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Articles

Effect of a Fluorinated Sodium Bis(2-ethylhexyl) Sulfosuccinate (Aerosol-OT, AOT) Analogue Surfactant on the Interfacial Tension of CO_2 + Water and CO_2 + Ni-Plating Solution in Near- and Supercritical CO_2

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The effect of a fluorinated sodium bis(2-ethylhexyl) sulfosuccinate (aerosol-OT, AOT) analogue surfactant (sodium salt of bis(2,2,3,3,4,4,5,5-octafluoro-1-pentanol) sulfosuccinate) on the interfacial layer of supercritical CO_2 + water and supercritical CO_2 + Ni-plating solution systems was investigated by measuring via the capillary rise method. These interfacial tensions were measured in the pressure range of (0.1 to 20.0) MPa at multiple temperatures for each of five interfaces: (1) CO_2 + water system at (293.15, 298.15, 311.15, and 344.15) K; (2) CO_2 + Ni-plating solution system at (313.15, 328.15, and 344.15) K; (3) CO_2 + Ni-plating solution + F-AOT surfactant (0.1 and 0.3 mass %) system at (313.15, 328.15, and 344.15) K; (4) CO_2 + Ni-plating solution + ethanol (10 and 20 vol %) system at 328.15 K; and (5) CO_2 + Ni-plating solution + F-AOT surfactant (0.1 mass %) + ethanol (10 vol %) system at (313.15, 328.15, and 344.15) K. The reliability of the apparatus was confirmed by comparing the experimental data with literature data for the CO_2 + water system at (311.15 and 344.15) K. The individual addition of the F-AOT surfactant and ethanol reduced the interfacial tension for the CO_2 + Ni-plating solution system; however, the simultaneous addition of these two substances caused the opposite effect on the interfacial tension.

1. Introduction

CO_2 is regarded as a useful chemical reagent for several reasons: it is cheap, nonflammable, nontoxic, chemically inert, and recyclable. In particular, CO_2 is readily accessible to the supercritical state ($T_c = 304.15$ K, $P_c = 7.38$ MPa) compared to other solvents such as H_2O ($T_c = 647.15$ K, $P_c = 22.12$ MPa), CH_3OH ($T_c = 512.6$ K, $P_c = 8.09$ MPa), and so forth.

Moreover, supercritical CO_2 has good solvating characteristics and provides greatly increased mass-transfer rates in various applications such as in organic synthesis,[1] electrochemical synthesis,[2] and polymerization.[3] CO_2 is also considered to be a poor solvent; however, its low dielectric constant and polarizability per volume permit only very low solubility of polar molecules. The use of CO_2 has thus not competed with water as a reaction solvent.

Many chemists and engineers are actively working to overcome the disadvantages of CO_2. One such effort is research into the formation by polar chemicals of nano- or micrometer-sized droplets and their dispersal in CO_2 (microemulsion or macroemulsion).[4,5] Johnston et al.[6] discovered that an ammonium carboxylate perfluoropolyether [$CF_3O(CF_2CF(CF_3)OCF_2COO{-}NH_4$, PEPF)] surfactant could support microemulsion in supercritical CO_2, whereas Harrison et al.[4] demonstrated that dichain surfactant [$(C_7H_{15})(C_7F_{15})CHSO_4^-Na^+$] could microemulsify up to its own mass in water. These emulsion phenomena in supercritical CO_2 have been applied to various fields ranging from reaction and separation to the electroplating process.[7,8]

Electroplating has been reported as an application by H. Yoshida et al.[7] They improved the qualities of plated ware by adding additives or changing the surfactant. For this study, the interfacial tension was considered to be an influential factor. Interfacial tension was related to the formation of emulsions between immiscible fluids such as aqueous plating solutions and CO_2.

The interfacial tension is an important thermodynamic property in supercritical fluid applications because the supercritical process is directly influenced by the change in interfacial tension. Affected applications include the formation of fibers, generation of foams, and macroemulsion and microemulsion processes in the supercritical state as well as the formation of nanoparticles using the rapid expansion of a supercritical solution. Therefore, the knowledge of the interfacial tension data is needed to understand the emulsion with CO_2 and the research of this property was reported.[9−11]

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Scheme 1. Structure of Sodium Salt of Bis(2,2,3,3,4,4,5,5-octafluoro-1-pentanol) Sulfosuccinate

