Effect of F-AOT surfactant on the interface between supercritical CO_2 and nickel plating solution

Ji-Young Park, Jong Sung Lim*

Supercritical Research Laboratory, KIST

***Department of Chemical Engineering, Sogang University**

Korea Institute of Science and Technology

INTRODUCTION

Interfacial tension (IFT) and surfactant

1. Why do surfactants tend to go to the interface of a medium ?

2. How do surfactants reduce the interfacial tension ?

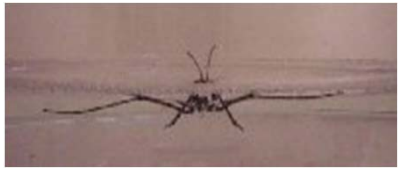
The surface of a liquid is defined as the boundary between two bulk phases, usually between the liquid and air. An interface is formed between two "immiscible" liquids when they are saturated with each other.

To explain why amphiphilic molecules tend to migrate to the interface of a system – we should understand that in general any system tends to evolve such that its lowers it potential energy and hence reach a stable state. An amphiphilic molecule at the interface places itself such that the head and taiare in different mediums according to their liking – this configuration is the one with lowest potential energy .

no surfactant

SDS* = 0.001M

0.002M



0.003M

0.004M

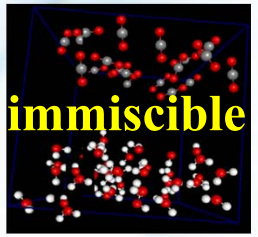
*SDS : Sodium Dodecyl Sulfate

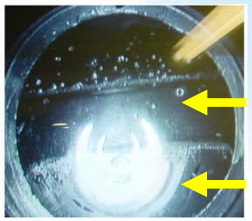
3. Why was IFT of Ni-plating solution/CO_2 measured ?

The electroplating by using supercritical CO_2 has lately attracted considerable attention, since it is environmentally friendly process.

This electroplating process uses the emulsion phenomena between plating solution and CO_2

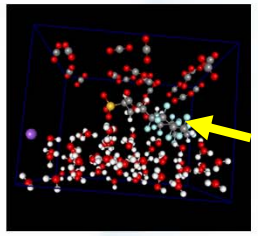
IFT data are requisite as a basic information to understand the emulsion phenomena.



