CAP.C534

Advanced Supercritical Fluid Process

（超臨界流体プロセス特論）

1. Fundamental Property of Supercritical Fluid

Department of Chemical Science and Engineering

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2018.9.27　Room 421 of South Buld. 4

Outline

New development of Chemical Process

- Reaction process : rapid, selective, simple
- Separation process : rapid, low energy, selective
- Material process : low cost and energy, functional material

How to use and design “Supercritical fluid medium”
for development of chemical process

Fundamentals

Reaction mechanism

Separation mechanism

Material design

Supercritical Fluid

Class Schedule

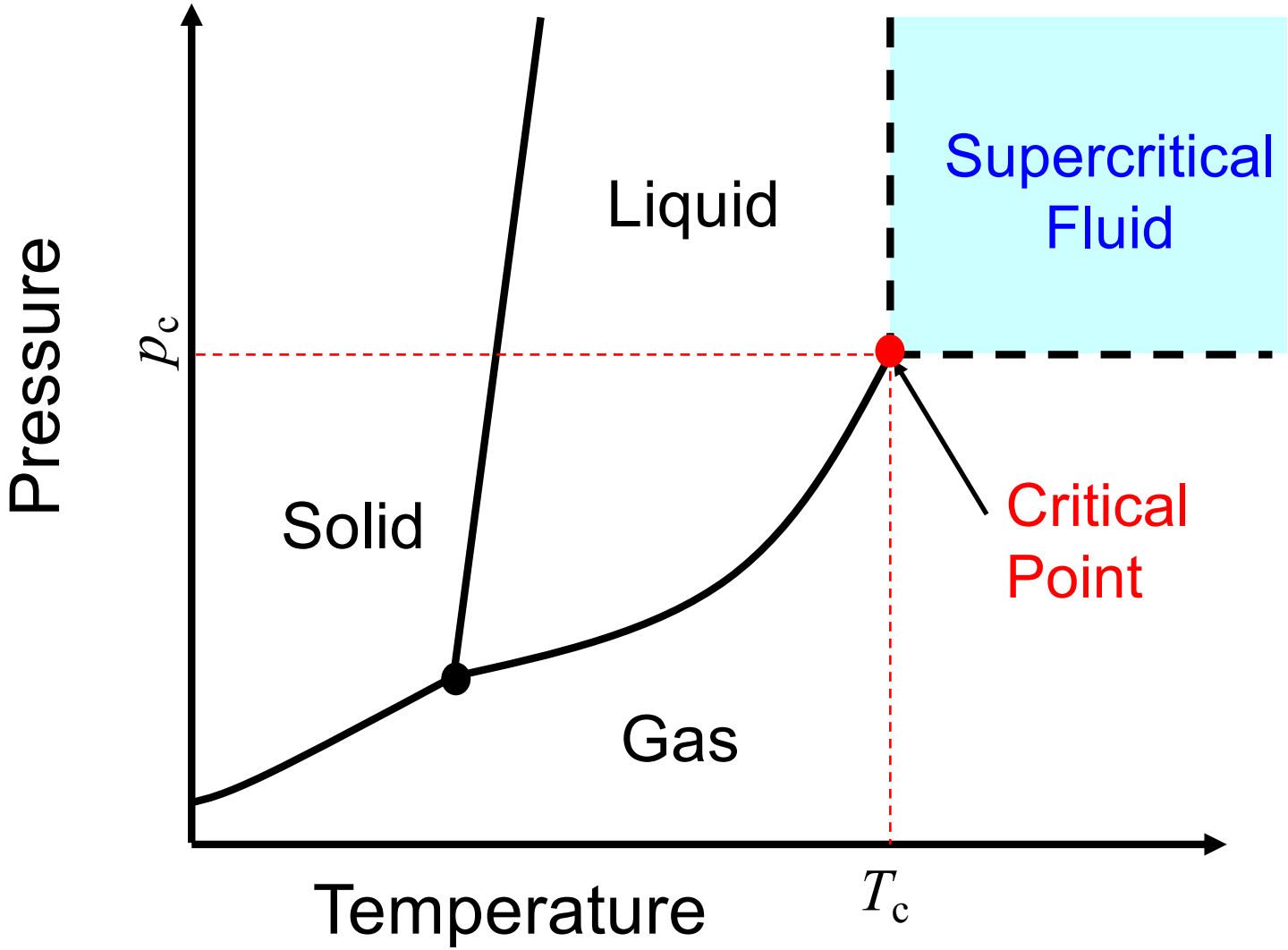
1. 9/27 Fundamental property of SCF
2. 10/4 Particle formation using SCF (I)
3. 10/11 Particle formation using SCF (II)
4. 10/18 Porous material formation using SCF (I)
5. 10/25 Porous material formation using SCF (II)
6. 11/1 Composite formation using SCF
7. 11/8 Film formation using SCF

11/22 Final report submission

Class document will be upload in OCW

Supercritical Fluid

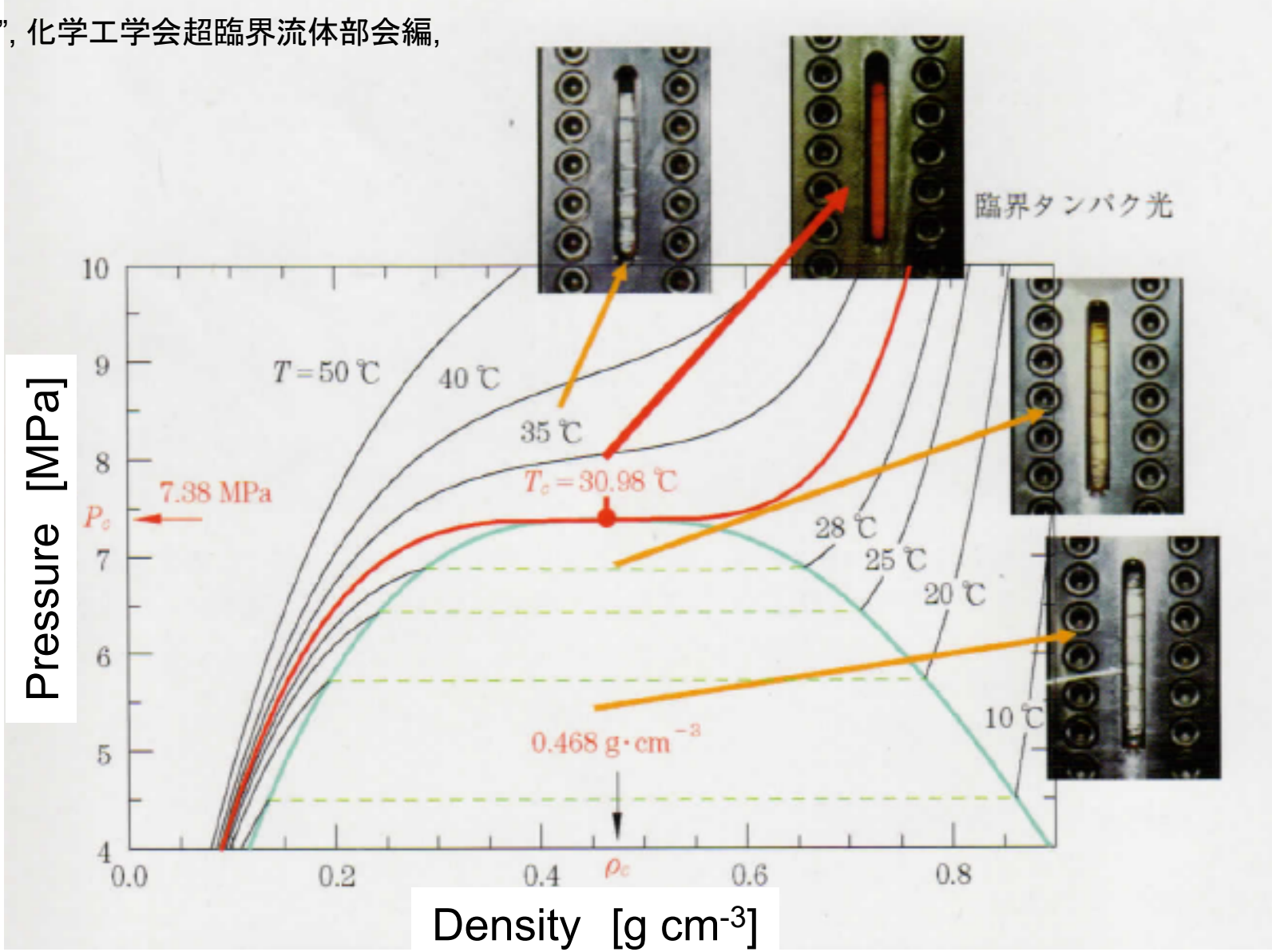
➢ Phase diagram of pure compound



Fundamental property of SCF

➢ Specific phase “color” change of SCF

“超臨界流体入門”, 化学工学会超臨界流体部会編, 丸善, 2008



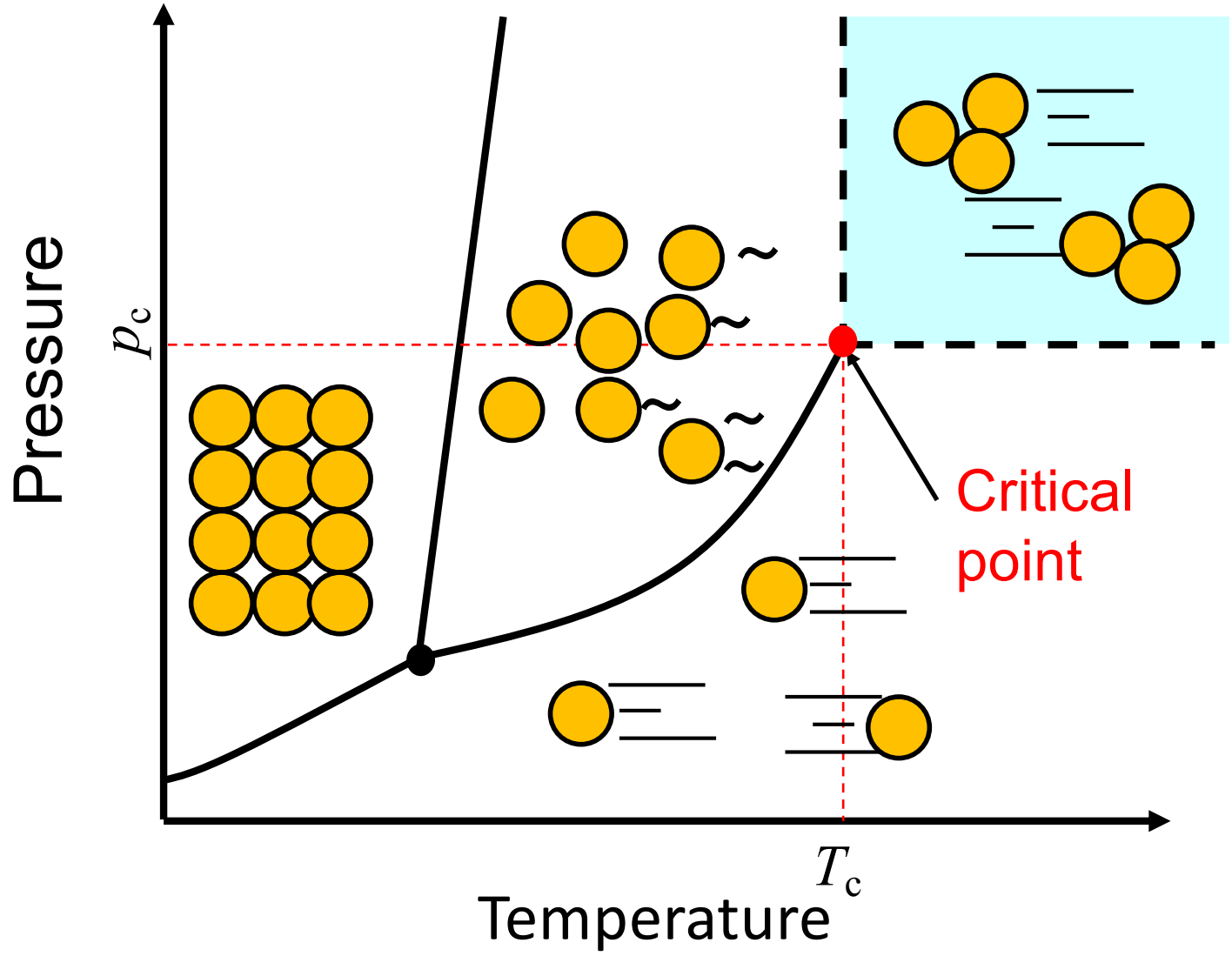
Fundamental property of SCF

- Critical temperature and pressure

Substance	T_c / ℃	p_c / MPa
H_2	-240.0	1.30
H_2O	374.1	22.04
CO_2	31.0	7.37
Toluene	318.5	4.11
Ethanol	239.4	8.09

