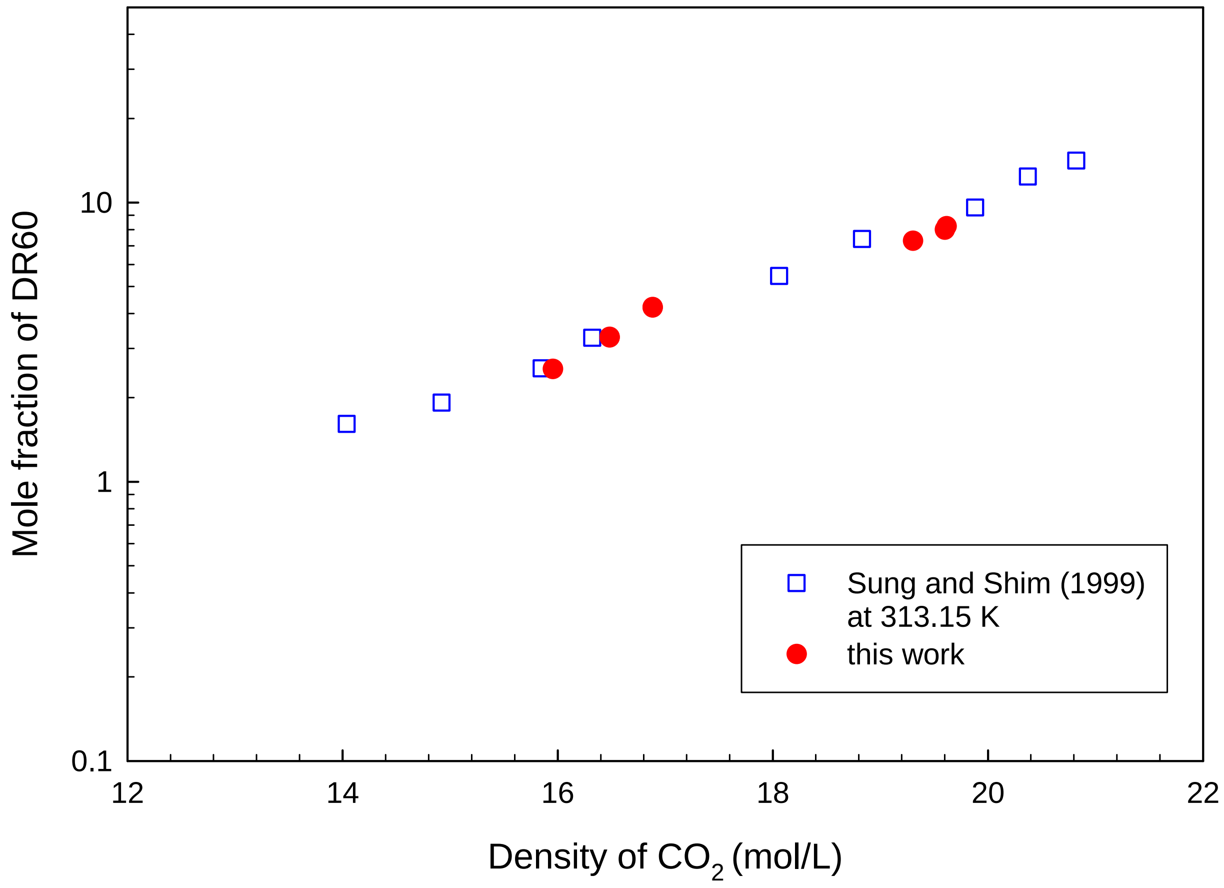
▶ Molar extinction coefficient of E-type dyes

	Dyestuff	Solvent	ε (mol/cm^2) ×10^6	λ_{max} (nm)
	DR60	Benzene	14.054	515
		Acetone	13.597	515
		Ethanol	14.060	517
	DB56	Benzene	21.128	624
E type		Acetone	24.403	657
		Ethanol	20.742	625
	DY54	Benzene	57.479	448
		Acetone	49.755	441
		Ethanol	44.455	442