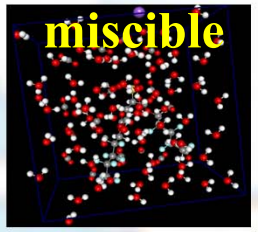


CO_2

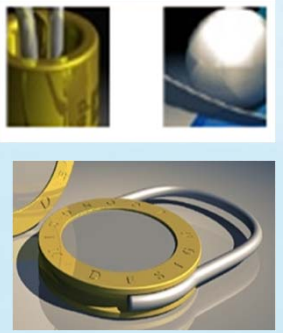
Ni-plating solution



Surfactant

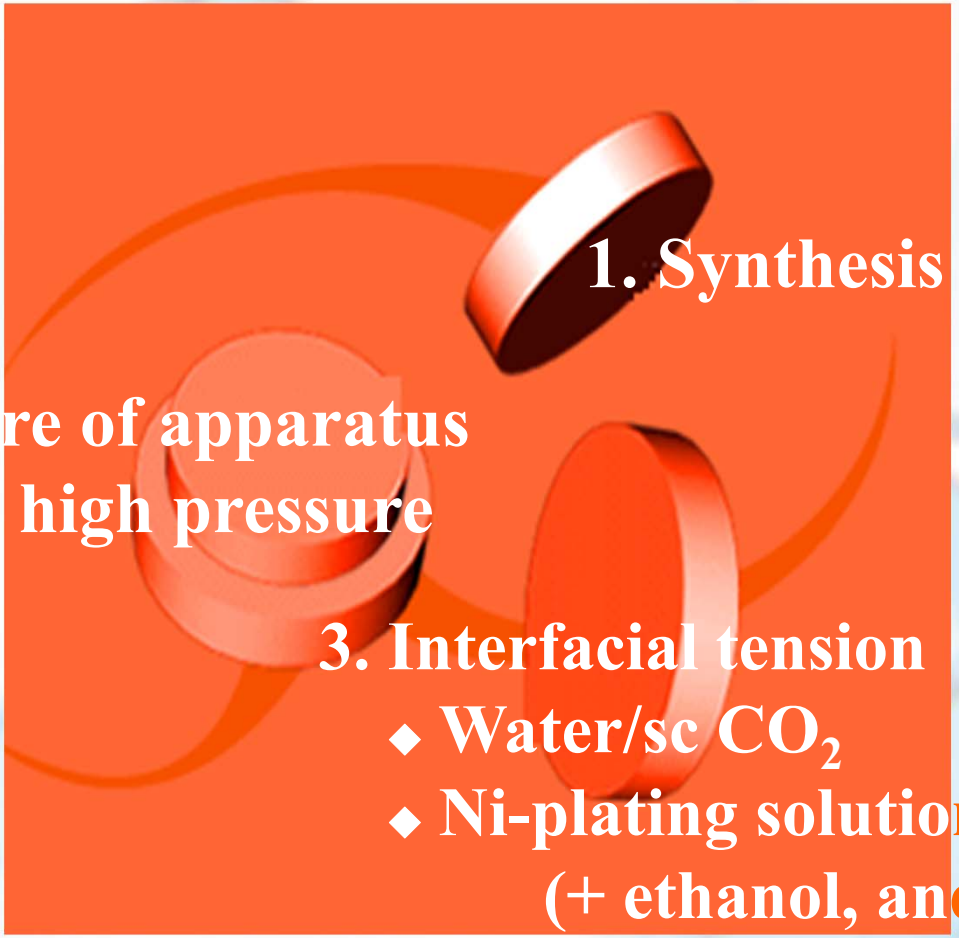


Electroplating by using emulsion



< plated ware >

Research contents



1. Synthesis of Surfactant

2. Manufacture of apparatus for IFT in high pressure

3. Interfacial tension measurement
   - Water/sc CO_2
   - Ni-plating solution/sc CO_2 (+ ethanol, and surfactant)

THEORY

IFT was measured by using capillary rise method and it was calculated by following equation.

$$8\pi r\gamma dr = \Delta P \cdot 4\pi r^2 dr$$

$$\Delta P = \Delta\rho gh = \frac{2\gamma}{r}$$

$$a^2 = \frac{2\gamma}{\Delta\rho g}$$

$$\Delta\rho gh = \frac{2\gamma\cos\theta}{r}$$

$$R = \frac{r}{\cos\theta}$$

$$\gamma = \frac{1}{2} rg(h)\frac{\Delta\rho}{\cos\theta}$$

$$a^2 = r\left(h + \frac{r}{3} - \frac{0.1288r^2}{h} + \frac{0.1312r^3}{h^2}\right)$$

$$\gamma = \frac{1}{2} rg\left(h + \frac{r}{3}\right)\frac{\Delta\rho}{\cos\theta}$$

r : the radius of the capillary [m]

g : the acceleration of gravity (m/sec^2)

h : the height of the meniscus [m]