Fundamental property of SCF

- Molecular motion on solid, liquid, gas and SCF



Fundamental Property of SCF

➢ Application of SCF : Extraction

Raw Material		Extracted solute
Coffee beans, tea leaf		Caffeine (alkaloid)
Algae		β-carotene, carotenoid
Aroma	Vanilla beans	vanilline
	Citrus skin	Citrus oil
	Tea, green tea	Aqueous aromatic compound
Red pepper, paprika		capsicin
Fish oil		EPA and DHA

"超臨界流体入門", 化学工学会超臨界流体部会編, 丸善, 2008

Fundamental Property of SCF

➢ Application of SCF : Extraction

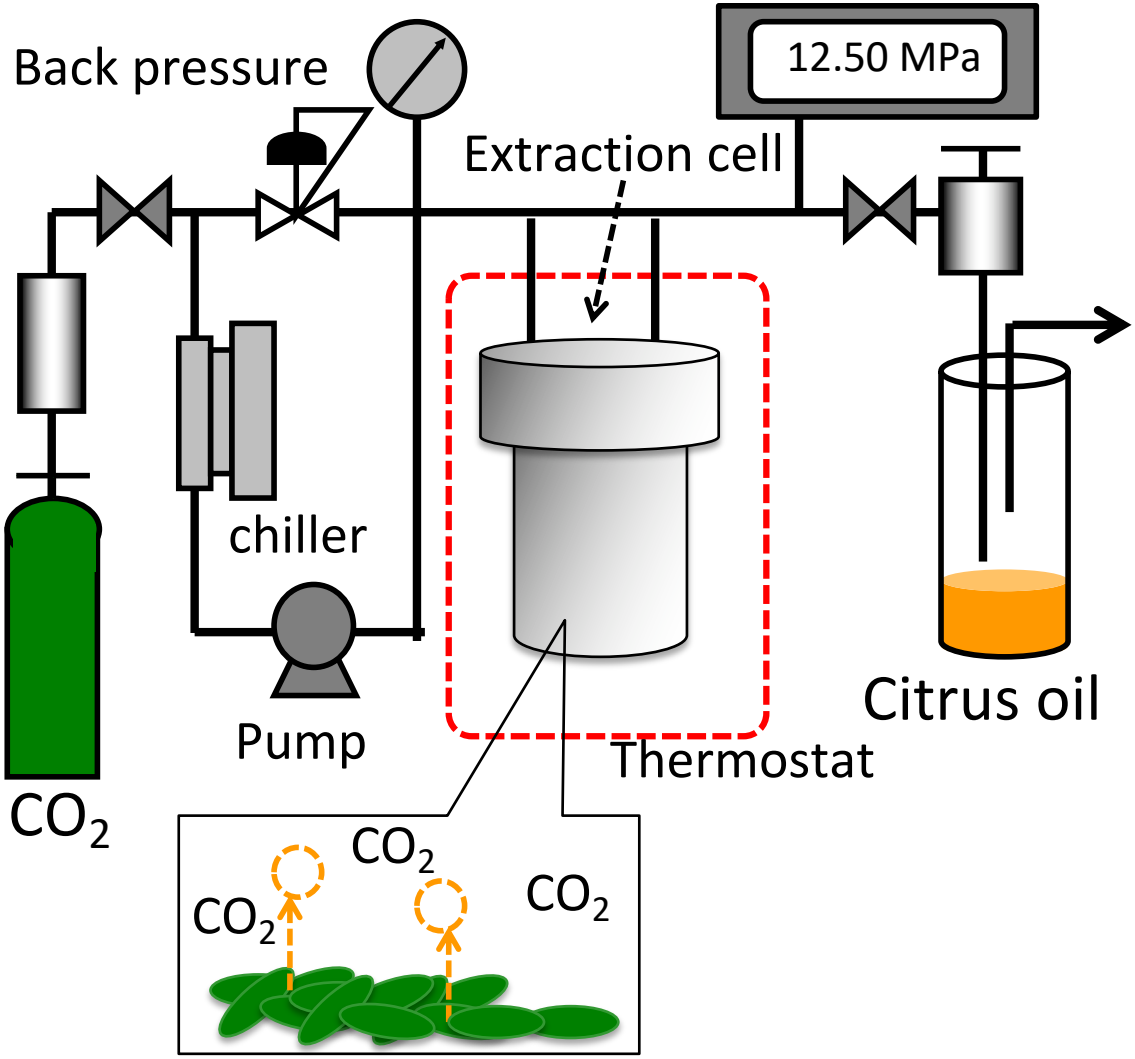
Raw material : Eucalyptus leaf

Condition : 50℃, 9 MPa

Extracted solute :

α-pinene (10.5 %)

1,8-cineole (62.6 %)



Flavor and Fragrance J., 14, 214 – 218 (1999).

Q 1-1. Application of SCF : Extraction

What is the advantage of extraction process using SCF compared to that using liquid solvent?

Fundamental Property of SCF

A 1-1. Application of SCF : Extraction

Fundamental Property of SCF

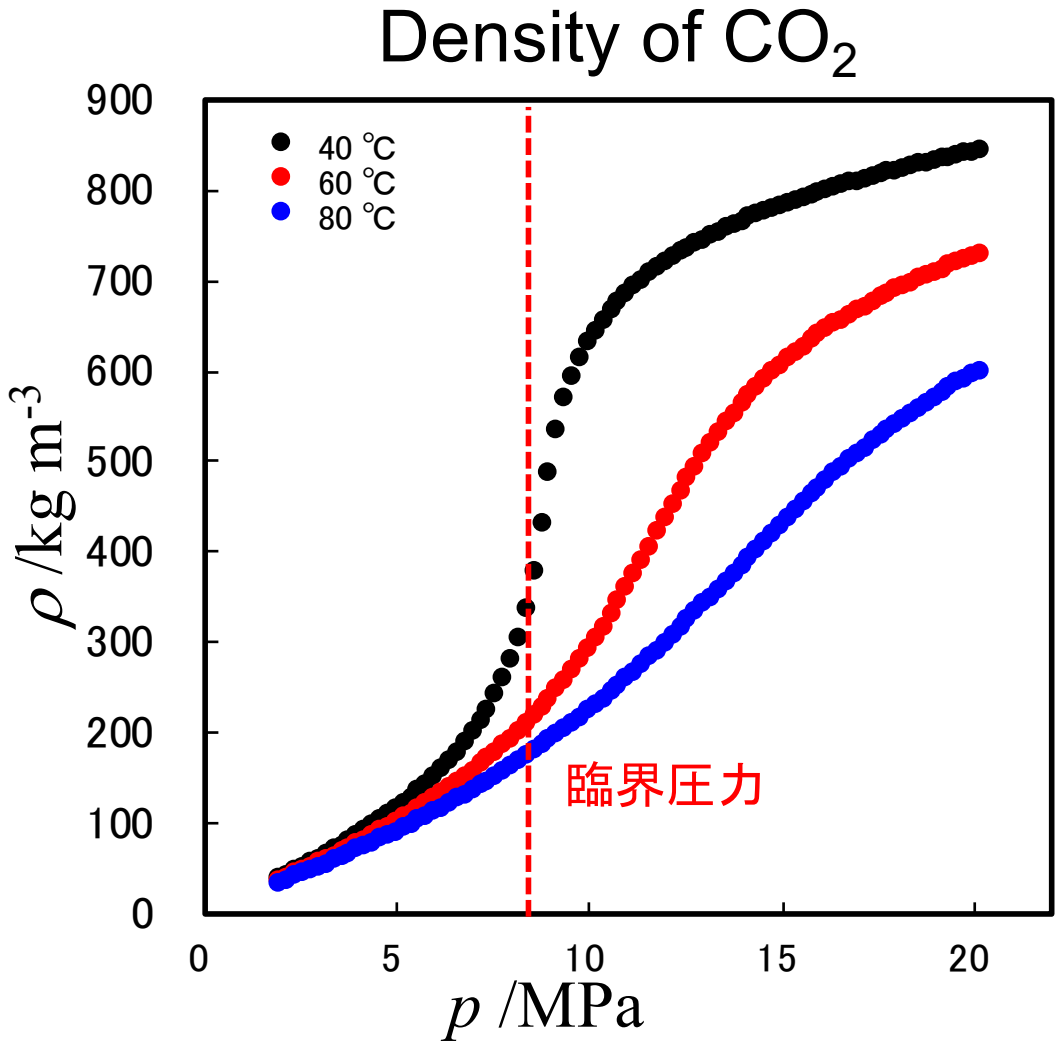
➢ Application of SCF : Reaction

Solvent	Reaction type
$SCCO_2$	Hydrogenation of unsaturated fatty acid (Ru, Rh catalyst)
	Hydroformylation (Rh, Co catalyst)
CO_2 expand liquid	Oxidation and Hydrogenation : Enhanced dissolution of O_2, H_2 to liquid phase
High temp. and press. water	Oxidation : Decomposition of toxic compounds
	Hydrogenation of heavy oil (NiMo, CoMo catalyst)
	Gasification of biomass (NaOH, KOH, Ni catalyst)
SCMeOH	Production of biodiesel from fat and oil

“超臨界流体入門”, 化学工学会超臨界流体部会編, 丸善, 2008

Fundamental Property of SCF

➢ Application of SCF : Material process

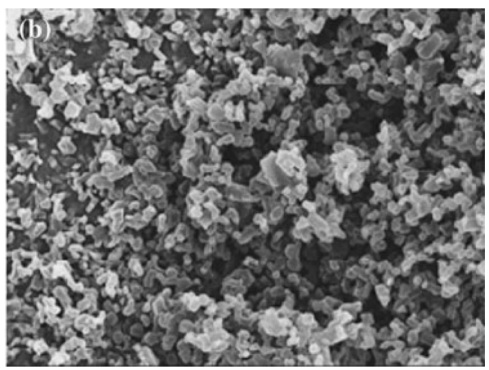


Diffusion coefficient, Viscosity

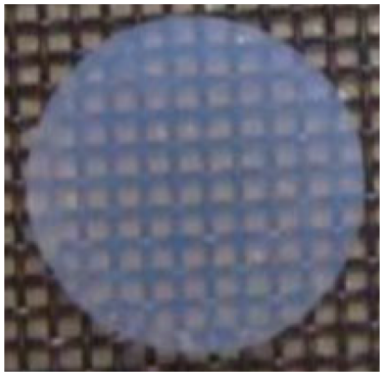
Solubility in supercritical CO_2

Phase equilibria and phase behavior

Design of Material Process



nanoparticle



Aerogel

Bozbag, S. E. et al., J. Mater. Sci., 47 (2012) 2995 – 3025.
Sanli, D. et al., J. Mater. Sci., 47 (2012) 3469 – 3492.