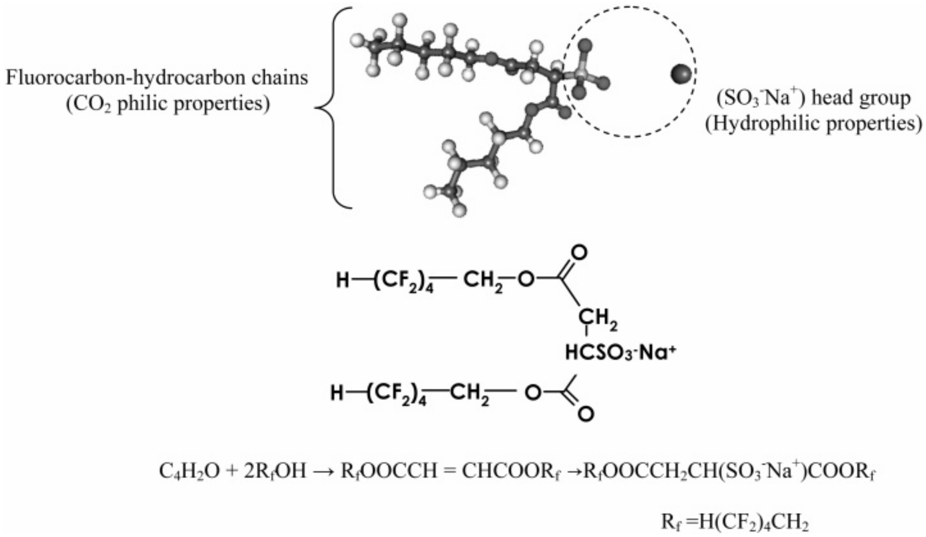


Table 1. Interfacial Tension of Chemicals

chemical	γ/mN·m^{-1a}	T/K
pure water	72.7	299.15
Ni-plating solution	43.0	299.15

[a] γ (mN/m): interfacial tension under atmospheric conditions.

In this work, we measured the interfacial tension between Ni-plating solution and CO_2 and investigated the effect of surfactant and an additive on the surface of the Ni-plating solution and CO_2 by the capillary rise method. The systems measured at high pressure were the CO_2 + water system at (293.15, 298.15, 311.15, and 344.15) K, the CO_2 + Ni-plating solution system at (313.15, 328.15, and 344.15) K, the CO_2 + Ni-plating solution + surfactant (0.1 and 0.3 mass %) system at (313.15, 328.15, and 344.15) K, the CO_2 + Ni-plating solution + ethanol (10 vol % and 20 vol %) system at 328.15 K, and the CO_2 + Ni-plating solution + surfactant (0.1 mass %) + ethanol (10 vol %) system at (313.15, 328.15, and 344.15) K in the range of (0.1 to 20.0) MPa. The accuracy of the experimental data was supported by a comparison with other published data of the CO_2 + water system at (311.15 and 344.15) K.

2. Experimental Section

Chemicals. Carbon dioxide (CO_2, ≥99.99%) was obtained from Duck Yang (Korea), *p*-toluenesulfonic acid monohydrate ($CH_3C_6H_4SO_3H{\cdot}H_2O$, ≥99%) was obtained from the Yakuri Chemical Company (Japan), maleic anhydride ($C_4H_2O_3$ ≥98%) was obtained from the Junsei Chemical Company(Japan), toluene ($C_6H_5CH_3$, ≥99.8%) was obtained from the J. T. Baker Company, and 2,2,3,3,4,4,5,5-octafluoro-1-pentanol ($F_2CH(CF_2)_3CH_2OH$, ≥98%) and sodium metabisulfite ($Na_2H_2SO_5$, a reagent) were obtained from the Aldrich Chemical Company. The interfacial tension of water and the Ni-plating solution measured at 0.1 MPa by the capillary rise method is listed in Table 1.

Composition of the Ni-Plating Solution. The Ni-plating solution was composed of 50 g of $NiCl_2{\cdot}6H_2O$, 200 g of $NiSO_4{\cdot}6H_2O$, 50 g of H_3BO_3, 10 mL of carrier, 2 mL of brighter, and 1 mL of an anti-pitting agent per 1000 mL of H_2O. Ni-sulfate ($NiSO_4{\cdot}6H_2O$) is the principal source of Ni ions, Ni-chloride ($NiCl_2{\cdot}6H_2O$) improves anode dissolution and increases solution conductivity, and boric acid (H_3BO_3) helps to produce smoother and more ductile deposits.