θ: the contact angle

Various methods for interfacial tension

→ In this work, capillary rise method was used

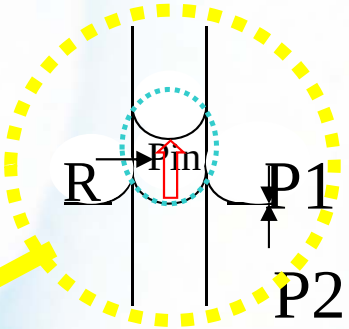
Powder contact angle method

Du Nouy ring method

Pendant drop method

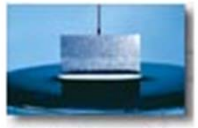
Spinning drop method

Dynamic Wilhelmy method



Capillary rise method

Drop volume method



Wilhelmy plate method

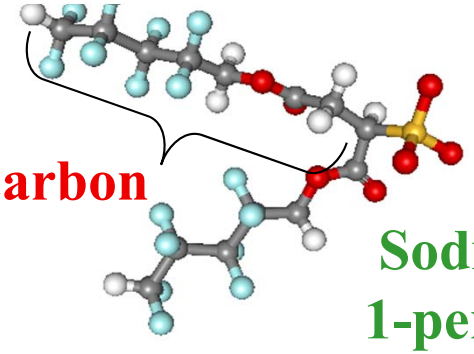
Sessile drop method

Bubble pressure method

EXPERIMENTAL

Synthesis of surfactant

We synthesized the fluorocarbon-hydrocarbon hybrid nonionic surfactants with both 'CO_2 philic' and 'hydrophilic' chain and form water (polar) in CO_2 (nonpolar) emulsion by using these surfactants



fluorocarbon-hydrocarbon chain

$(SO_3Na)^+$ head group

Sodium salt of bis(2,2,3,3,4,4,5,5-octafluoro-1-pentyl) sulfosuccinate → di-HCF4

$$C_4H_2O + 2R_fOH \xrightarrow{H^+/\text{toluene}} R_fOOCCH{=}CHCOOR_f \xrightarrow{NaHSO_3/1,4\text{-dioxane}} R_fOOCCH_2CH(SO_3Na)COOR_f$$

; $R_f = H(CF_2)_4CH_2$ (di-HCF4)