▶ Molar extinction coefficient of S-type dyes

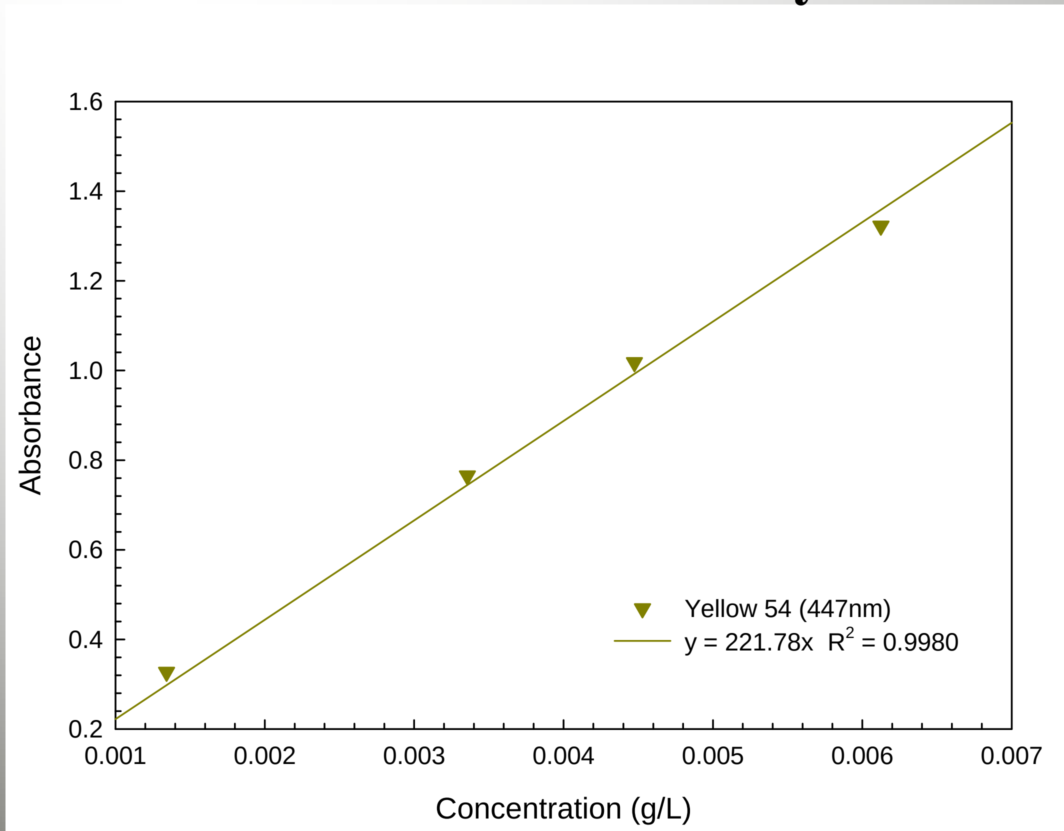
	Dyestuff	Solvent	ε (mol/cm^2) ×10^6	λ_{max} (nm)
	DR360	Benzene	32.165	489
		Acetone	39.310	504
		Ethanol	7.991	498
	DB79.1	Benzene	34.710	593
S type		Acetone	33.992	581
		Ethanol	13.467	575
	DY114	Benzene	36.021	428
		Acetone	41.526	420
		Ethanol	10.804	415