Synthesis of Sodium Salt of Bis(2,2,3,3,4,4,5,5-octafluoro-1-pentanol) Sulfosuccinate(F-AOT) Surfactant. The synthesis of a fluorinated AOT analogue surfactant, the sodium salt of bis(2,2,3,3,4,4,5,5-octafluoro-1-pentanol) sulfosuccinate (F-AOT), was reported by Liu and Erkey,[12] who prepared it by this method. This surfactant can form the water + CO_2 microemulsion because it has both two "CO_2-philic" chains and a "hydrophilic" headgroup. The method for synthesizing the surfactant was expressed as follows. A mixture of 2,2,3,3,4,4,5,5-octafluoro-1-pentanol, maleic anhydride, and *p*-toluenesulfonic acid monohydrate as the catalyst in toluene was refluxed. After this esterification reaction, the solvent was evaporated, and the remaining solids were washed with water. Crystallization gave a white solid, bis(2,2,3,3,4,4,5,5-octafluoro-1-pentyl) maleate. A solution of bis(2,2,3,3,4,4,5,5-octafluoro-1-pentyl) maleate in ethanol was added to an aqueous sodium hydrogen sulfite solution. The mixture was refluxed under stirring. After the evaporation of the solvent, a crude solid of bis(2,2,3,3,4,4,5,5-octafluoro-1-pentanol) sulfosuccinate was obtained after drying under vacuum overnight. After several purification processes, a white solid of bis(2,2,3,3,-4,4,5,5-octafluoro-1-pentanol) sulfosuccinate was finally obtained. The molecular weight is 688, and the chemical structure of the surfactants is shown in Scheme 1.

Measurement of the Interfacial Tension. The interfacial tension was obtained by using the capillary rise method. An approximate treatment of the capillary rise phenomenon is made in terms of the Young–Laplace equation.[13] If the liquid wets the wall of the capillary, then the liquid surface is thereby constrained to lie parallel to the wall, and the complete surface must therefore be concave in shape. If the capillary is circular in cross section and not too large in radius, then the meniscus will be approximately hemispherical. The two radii of curvature are thus equal to each other and to the radius of the capillary. We can express this as follows.

$$\Delta P = \frac{2\gamma}{r} \tag{1}$$

where r is the radius of the capillary. If h denotes the height of the meniscus above a flat liquid surface (for which ΔP must be zero), then ΔP in eq 1 must also equal the hydrostatic pressure drop in the column of liquid in the capillary. Thus, $\Delta P = \Delta\rho g h$, where $\Delta\rho$ denotes the difference in density between the liquid and gas phases and g is

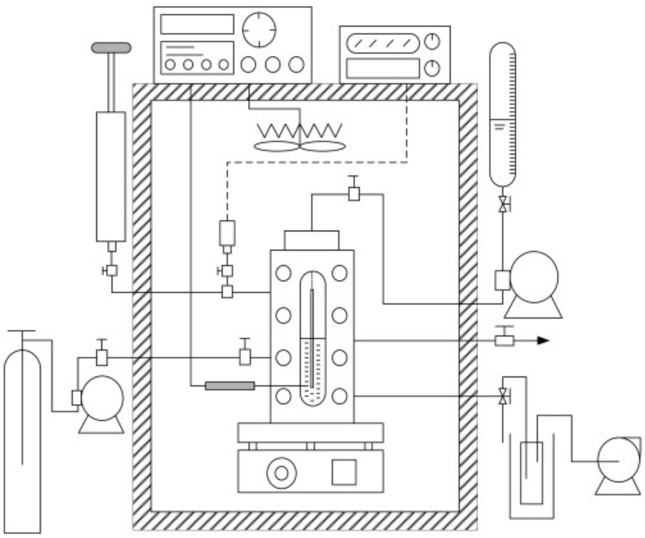


Figure 1. Experimental apparatus for measuring the interfacial tension at high pressure: (1) high-pressure viewing cell; (2) capillary tube; (3) precision pressure indicator; (4) thermocouple; (5) temperature controller; (6) fan; (7) pressure generator; (8) solution reservoir; (9) high-pressure pump; (10) carbon dioxide cylinder; (11) high-pressure pump; (12) magnetic stirrer; (13) trap; (14) vacuum pump; (15) thermostatic air bath.