Scheme 1. Synthesis of fluorocarbon-hydrocarbon hybrid surfactant

Apparatus for IFT measurement in high pressure

< schematic diagram >

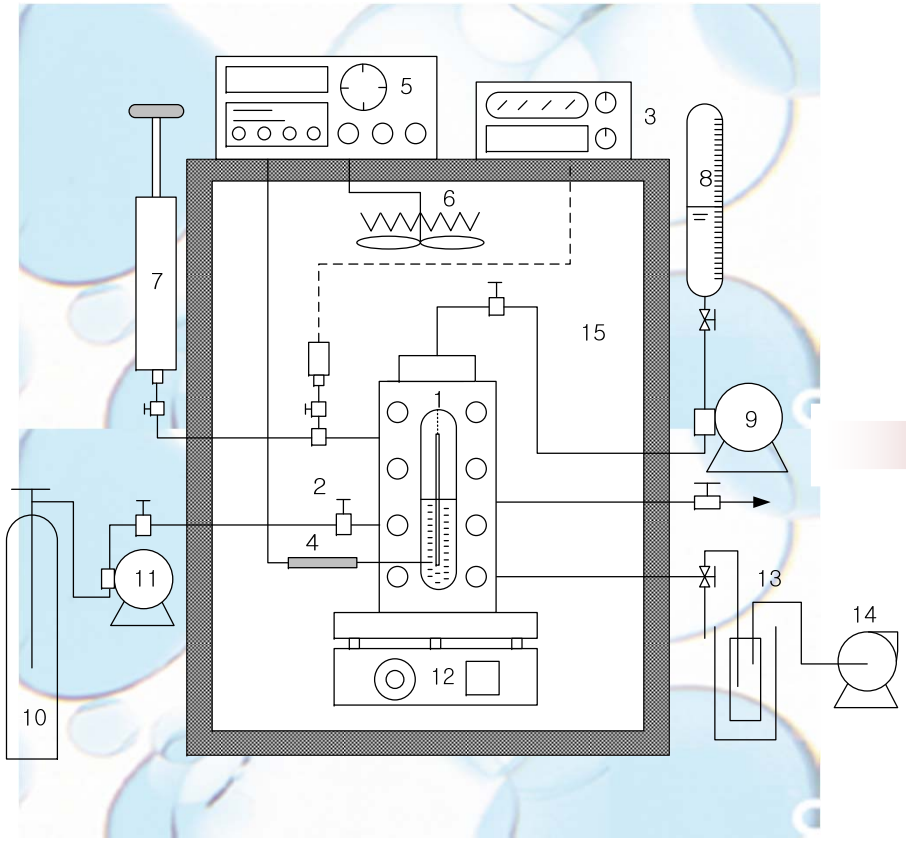


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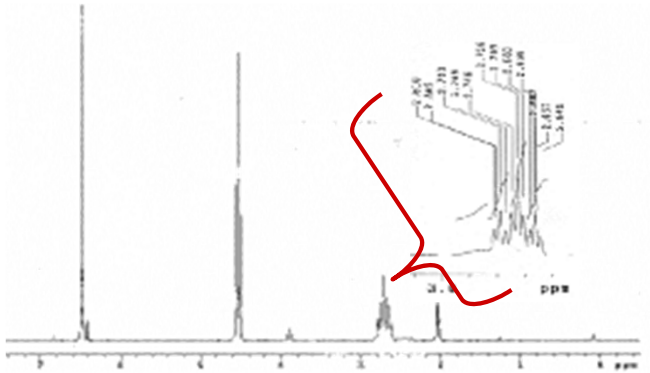
Fig. 2 Experimental apparatus