Fundamental Property of SCF

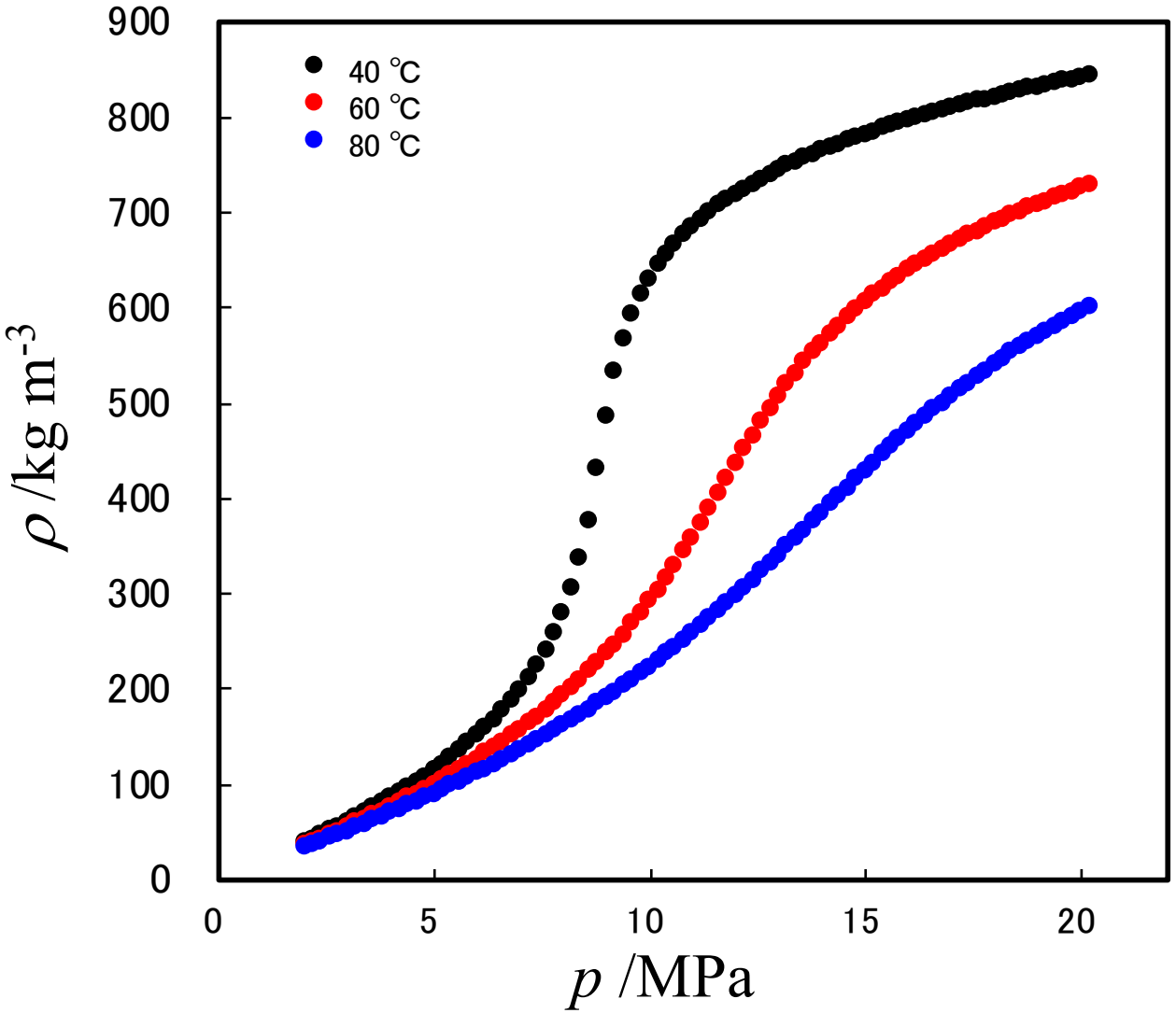
- Property of gas, liquid and supercritical fluid

	Gas	Supercritical Fluid	Liquid
density / kg m^{-3}	0.6 – 2	300 – 900	700 – 1600
diffusion coefficient/ 10^{-9} m^2 s^{-1}	1000 – 4000	20 – 700	0.2 – 2
Viscosity / 10^{-5} Pa s	1 – 3	1 – 9	200 – 300
Thermal conductivity /10^{-3} W m^{-1} K^{-1}	1	1 – 100	100

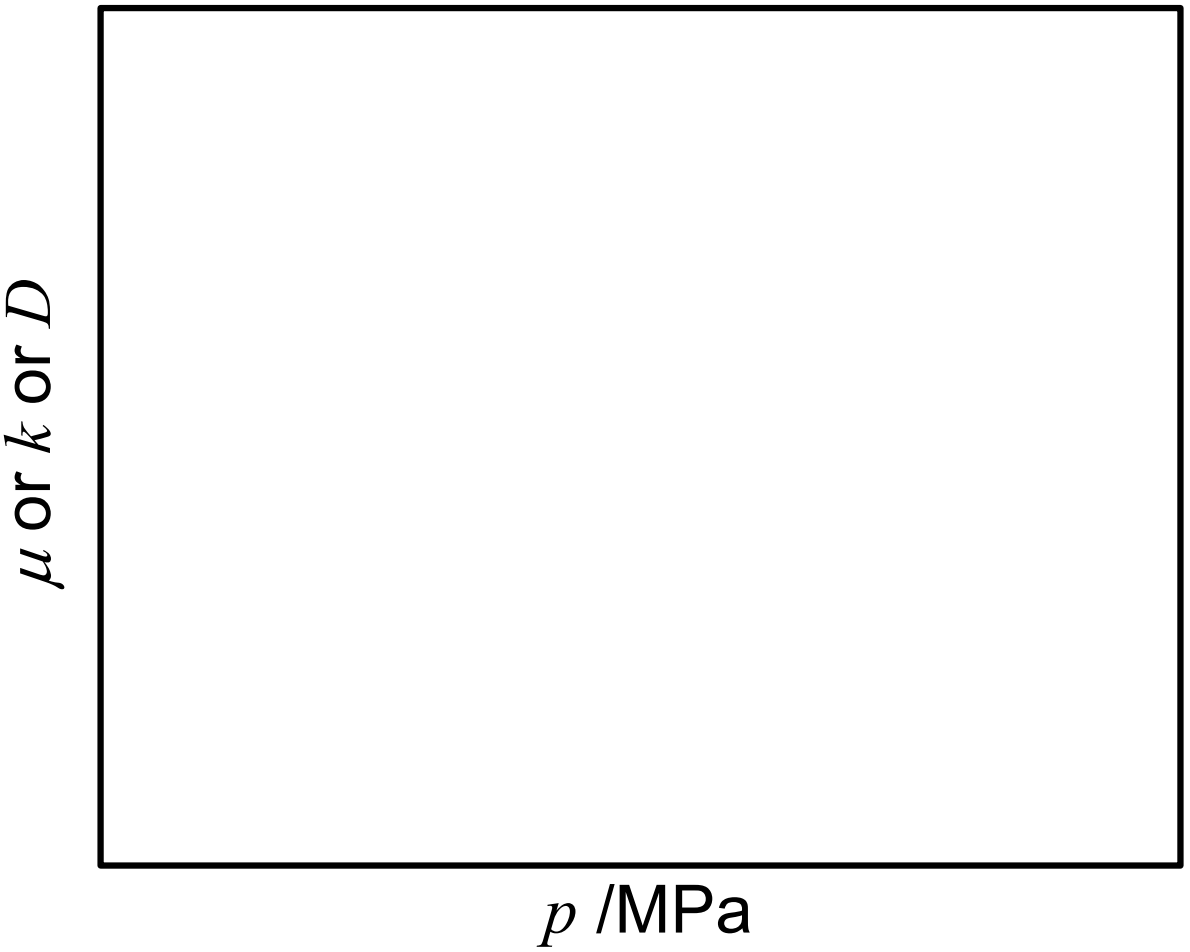
Fundamental Property of SCF

➢ Density of CO_2

R. Span and W. Wagner,
J. Phys. Chem. Ref. Data 25(6), 1509–1596 (1996).



Q.1-2: What is the behavior of viscosity μ, thermal conductivity k and diffusion coefficient D as the function of pressure at constant temperature?

