초임계 CO_2 내에서 CO_2와 nickel 도금액 계면에 미치는 비이온 계면활성제의 영향

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Effect of nonionic surfactant on interface between CO_2 and nickel plating solution in supercritical CO_2

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Introduction

Carbon dioxide(CO_2) has been regarded as a useful chemical having many advantages that it is cheap, nonflammable, nontoxic, chemically inert, recyclable, and readily accessible to supercritical region (T_C=31°C, P_C=7.38MPa)[1]. Especially, supercritical CO_2 have interesting solvating characteristics and provide greatly increased mass transfer rates in various fields such as an organic synthesis [2], electrochemical synthesis[3], and polymerization [4], etc. In spite of these advantages, CO_2 is also regarded as a poor solvent because the solubility of polar chemicals in CO_2 which is nonpolar is very low[5]. For this reason, the usage of CO_2 as a reaction solvent with water has lagged. Recently, the efforts to overcome these disadvantages of CO_2 are lively carried out by many chemists and engineers. One of these is the research about the formation of emulsion that polar chemicals of nano(nm) or micro(μm) size droplets in diameter were dispersed in CO_2[6-8]. It is desired that many polar chemicals will be soluble in CO_2, therefore, it is applied in various fields such as reaction, separation, electroplating process[9] etc. in supercritical CO_2. Among these, the electroplating process in supercritical CO_2 used the emulsion phenomena have been researched in my laboratory and this process will be resulted in reducing the aqueous plating solution. In formation of emulsion of immiscible phases like water or the aqueous plating solution and CO_2 emulsion, the interfacial tension (IFT) has an influence in formation of emulsion. Therefore these data are requisite as a basic information to understand the emulsion with CO_2. Unfortunately, the measurement of the IFT in high pressure CO_2 was hardly carried out except for several studies[10-11]. In this research, we manufactured the apparatus for IFT by using the capillary rise method in high pressure and measured the IFT of 1)water+CO_2 at 71°C, 2)nickel plating solution+CO_2 at 55°C, 3)nickel plating solution+CO_2+surfactant (0.1, 0.3 wt%) at 40°C, and 55°C, 4)Nickel plating solution+CO_2+ethanol (10, 20 vol%) at 55°C, and 5) nickel plating solution+CO_2+surfactant (0.1, 0.3 wt%)+ ethanol(10 vol%) at 40°C, and 55°C in the ranges of 0.1MPa~20.0 MPa by using the capillary rise method. The consistency of experimental data of water+CO_2 was confirmed by comparing of experimental data and others data[10-11] at 71°C.

Theory

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

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

γ(mN/m) is interfacial tension, r(m) is the radius of the capillary, h(m) is the height of the meniscus above a flat liquid surface (for which ΔP must be zero), (g/ml) is the difference between density of CO_2 and density of water (or nickel plating solution), g(m/sec^2) is the acceleration of gravity, θ is the contact angle (it is assumed as a 0^o).

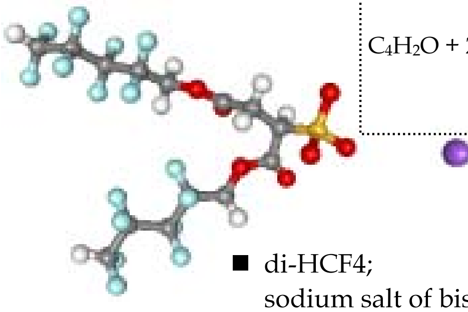
Experimental

Synthesis of surfactant and measurement of solubility The synthesis of fluorocarbon-hydrocarbon hybrid nonionic surfactants such as sodium salt of bis(2,2,3,3,4,4,5,5-octafluoro-1-pentanol) sulfosuccinate (di-HCF4) and the sodium salt of bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-octyl)-2-sulfosuccinate (di-HCF7) was reported by Zhao-Tie Liu and Can Erkey[13] and the measurement of solubility was expressed in previous paper[1] in detail.