▶ Reliability of the experimental technique

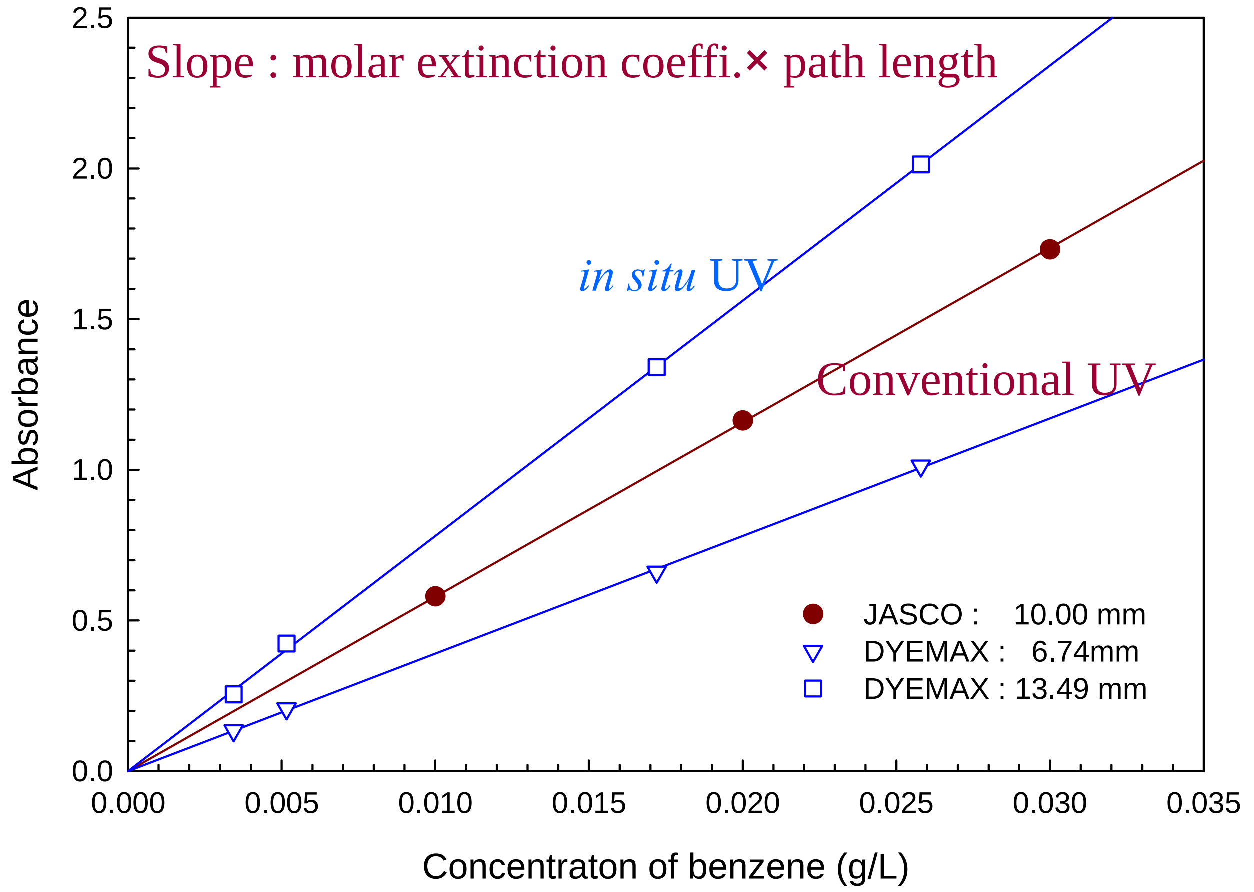


▶ Measurement of the solubility for DY54 in SC-CO_2 by using *in situ* UV-Visible spectroscopy