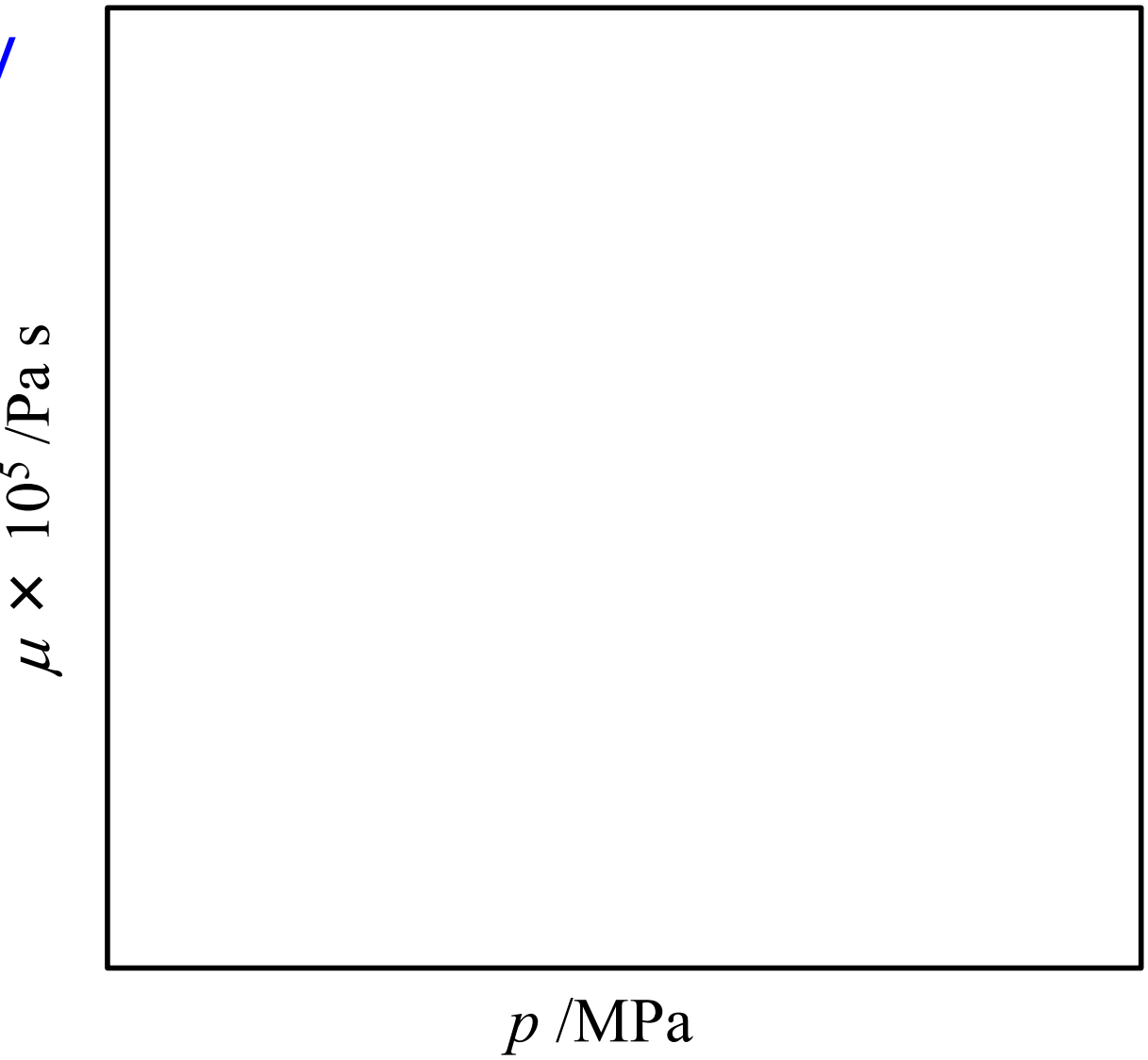


Fundamental Property of SCF

A. 1-2

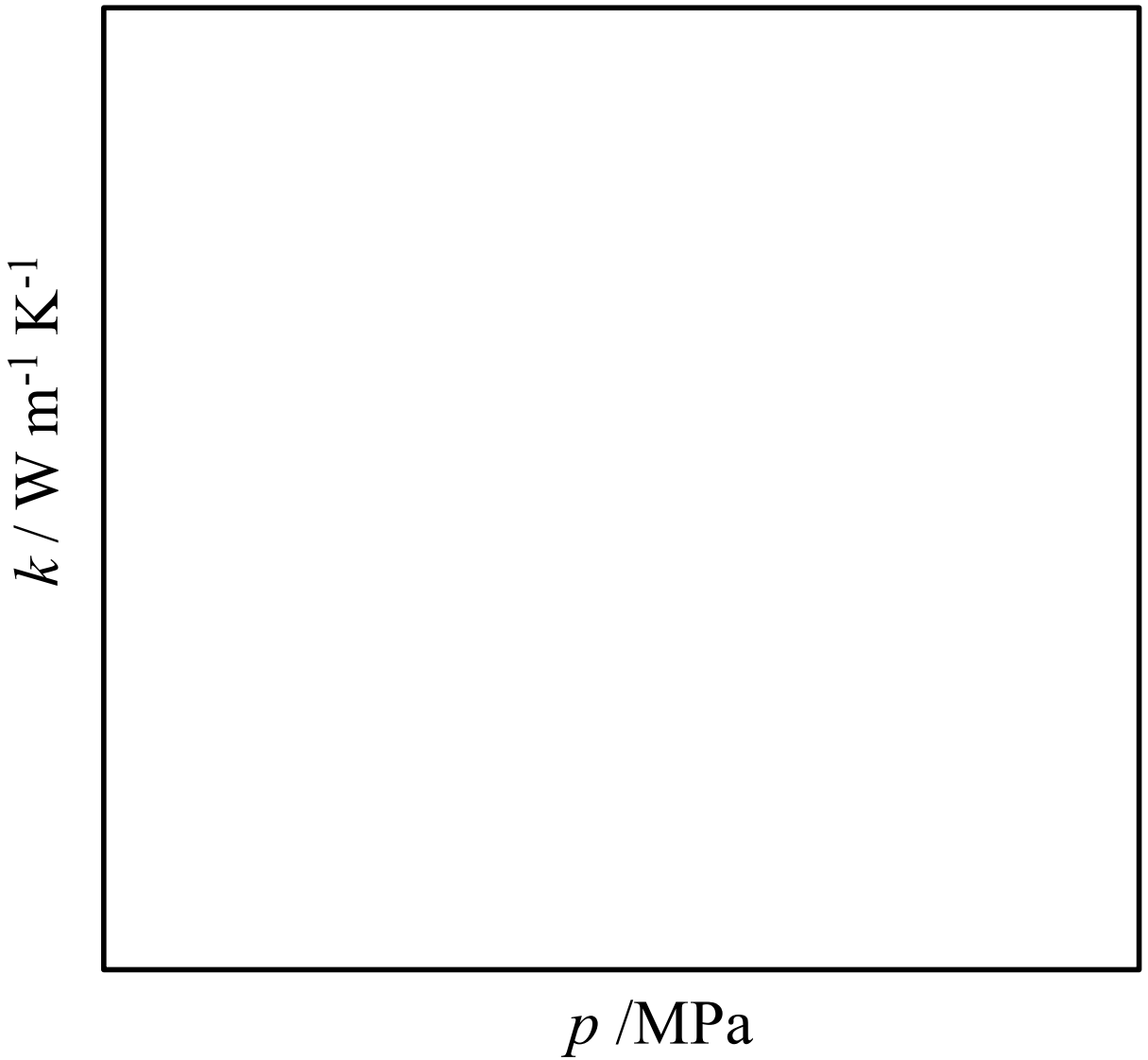
R. Span and W. Wagner,
J. Phys. Chem. Ref. Data 25(6), 1509–1596 (1996).