Table 2. Thermodynamic Properties and Parameters of Pure Chemicals for Calculating the Rackett Equation

	T_c/K	P_c/bar	ω_{SRK}	V^*/cm^3·mol^{-1}	Z_{RA}	V_c/cm^3·mol^{-1}
ethanol	516.16	61.37	0.6378	175.2	0.2502	168
water	647.37	220.6	0.3852	43.6	0.2338	56

the acceleration of gravity. Equation 1 becomes

$$\Delta\rho g h = \frac{2\gamma}{r} \tag{2}$$

$$a^2 = \frac{2\gamma}{\Delta\rho g} = rh \tag{3}$$

$$\Delta\rho g h = \frac{2\gamma\cos\theta}{r} \tag{4}$$

γ is the interfacial tension, r is the radius of the capillary, h is the height of the meniscus above a flat liquid surface (for which ΔP must be zero), $\Delta\rho$(g·cm^{-3}) is the difference between the density of CO_2 and the density of water (or the Ni-plating solution), g (m·s^{-2}) is the acceleration of gravity, and θ is the contact angle (assumed to be 0°). These approximate solutions have been obtained by Rayleigh.[14] It is that of a series approximation. The derivation is not repeated here, but for the case of a nearly spherical meniscus, that is, $r \ll h$, expansion around the a deviation function led to eq 5.

$$a^2 = r\left(h + \frac{r}{3} - \frac{0.1288r^2}{h} + \frac{0.1312r^3}{h^2}\right) \tag{5}$$

The third and fourth terms can be omitted in eq 5. We can get the final equation for interfacial tension by the capillary rise method.

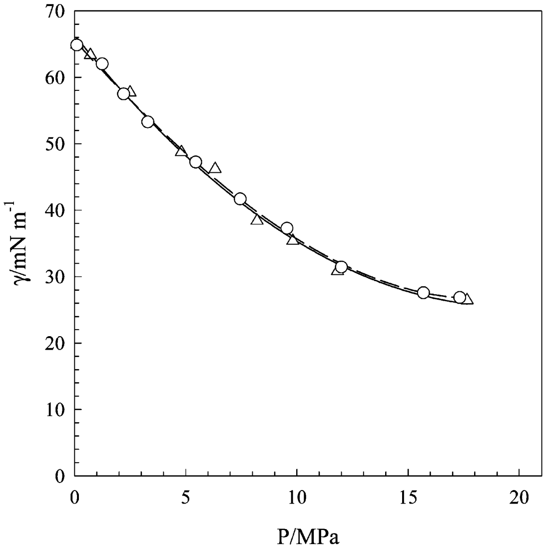


Figure 2. Interfacial tension of the water + CO_2 system measured at 344.15 K: ○, exp 1; △, exp 2.

$$\gamma = \frac{1}{2}rg\left(h + \frac{r}{3}\right)\frac{\Delta\rho}{\cos\theta} \tag{6}$$

Density of Chemicals. The density of fluid at high pressure is needed for the determination of the interfacial tension. The density of CO_2 was obtained from the NIST webbook,[15] and the compressed liquid densities of water and ethanol were fit by a modified Rackett−Hankinson equation with temperature- and pressure-dependent parameters. The modified Rackett equation for mixtures at their bubble points is expressed as follows.[16,17]

$$V_m = R\left(\sum_i \frac{x_i T_{ci}}{P_{ci}}\right) Z_{RAm}{}^{[1-(1-T_r)^{2/7}]} \tag{7}$$

$$Z_{RAm} = \sum_i x_i Z_{RAi} \tag{8}$$

where $T_r = T/T_{cm}$ and the Chueh−Prausnitz rules are recommended[17] for T_{cm}:

$$T_{cm} = \sum_i \sum_j \phi_i \phi_j T_{cij} \tag{9}$$

$$\phi_j = \frac{x_i V_{ci}}{\sum_i x_i V_{ci}} \tag{10}$$

$$T_{cij} = (1 - k_{ij})(T_{ci}T_{cj})^{1/2} \tag{11}$$

$$1 - k_{ij} = \frac{8(V_{ci}V_{cj})^{1/2}}{(V_{ci}{}^{1/3} + V_{cj}{}^{1/3})^3} \tag{12}$$

Table 3. Thermodynamic Properties and Parameters of Water + Ethanol Mixtures for Calculating Density

T_{cm}/K		P_{cm}/bar		ω_{SRKm}		V^*_m/ cm^3·mol^{-1}		Z_{RAm}	
632.7048		291.1124		0.3932832		46.8976		0.2343248	
T	T_{rm}	T_{rm}	β	α	$P_{rm}{}^{(0)}$	$P_{rm}{}^{(1)}$	log(P_{rm})	P_{rm}	P_{vpm}
313.15	0.494	0.494	11.070	−8.176	−1.696	−1.790	−2.401	0.003	1.156
328.15	0.518	0.518	10.382	−6.812	−1.578	−1.641	−2.224	0.005	1.737
344.15	0.543	0.543	9.660	−5.577	−1.458	−1.494	−2.046	0.008	2.615