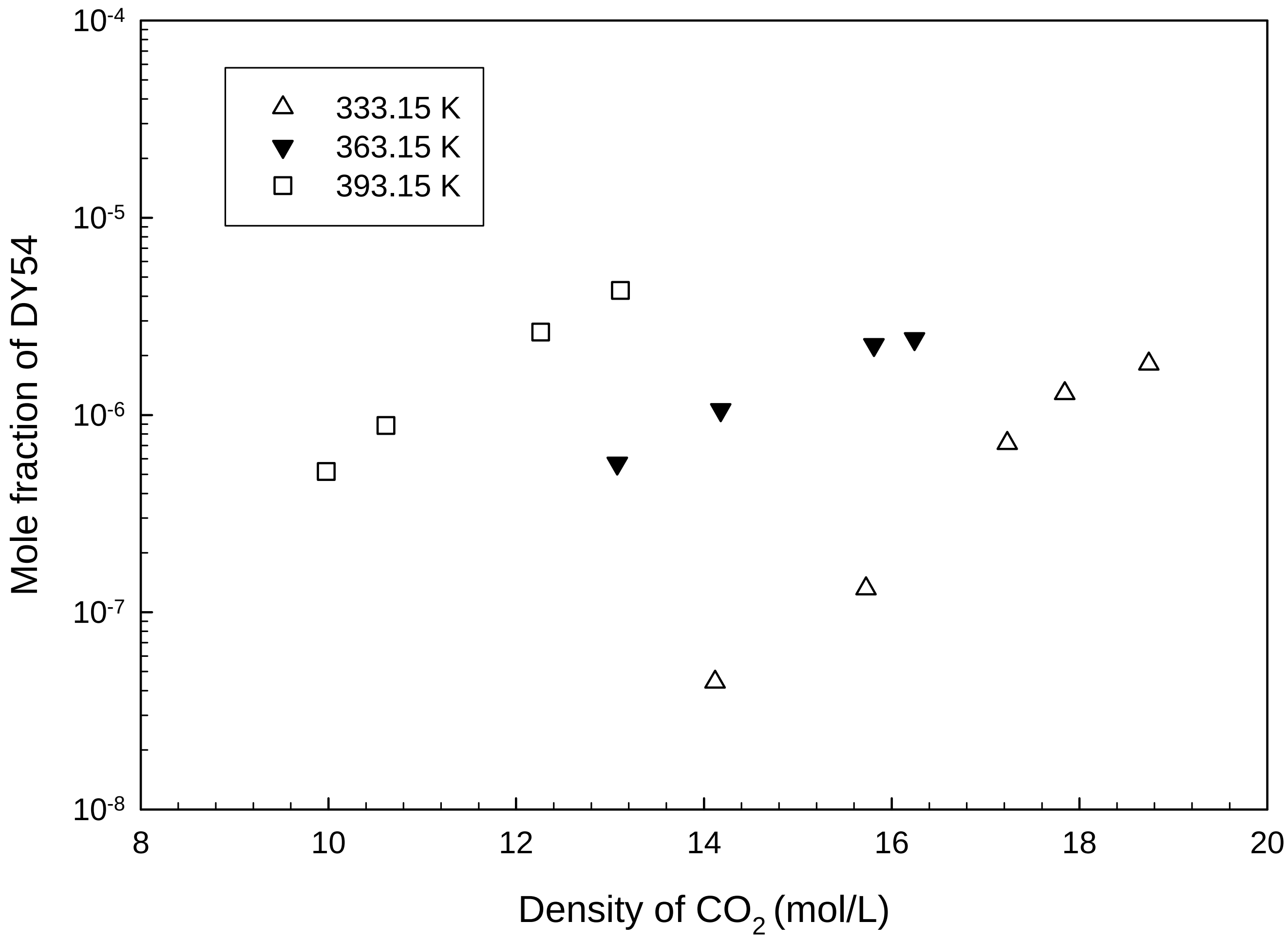
● Determination of ε for DY 54-hexane system



● Determination of path length
for *in situ* UV-Visible spectroscopy



● Solubility data of DY54 in $SC\text{-}CO_2$



● Solubility data of DY54 in SC-CO_2

Temperature (K)	Pressure (MPa)	Density of CO_2 (mol/L)	Solubility of dye (y fraction)
333.15	14.81	14.1191	4.4326e-8
	17.67	15.7278	1.3171e-7
	22.36	17.2315	7.1913e-7
	25.01	17.8435	1.2860e-6
	30.04	18.7392	1.8146e-6
363.15	21.53	13.0766	5.6917e-7
	24.05	14.1784	1.0620e-6
	29.42	15.8117	2.2720e-6
	31.28	16.2426	2.4283e-6
393.15	21.57	9.9775	5.1743e-7
	22.81	10.6129	8.8372e-7
	26.60	12.2605	2.6317e-6
	29.04	13.1108	4.2822e-6