Viscosity



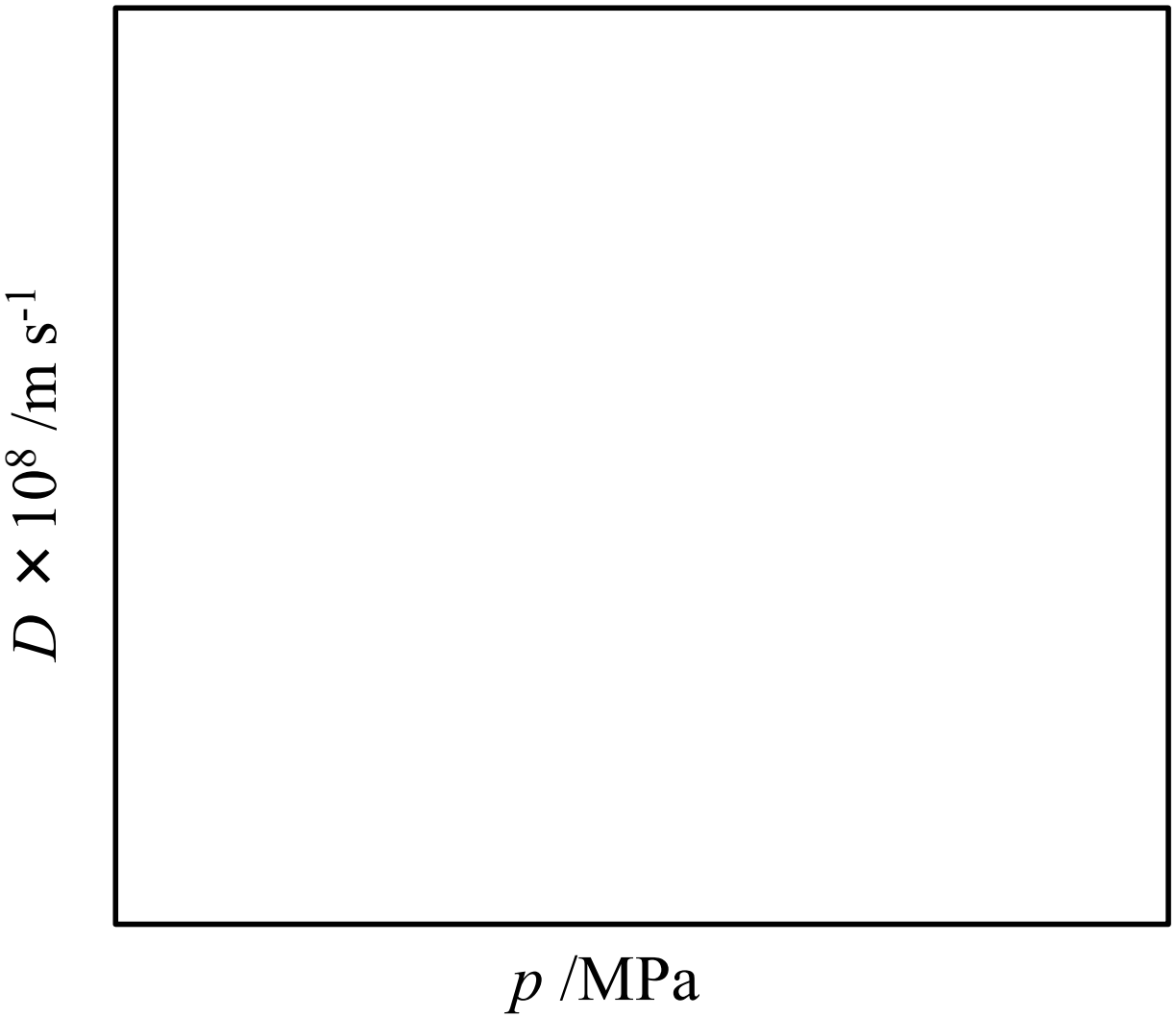
A. 1-2

Thermal conductivity



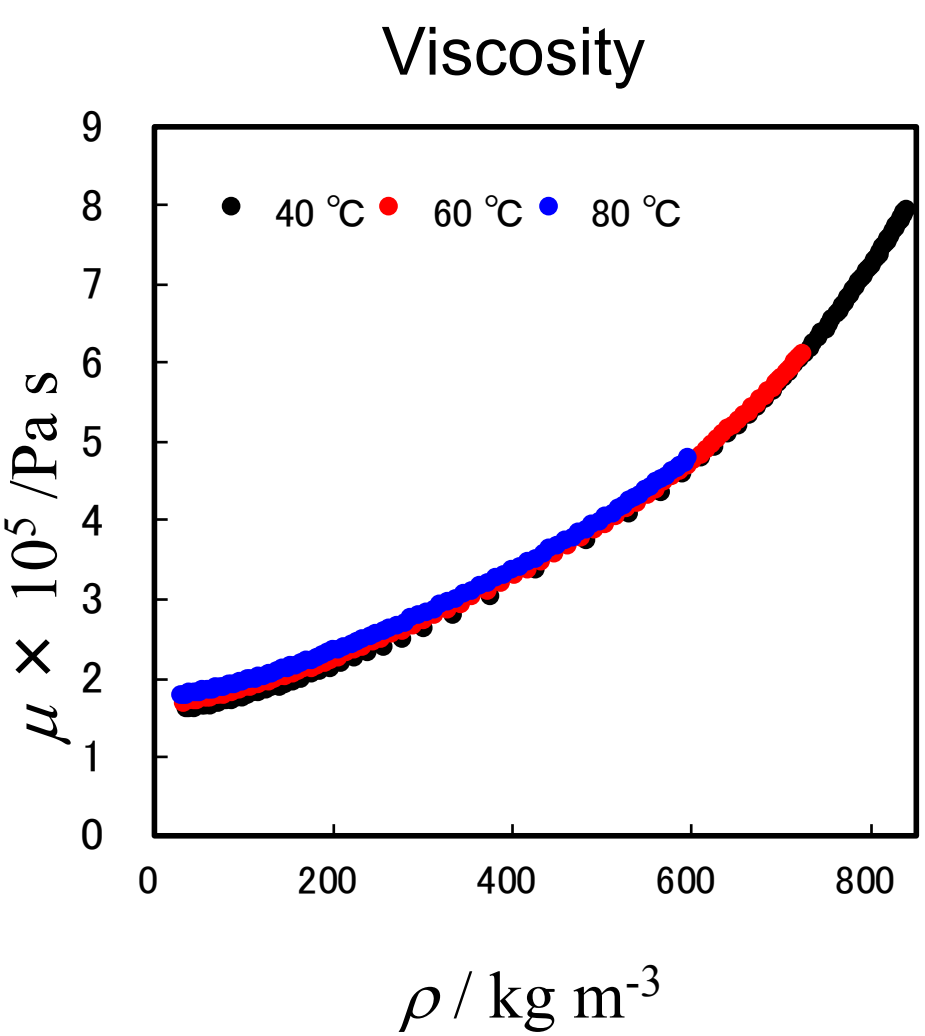
A. 1-2

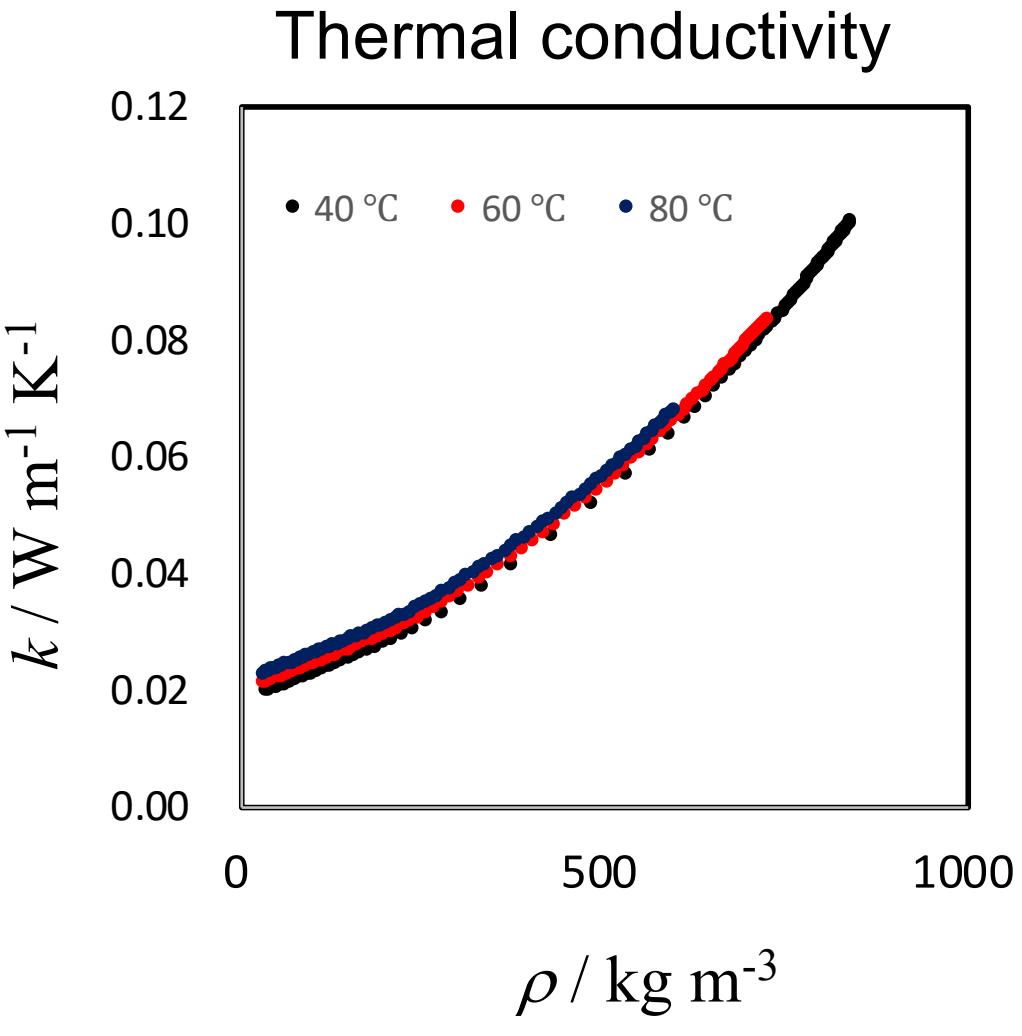
Diffusion coefficient of naphthalene



Fundamental Property of SCF

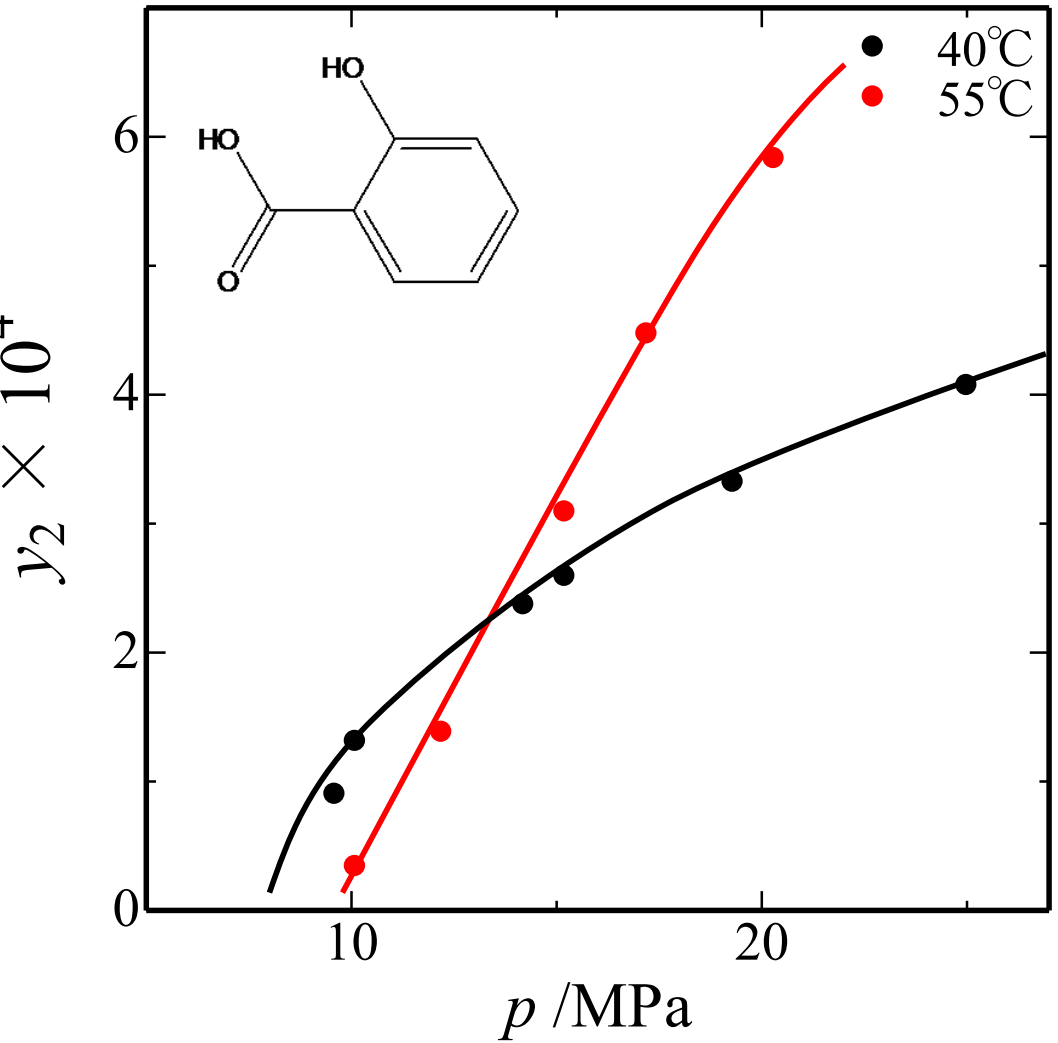
- If the function of density,





Solubility of salicylic acid in supercritical CO_2

Haung, Z., J. Chem. Eng. Data, 49 (2009) 1323 – 1327.



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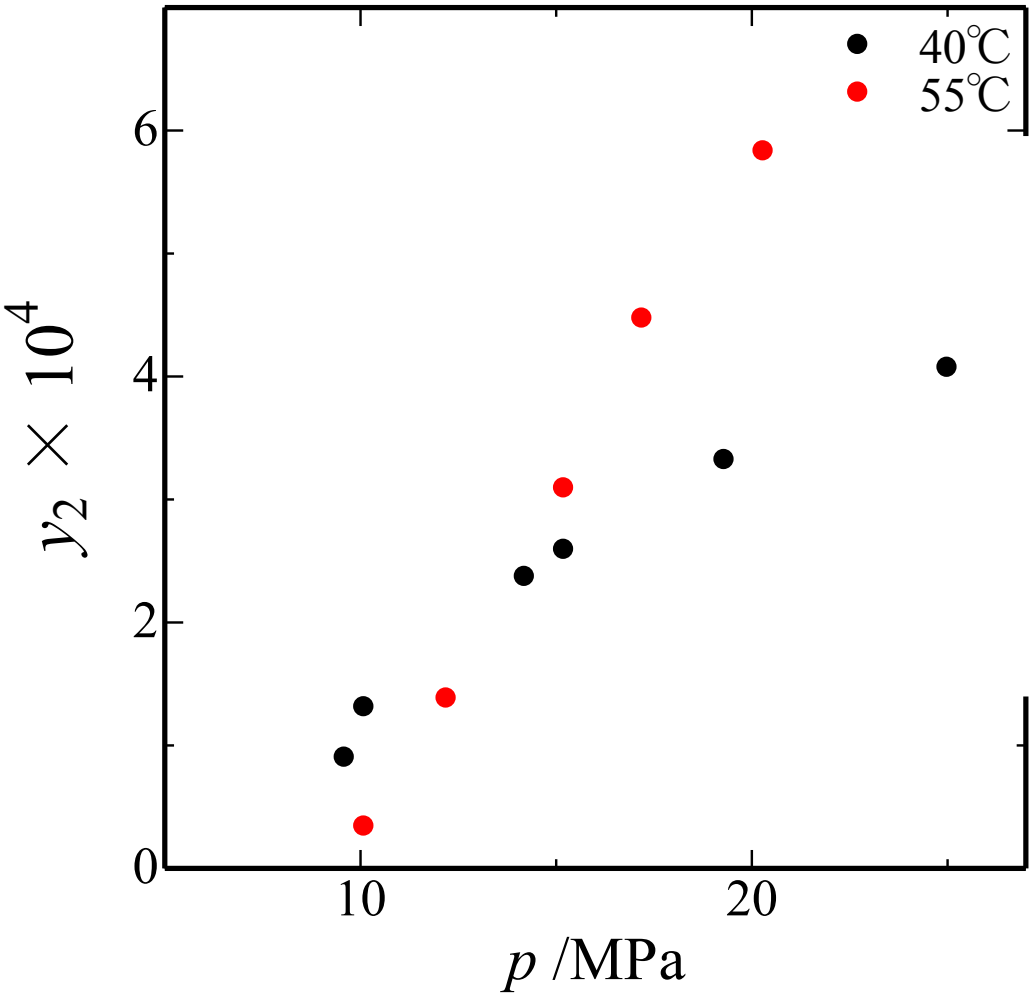
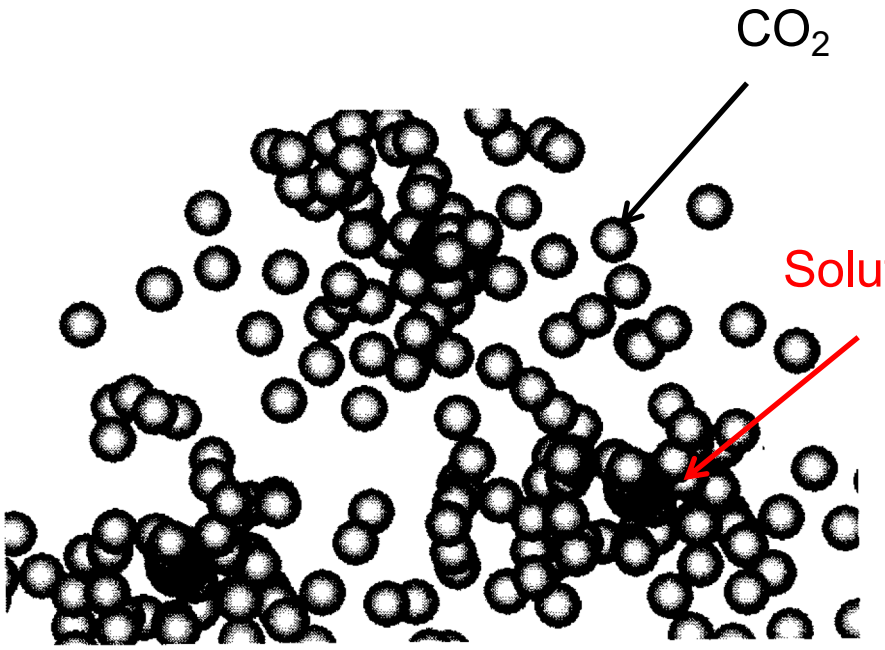
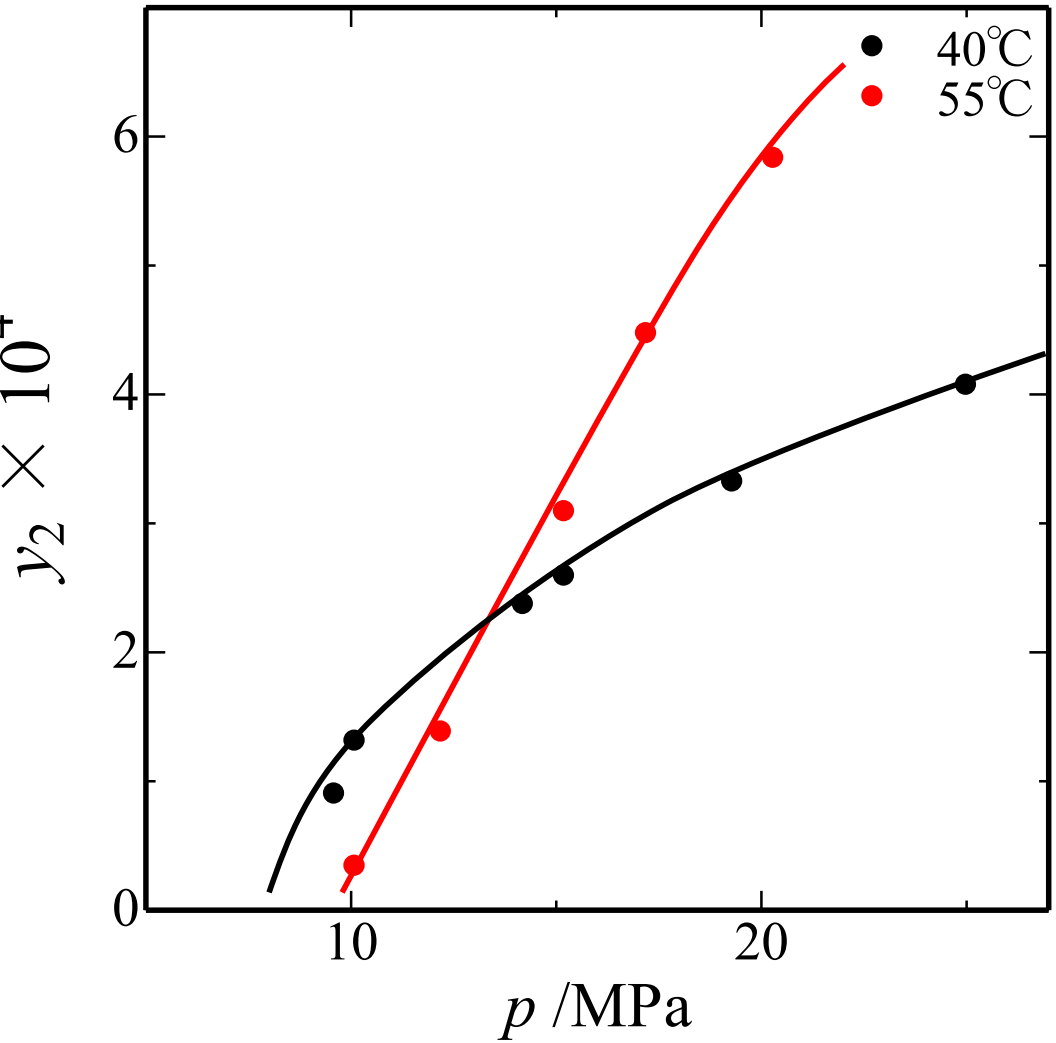