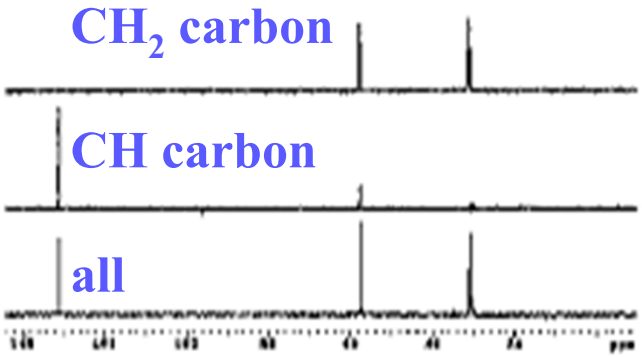
RESULTS AND DISCUSSION

Identification of surfactant by NMR analysis

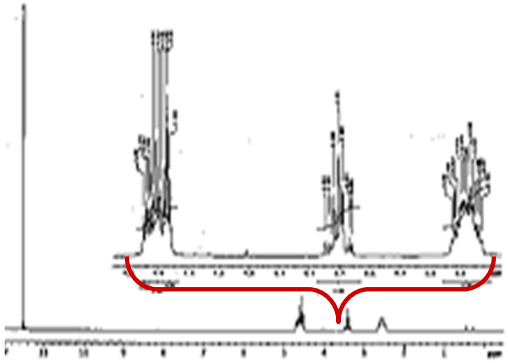
(a) ^{1}H NMR of di-HCF4 1st



(c) ^{13}C NMR of di-HCF4 2nd



(b) ^{13}C NMR of di-HCF4 1st



(d) DEPT of di-HCF4 2nd

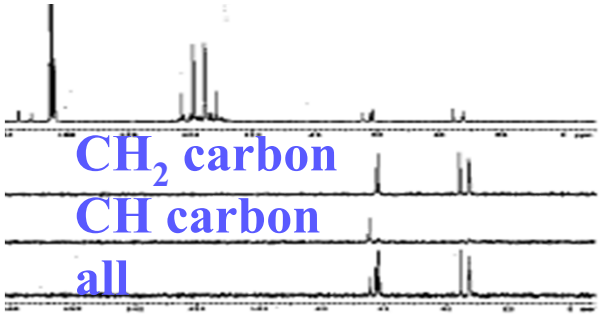
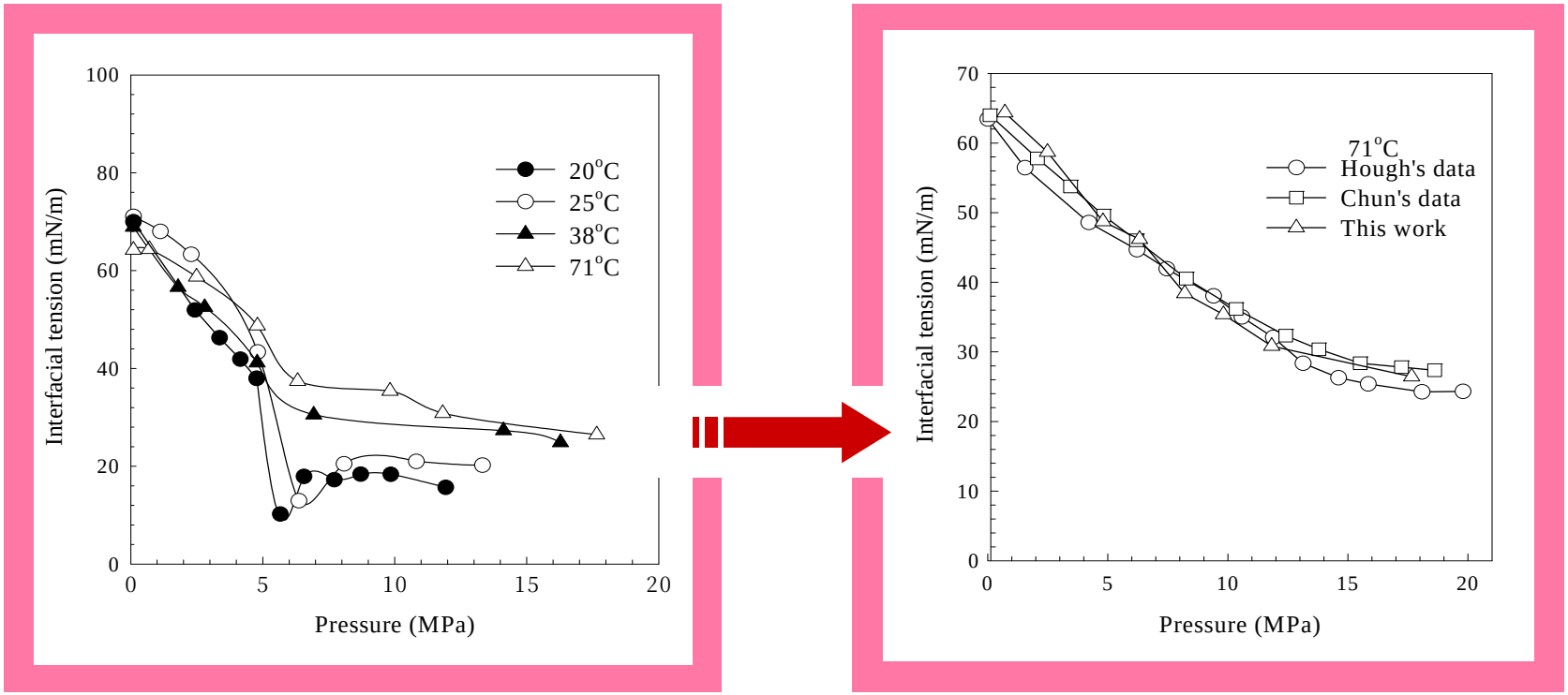


Fig. 3. Results of NMR spectra (500MHz)