Interfacial tension measurement The procedure for IFT measurement is shown in Chun's paper in detail[ref].

$$C_4H_2O + 2R_fOH \xrightarrow{H^+/\text{toluene}} R_fOOCCH = CHCOOR_f \xrightarrow{NaHSO_3/1,4\text{-dioxane}} R_fOOCCH_2CH(SO_3^-Na^+)COOR_f$$

R_f=$F(CF_2)_6CH_2CH_2$ (di-HCF7), $H(CF_2)_4CH_2$ (di-HCF4)



- di-HCF4;
sodium salt of bis(2,2,3,3,4,4,5,5-octafluoro-1-pentyl) sulfosuccinate >

Results and Discussion

Two surfactants with 'CO_2 philic group' and hydrophilic group were synthesized. According to Tie Liu and Can Erkey's experiment, di-HCF 4 is soluble with an added water and better than di-HCF 7 in the water/CO_2 emulsion formation among these. By this result, di-HCF4 surfactant was chosen and used in measurement of IFT .

Interfacial tension measurement In this study, we measured the IFT of various systems such as 1) water + CO_2, 2) nickel plating solution + CO_2, 3) nickel plating solution + surfactant (di-HCF 4) + CO_2, 4)Nickel plating solution+CO_2+ethanol (10, 20 vol%)at 55^{o}C, and 5) nickel plating solution + surfactant (di-HCF 4) + ethanol + CO_2. We considered the effect of temperature, surfactant, and ethanol on interface between CO_2 and nickel plating solution in supercritical CO_2.

Table 1. Properties of chemicals

chemical	$^a\gamma$(mN/m)	T(K)
Pure water	72.7	299.15
Nickel plating solution	43.0	299.15

$^a\gamma$(mN/m) : interfacial tension in atmospheric condition

1)w*ater + CO_2 system* IFT of water + CO_2 system was measured at 71°C for data consistency. IFT data of water + CO_2 at 71°C were compared with Hough's data [12] and Chun's data [13] and represented in Figure 1

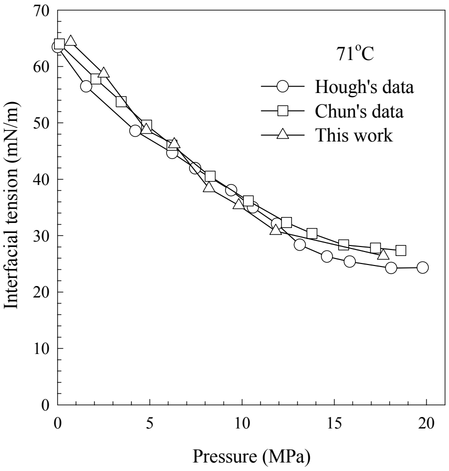


Figure 1. Comparison of IFT for CO_2 + Water mixture at 71°C

2) *Nickel plating solution + CO_2 system* IFT of nickel plating solution + CO_2 system was measured at 55°C. IFT of this system was lower than that of water + CO_2 system because nickel ions that dissolved in water work as electrolytes. This result was shown in Figure 2.

3) *Nickel plating solution + CO_2 + di-HCF4 surfactant system* To investigate the effect on the concentration of di-HCF 4 surfactant, we added the 0.1wt% and 0.3wt% in nickel plating solution and measured IFT of nickel plating solution + CO_2 + di-HCF 4 system at 40°C, and 55°C. As the concentration of surfactant was higher, the IFT on between two fluids became lower. This result was shown in Figure 3.

4) ***Nickel plating solution + CO_2 + ethanol system***
IFT of nickel plating solution + CO_2 + ethanol (10vol%) system were measured at 55°C. Ethanol reduced IFT like Chun's study[13] that alcohol such as isopropyl alcohol, ethanol, methanol, and butanol reduce the IFT of water +CO_2. This result was shown in Figure 4.

5) Nickel plating solution + CO_2 + di-HCF 4 surfactant + ethanol system To look into effect ethanol and surfactant at the same time, IFT of nickel plating solution + CO_2 + di-HCF 4 surfactant (0.1, 0.3 wt %) + ethanol (10vol%) system were measured at 40°C, and 55°C. By experiments 3) and 4), the double effects of reduction in IFT was predicted. But, when IFT of solution with both ethanol and di-HCF4,it was increased. These results were shown in Figures 4 and 5.