Cluster structure from molecular simulation

Q. 1-3: Why is the cross over point of solubility in supercritical carbon formed?

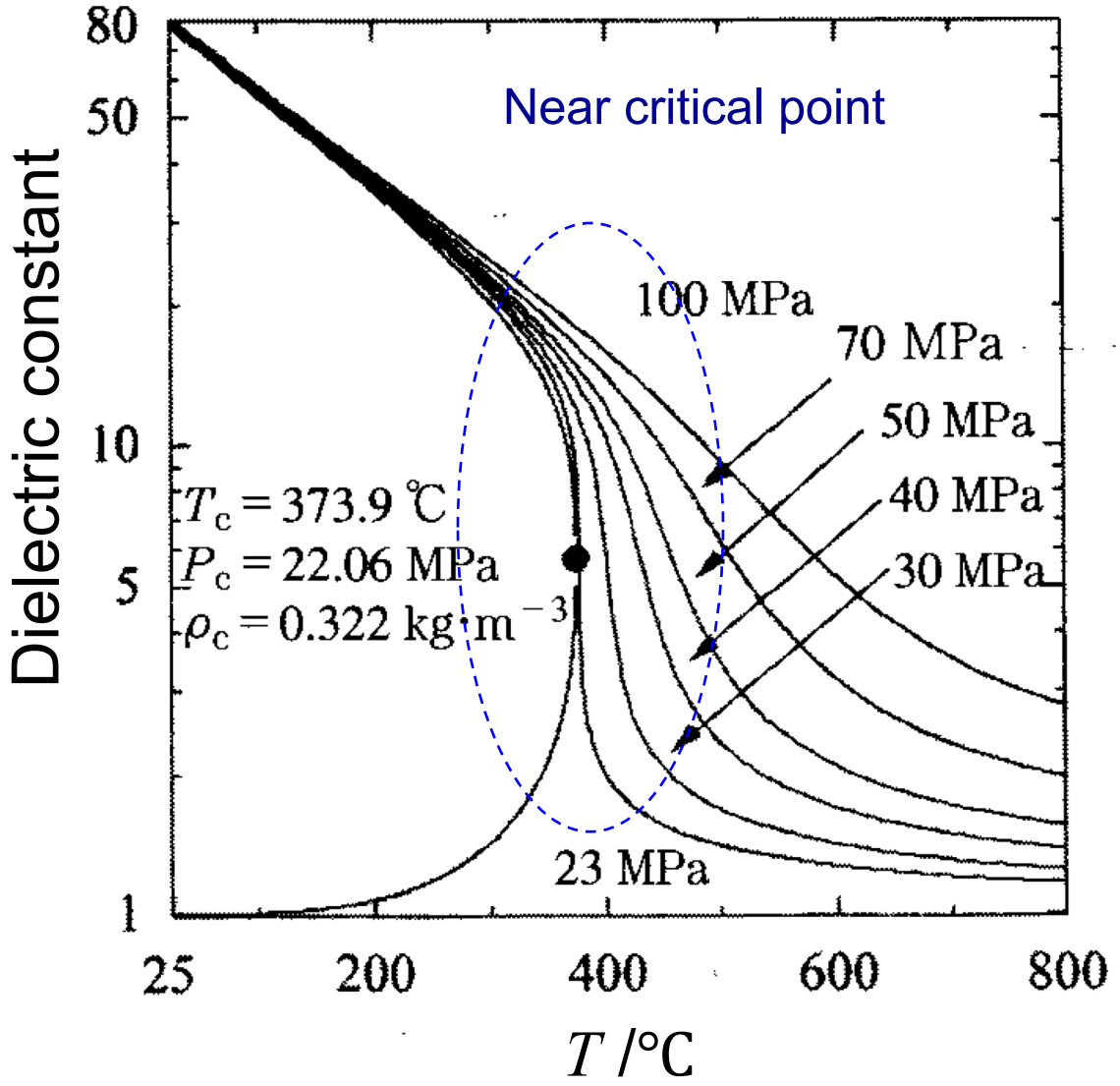


Fundamental Property of SCF

A. 1-3：

Fundamental Property of SCF

- Supercritical water (high temperature and pressure water)



Fundamental Property of SCF

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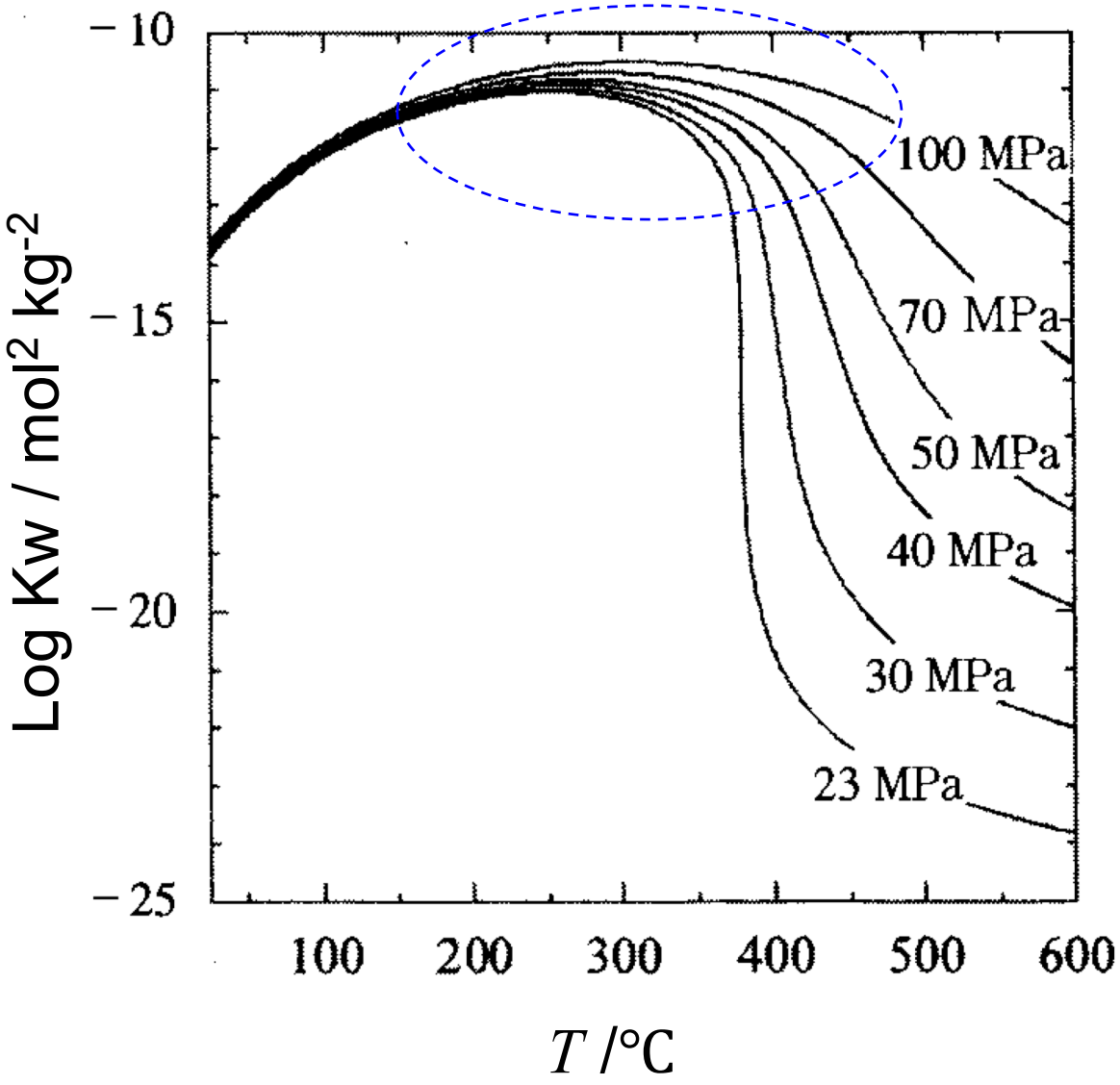


Dissociation of water

$$H_2O \longrightarrow H^+ + OH^-$$

Kw : Ionic product

- Maximum at 300 °C
- Enhancement of hydrolysis

Fundamental Property of SCF

- Supercritical water (high temperature and pressure water)

Ultraheavy oil*

- ✓ Canada: Oilsand
  333 Billion Barrel
- ✓ Venezuela: Oinoco Tar
  289 Billion Barrel
- ✓ Current Oil: 1000 Billion Barrel

Oilsand
(Canada)

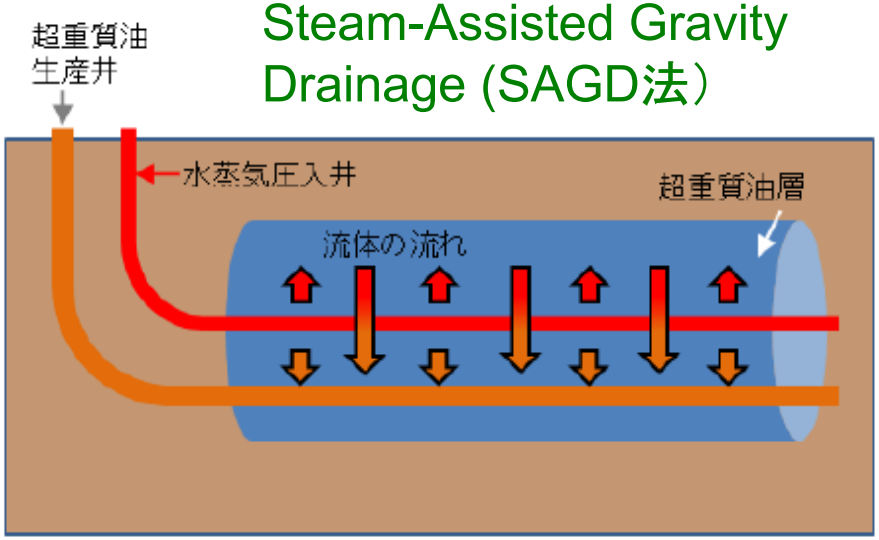
Orinoco Tar
(Venezuela)