Consistency of interfacial tension data

- Comparison with literature data



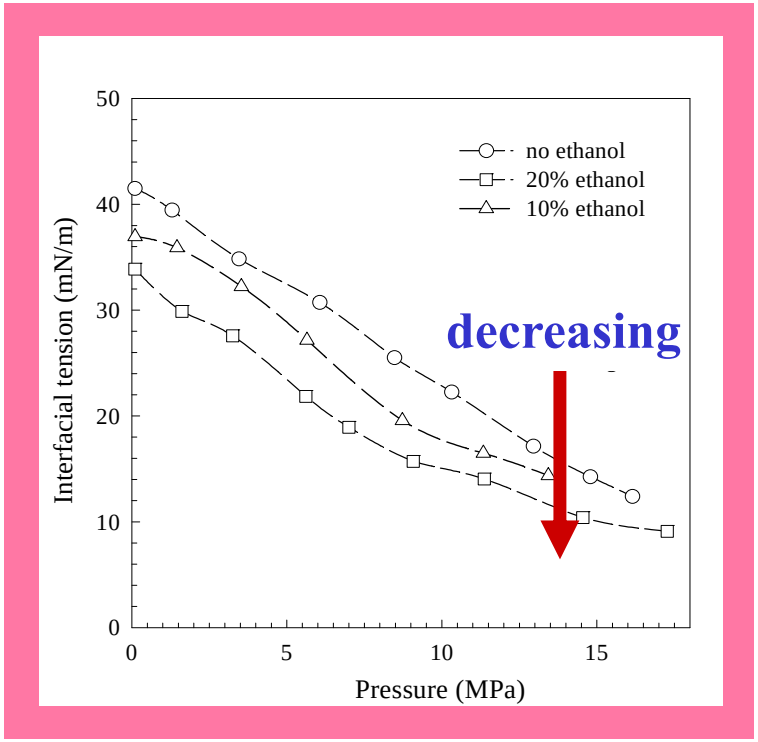
(a) (b)

Fig. 4. Comparison of interfacial tension for Water + CO_2 system; (a) IFT of water + CO_2 at 38°C, (b) IFT of water + CO_2 at 71°C

Measurement of interfacial tension in sc state

- Ni-plating solution + CO_2 + ethanol system -

Ethanol effect



The IFT of water + CO_2 + ethanol system was lower than that of water + CO_2 system. The cohesive force of ethanol was low compared with that of water remarkably

→ IFT of Ni-plating solution + CO_2 + ethanol was decreased by adding ethanol because ethanol weakens the interfacial tension.

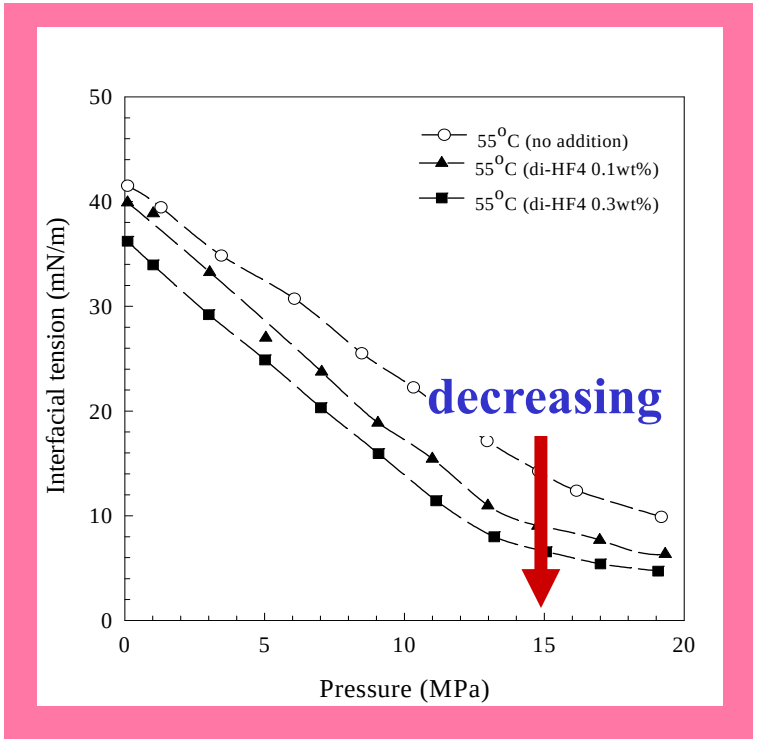
→ Interfacial tension of solution was dependent on ethanol volume.