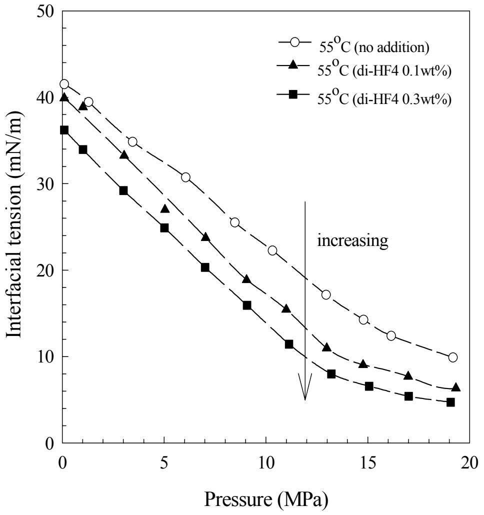


Figure 2. IFT of CO_2 + Nickel plating solution + di-HCF 4 at 55°C

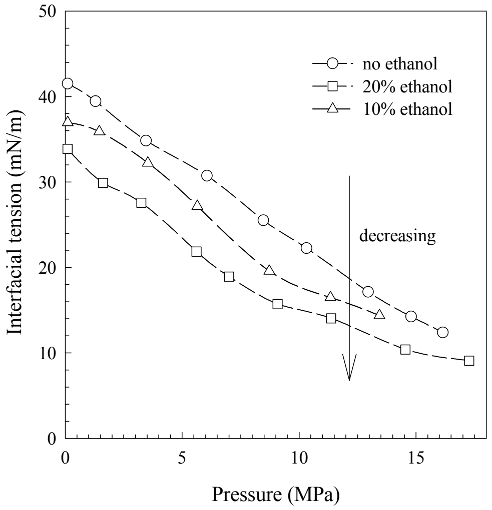


Figure 3. IFT of CO_2 + Nickel plating solution + ethanol at 55°C

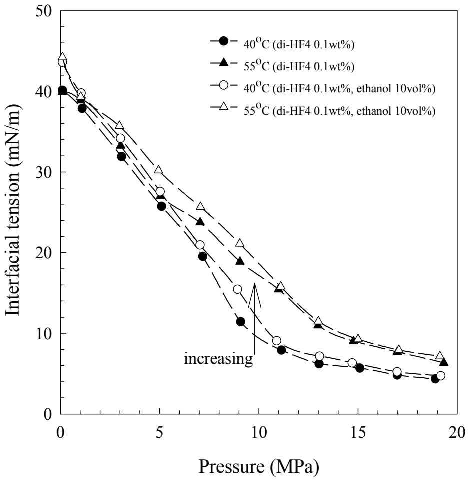


Figure 4. IFT of CO_2 + Nickel plating solution + di-HCF 4 + ethanol at 40°C, and 55°C

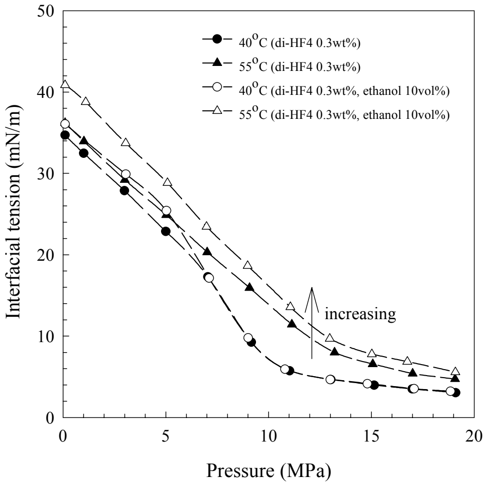


Figure 5. IFT of CO_2 + Nickel plating solution + di-HCF 4) + ethanol at 40°C, and 55°C.

Conclusion

We synthesized two nonionic H-F hybrid surfactants which have CO_2 philic tail and hydrophilic tail and measured the solubility of this surfactant in CO_2 and 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 be up to the expectation of a help for understanding interface phenomena between CO_2 and polar chemicals such as water or nickel plating solution in supercritical CO_2.

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