Upgrading of Ultraheavy oil*

SAGD : Using high-temperature and pressure water

Upgrading : reduction of viscosity, light oil production, desulfarization

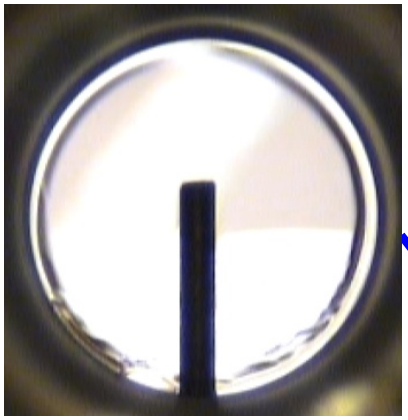
Steam-Assisted Gravity Drainage (SAGD法)



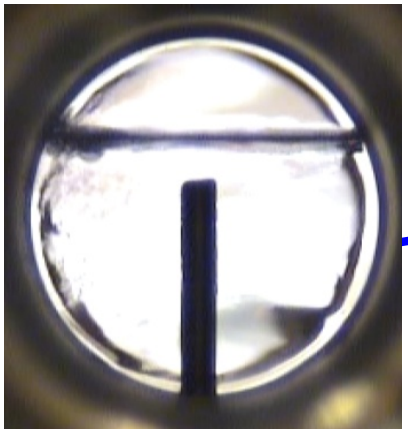
＊石油天然ガス・金属鉱物資源機構　技術部開発技術課報告書 (2011)

Fundamental Property of SCF

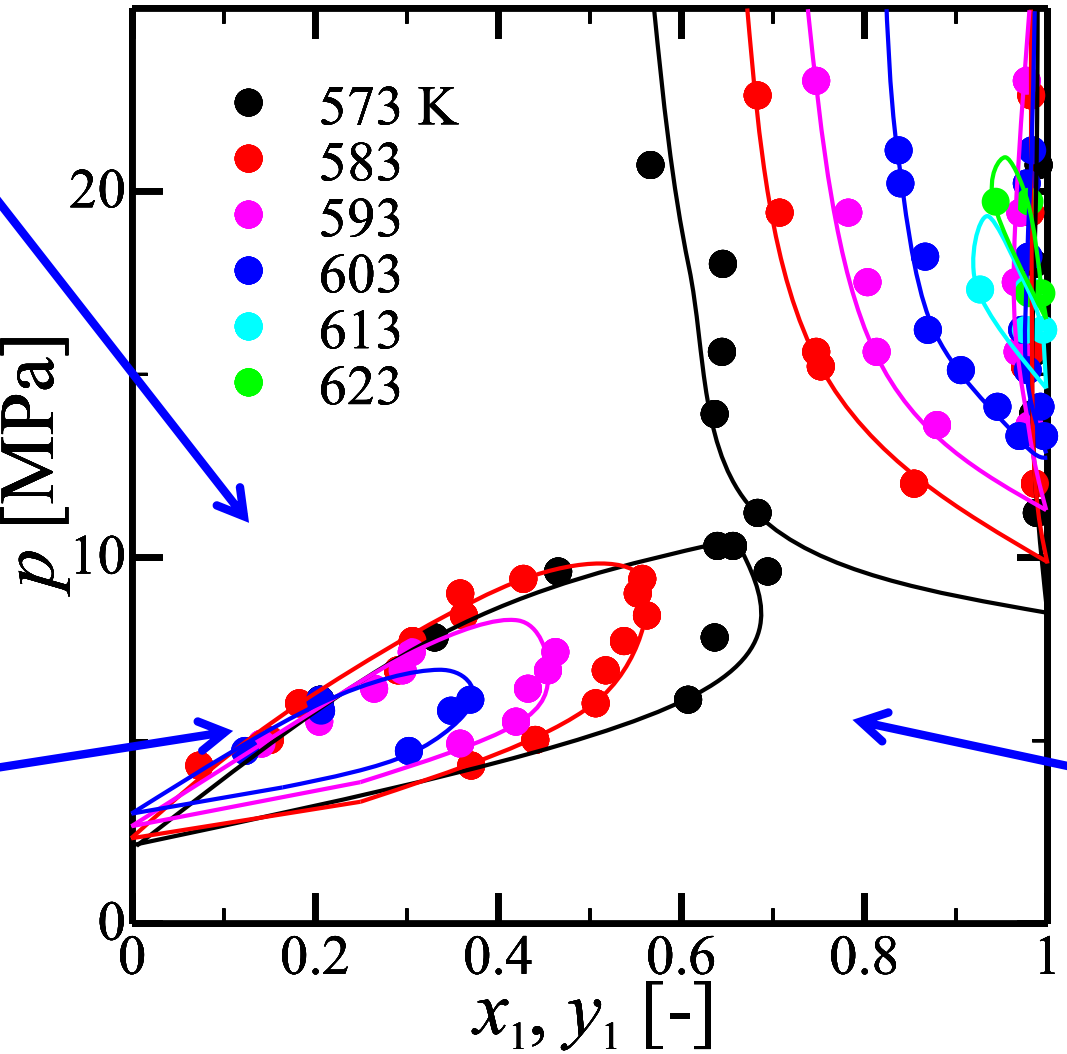
- Supercritical water (high temperature and pressure water)

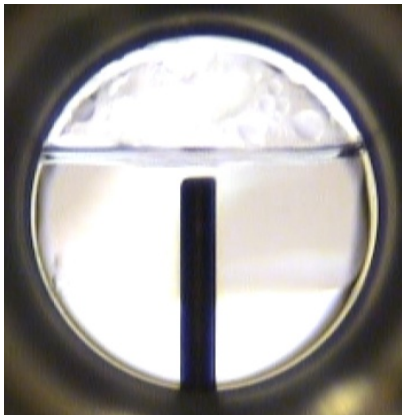


Homogeneous

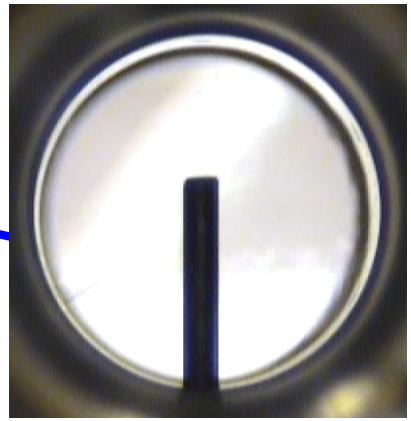


Vapor-liquid





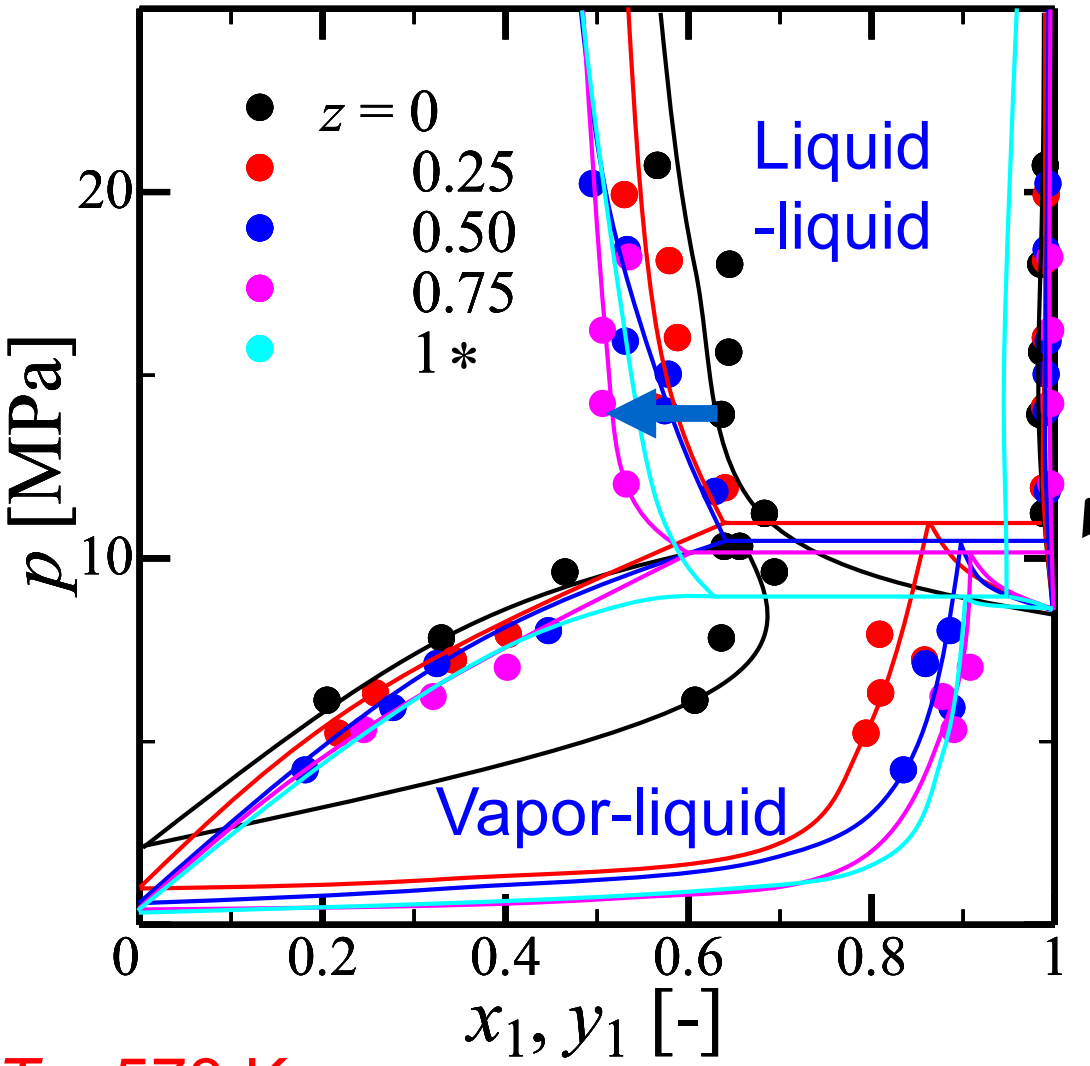
Liquid-liquid



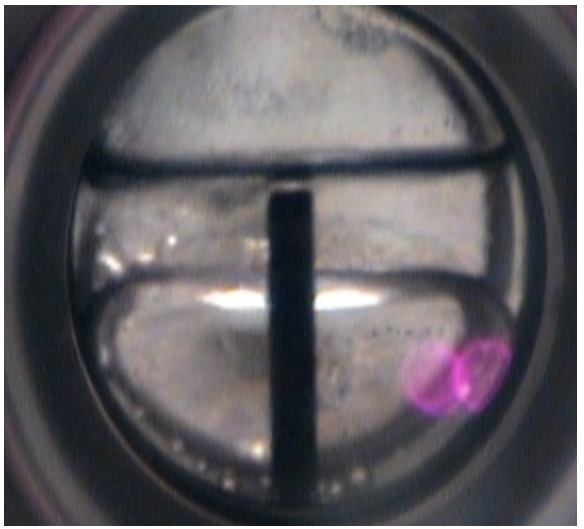
Homogeneous

Fundamental Property of SCF

- Supercritical water (high temperature and pressure water)