Fig. 5. Ethanol effect in IFT of Ni-plating solution + ethanol + CO_2(10, 20vol%) at 55°C

Measurement of interfacial tension in sc state

- Ni-plating solution + CO_2 + surfactant system -

Surfactant effect



To investigate the effect on the concentration of surfactant, we added the 0.1wt% and 0.3wt% in Ni-plating solution

As the concentration of surfactant was higher, the interfacial tension between two fluids became lower.

Surfactant promotes the adsorption on surface between CO_2 and water.

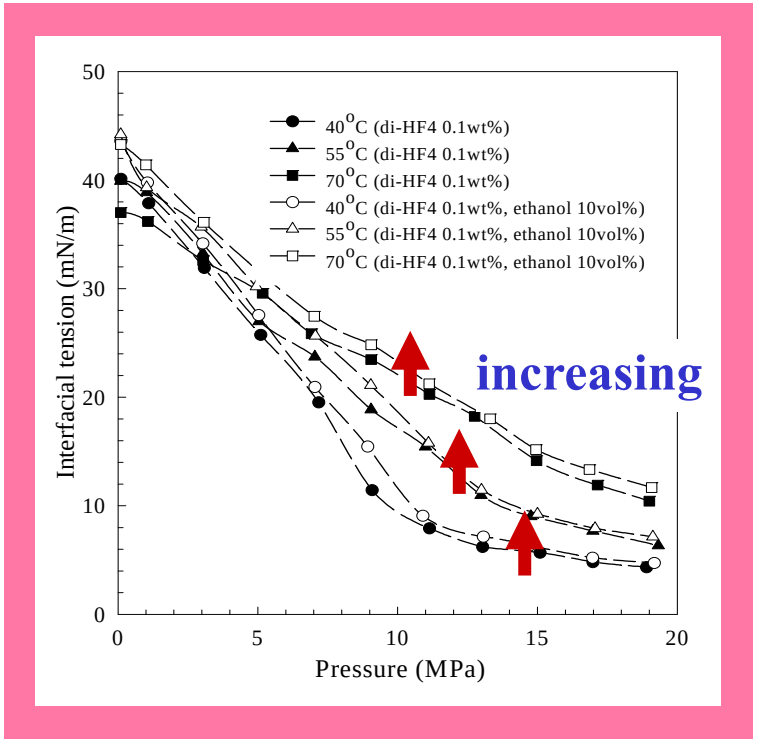
→ Interfacial tension of solution was dependent on surfactant concentration

Fig. 6. Surfactant effect in IFT of Ni-plating solution + surfactant + CO_2 (0.1wt% and 0.3wt%) at 55°C

Measurement of interfacial tension in sc state

- Ni-plating solution + CO_2 + ethanol + surfactant -

Surfactant + ethanol effect



IFT of Ni-plating solution + CO_2 + surfactant (0.1, 0.3wt %) + ethanol (10vol%) system were measured at 40°C, 55°C and 70°C.

It is known for alcohol such as isopropyl alcohol, ethanol, methanol, and butanol to reduce the IFT.