Table 4. Point-to-Point Comparison between Interfacial Tension Data for the Water + CO_2 System Measured Two Times at 344.15 K

experimental data				comparison by point-to-point				
P/MPa	exp 1 γ/mN·m^{-1}	P/MPa	exp 2 γ/mN·m^{-1}	P/MPa	exp 1 γ/mN·m^{-1}	exp 2 γ/mN·m^{-1}	deviation[a]	absolute deviation[b]
0.10	64.84	0.10	64.90	0.1	65.13	65.20	0.00	0.00
1.23	62.00	0.71	63.35	1.0	62.24	61.90	−0.01	0.01
2.20	57.49	2.49	57.70	2.0	58.96	58.35	−0.01	0.01
3.29	53.27	4.80	48.72	3.0	55.65	54.94	−0.01	0.01
5.44	47.23	6.32	46.18	4.0	52.35	51.67	−0.01	0.01
7.45	41.68	8.20	38.40	5.0	49.09	48.56	−0.01	0.01
9.54	37.25	9.81	35.37	6.0	45.90	45.61	−0.01	0.01
12.00	31.42	11.82	30.82	7.0	42.83	42.84	0.00	0.00
15.69	27.57	17.65	26.43	8.0	39.91	40.25	0.01	0.01
17.32	26.83			9.0	37.17	37.85	0.02	0.02
				10.0	34.66	35.66	0.03	0.03
				11.0	32.39	33.68	0.04	0.04
				12.0	30.42	31.93	0.05	0.05
				13.0	28.78	30.41	0.05	0.05
				14.0	27.49	29.14	0.06	0.06
				15.0	26.61	28.12	0.05	0.05
				16.0	26.15	27.36	0.04	0.04
				17.0	26.17	26.88	0.03	0.03
				17.65	26.45	26.71	0.01	0.01
								av = 0.02

[a] Deviation = [exp(1) − exp(2)]/exp(1). [b] Absolute deviation = |exp(1) − exp(2)|/exp(1).

Table 5. Interfacial Tension Data for the Water + CO_2 System Measured at (293.15, 298.15, 311.15, and 344.15) K

T/K = 293.15		T/K = 298.15		T/K = 311.15		T/K = 344.15	
P/MPa	γ/mN·m^{-1}	P/MPa	γ/mN·m^{-1}	P/MPa	γ/mN·m^{-1}	P/MPa	γ/mN·m^{-1}
0.10	65.69	0.10	78.01	1.79	56.61	0.10	64.84
2.43	51.95	1.12	70.30	2.80	52.50	1.23	62.00
3.36	46.27	2.29	63.30	4.79	41.17	2.20	57.49
4.15	41.91	4.81	43.34	6.93	30.53	3.29	53.27
4.77	37.95	6.37	12.94	14.12	27.28	5.44	47.23
5.66	10.22	8.08	20.48	16.28	24.85	7.45	41.68
6.56	17.92	10.82	14.76	20.28	20.55	9.54	37.25
7.71	17.24	13.32	11.83			12.00	31.42
8.71	18.37					15.69	27.57
9.85	18.36					17.32	26.83
11.93	15.68						

Mixing rules recommended[18] for the Handison−Brobst−Thomson equation are

$$T_{\mathrm{cm}} = \frac{\sum_i \sum_j x_i x_j V^*_{ij} T_{\mathrm{c}ij}}{V^*_{\mathrm{m}}} \tag{13}$$

$$V^*_{\mathrm{m}} = \frac{1}{4}\left[\sum_i x_i V^*_i + 3\left(\sum_i x_i V^{*\,2/3}_i\right)\left(\sum_i x_i V^{*\,1/3}_i\right)\right] \tag{14}$$

$$V^*_{ij} T_{\mathrm{c}ij} = (V^*_i T_{\mathrm{c}i} V^*_j T_{\mathrm{c}j})^{1/2} \tag{15}$$

$$\omega_{\mathrm{SRKm}} = \sum_i x_i \omega_{\mathrm{SRK}i} \tag{16}$$

$$P_{\mathrm{cm}} = \frac{(0.291 - 0.080\omega_{\mathrm{SRKm}})RT_{\mathrm{cm}}}{V^*_{\mathrm{m}}} \tag{17}$$