T = 573 K

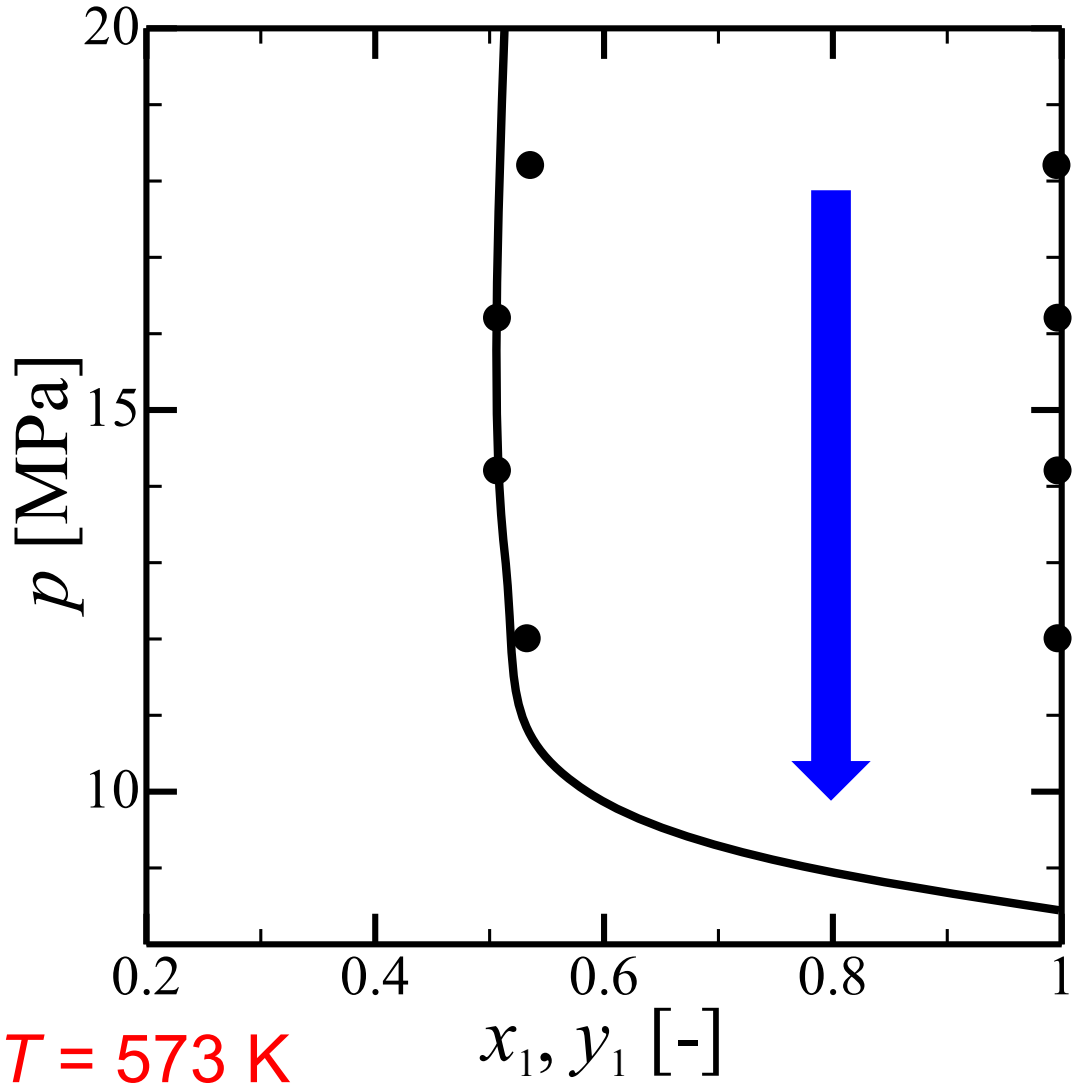


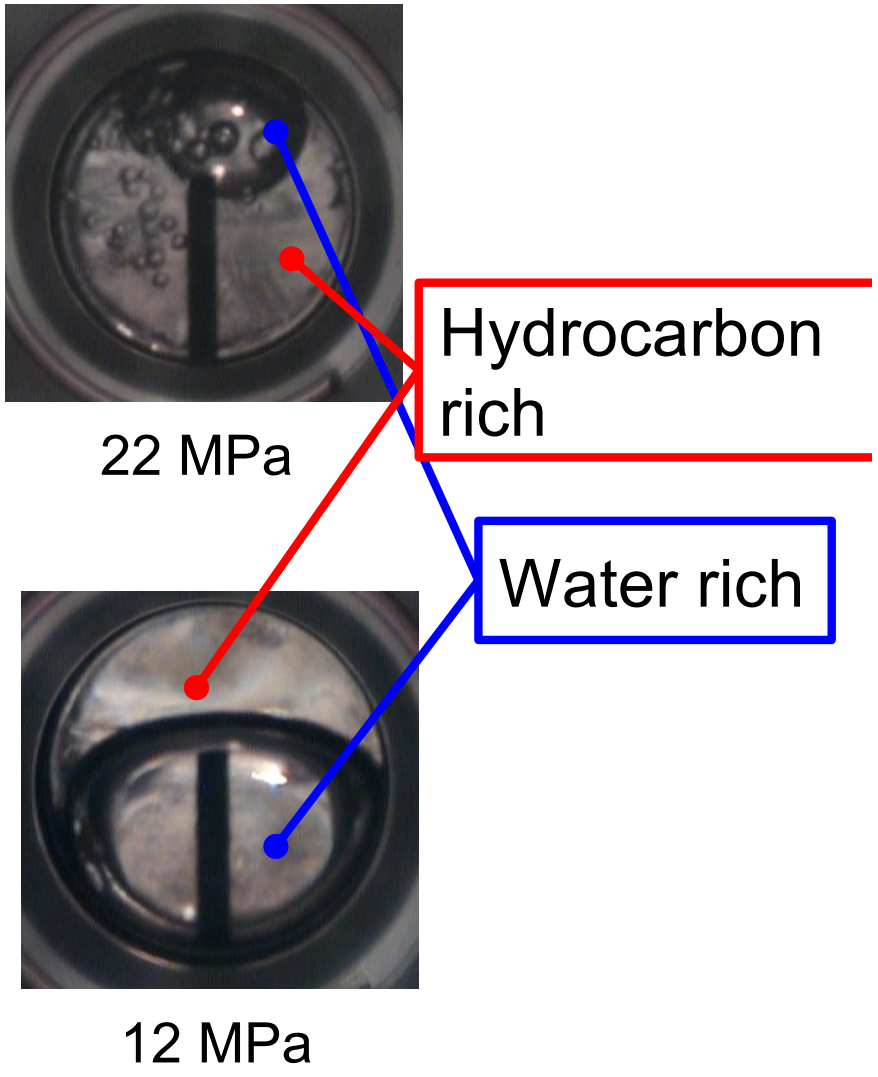
Vapor-liquid-liquid
(VLLE)

Fundamental Property of SCF

- Supercritical water (high temperature and pressure water)

Phase transition on liquid-liquid equilibria





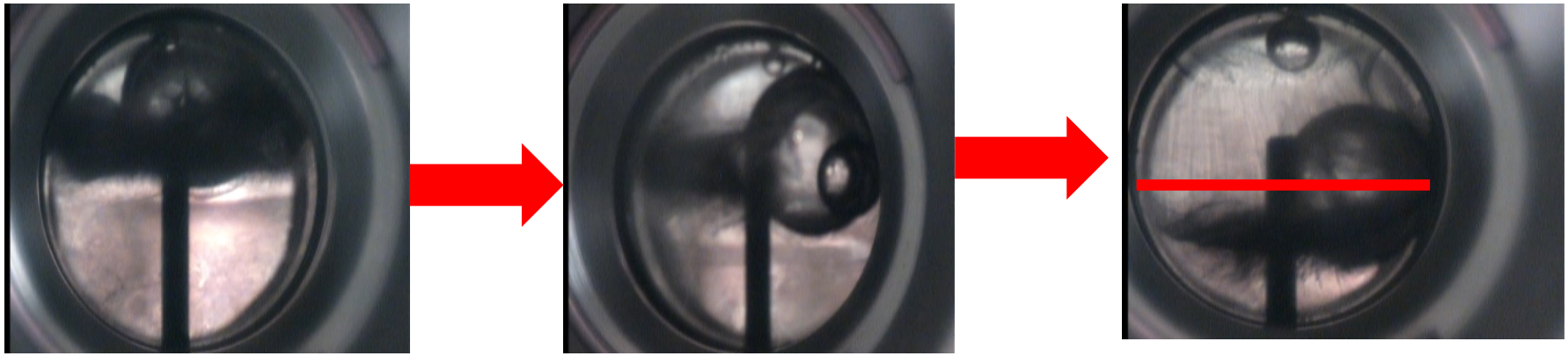
Fundamental Property of SCF

- Supercritical water (high temperature and pressure water)

Mole ratio heavy oil / light oil = 0.75

25.0MPa　　24.5MPa　　24.4MPa

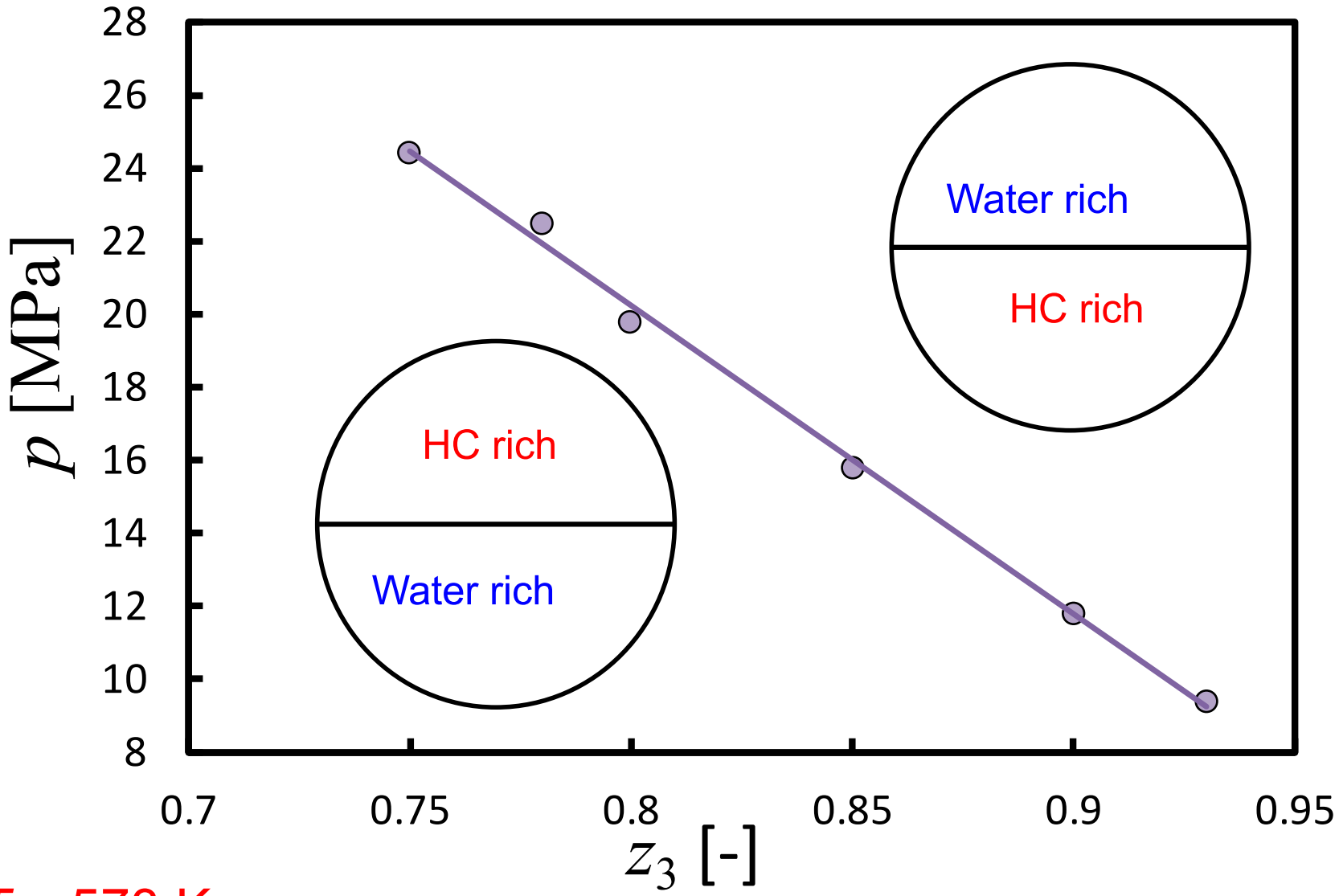
Mole ratio heavy oil / light oil = 0.80



20.5MPa　　20.1MPa　　19.9MPa

Fundamental Property of SCF

- Supercritical water (high temperature and pressure water)



T = 573 K

Q. 1-4 : Why is this phase transition on liquid-liquid two phase region formed?

High pressure

Low pressure