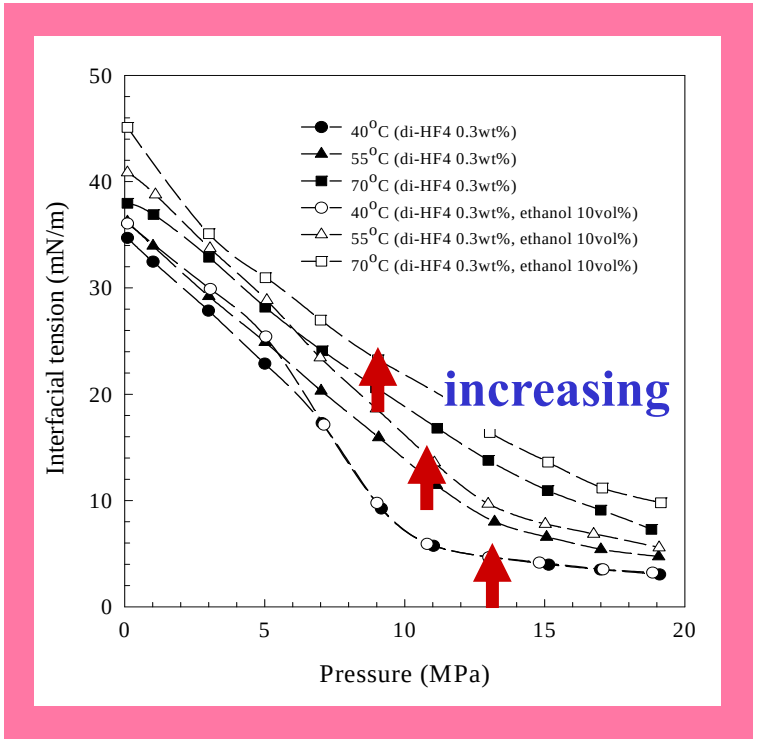
By means of addition of the ethanol of 10vol% into Ni-plating solution + CO_2 + surfactant system, we expected the synergy effect for reduction of IFT.

Fig. 7. IFT of CO_2 + Ni-plating solution + ethanol(10vol%) + di-HCF4(0.1wt%) at 40°C, 55°C, and 70°C.

Measurement of interfacial tension in sc state

- Ni-plating solution + CO_2 + ethanol + surfactant -

Surfactant + ethanol effect



But, when we compared with IFT in solution with ethanol, IFT was increased. By adding ethanol in surfactant + Ni-plating solution + CO_2 system, ethanol obstructs the adsorption of surfactant dissolved in water.

As a result, interfacial tension was increased.

Researches on mechanism of interface between CO_2 and aqueous solution with both alcohol and surfactant are in progress.

Fig. 8. IFT of CO_2 + Ni-plating solution + ethanol(10vol%) + di-HCF4(0.3wt%) at 40°C, 55°C, and 70°C.

Summary of Results

1) Water + CO_2 system; IFT of this system was measured at 20°C, 25°C, 38°C, and 71°C. The IFT of water + CO_2 decreased with rising pressure and increased with rising temperature at higher pressures.

2) Ni-plating solution + CO_2 system; IFT of this system was measured at 40°C, and 55°C. → As the temperature rose, the IFT were increased at constant pressure.

3) Ni-plating solution + CO_2 + surfactant system; IFT of this system was measured at 40°C, 55°C and 70°C.

→ As the concentration of surfactant was higher, the IFT between two fluids became lower. Surfactant promotes the adsorption on surface between CO_2 and water.

4) Ni-plating solution + CO_2 + ethanol system; IFT of this system was decreased by adding ethanol because ethanol weakens the interfacial tension.

5) Ni-plating solution + CO_2 + surfactant + ethanol system; IFT of this system was measured at 40°C, 55°C and 70°C. By adding ethanol in surfactant + water + CO_2 system, ethanol obstructs the adsorption of surfactant dissolved in water. As a result, interfacial tension was increased.

CONCLUSION

We synthesized the nonionic H-F hybrid surfactant which have both CO_2 philic and hydrophilic tail and measured the IFT of CO_2/water and CO_2/nickel plating solution system. In IFT measurement, the effect of surfactant and ethanol was investigated.

This research is will expected to be helpful for understanding the interface phenomena between CO_2 and polar chemicals such as water or nickel plating solution in supercritical CO_2.