▶ Model equation for correlating the solubility

$$\ln(xP/P_{ref}) = A + c(\rho - \rho_{ref})$$

by Bartle et al., 1991

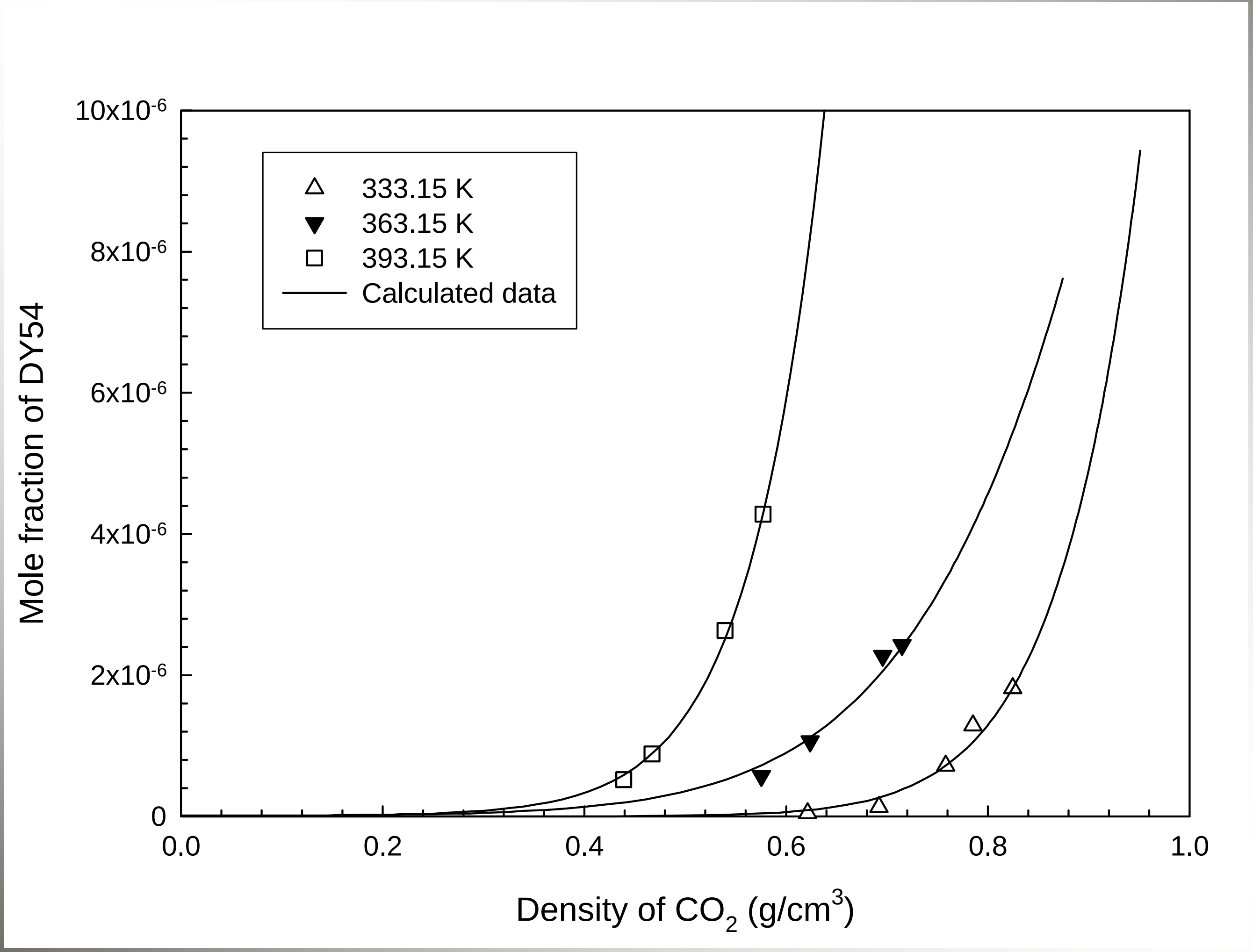
where,

x : mole fraction of solubility, P : system pressure,

P_{ref} : standard pressure of 1 bar, ρ : solution density,

ρ_{ref} : reference density (700 kg/m^3)

● Correlation – empirical equation



CONCLUDING REMARKS

- Molar extinction coefficient of dyestuffs in organic solvents were calculated from the slope of linear calibration curves of absorbance.

- Molar extinction coefficient for carbon dioxide was determined by using standard solution of C. I. Disperse Yellow 54.

- Solubility of the dye C. I. Disperse Yellow 54 in supercritical carbon dioxide have been measured in the temperature range from (333.15 to 393.15) K and at pressure from (14.81 to 30.04) MPa.

- Solubility data of the C. I. Disperse Yellow 54 in supercritical carbon dioxide were correlated in terms of the density (g/cm^3) of carbon dioxide using an empirical equation of Bartle et al.

감 사 드 립 니 다.