In the HBT compressed-liquid correlation equation,

$$V = V_{\mathrm{s}}\left(1 - c\ \ln\frac{\beta + P}{\beta + P_{\mathrm{vp}}}\right) \tag{18}$$

V_s, the saturated liquid volume at vapor pressure P_{vp}, should be obtained from following equations. Hankinson and Thomson present the following correlation for the saturated densities of liquids:

$$\frac{V_{\mathrm{s}}}{V^*} = V^{(0)}R[1 - \omega_{\mathrm{SRK}} V^{(\delta)}_{\mathrm{R}}] \tag{19}$$

$$V^{(0)}_{\mathrm{R}} = 1 + a(1 - T_{\mathrm{r}})^{1/3} + b(1 - T_{\mathrm{r}})^{2/3} + c(1 - T_{\mathrm{r}}) + d(1 - T_{\mathrm{r}})^{4/3} \qquad 0.25 < T_{\mathrm{r}} < 0.95 \tag{20}$$

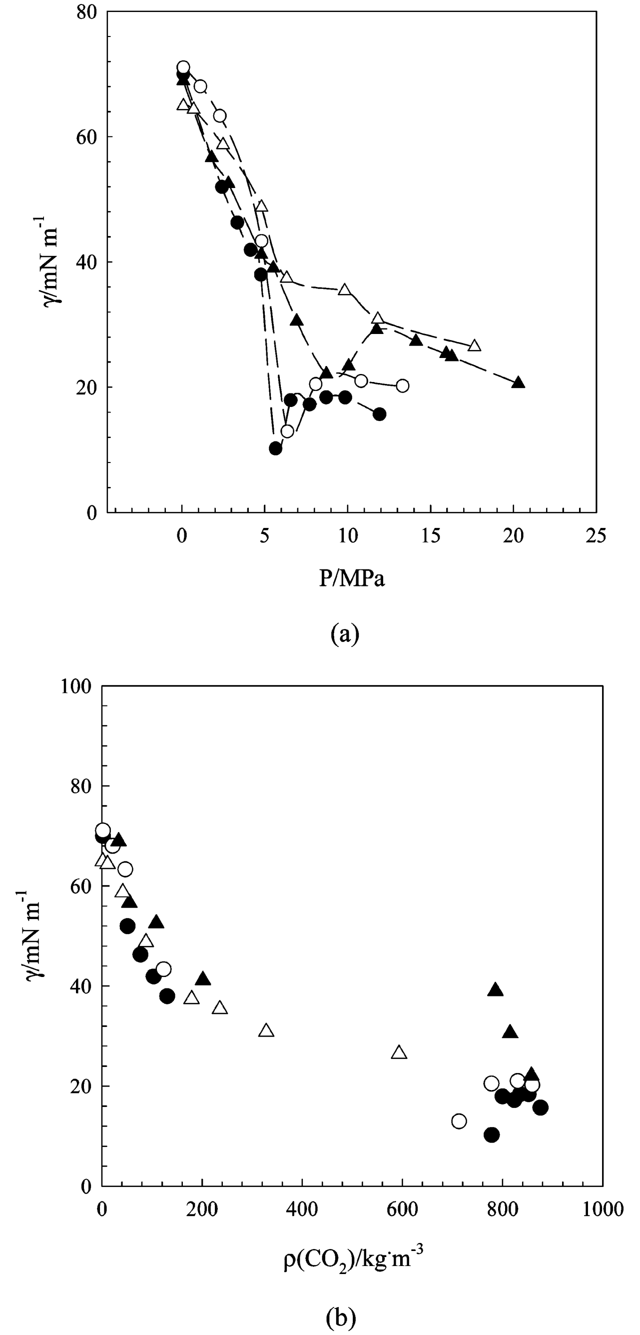
$$V^{(\delta)}_{\mathrm{R}} = \frac{e + fT_{\mathrm{r}} + gT_{\mathrm{r}}^2 + hT_{\mathrm{r}}^3}{T_{\mathrm{r}} - 1.00001} \qquad 0.25 < T_{\mathrm{r}} < 1.0 \tag{21}$$

When computing T_r, T_c should be obtained from Table 2. Values of the constants are $a = -1.5281$, $b = 1.4397$, $c = -0.8144$, $d = 0.1904$, $e = -0.2961$, $f = 0.3869$, $g = -0.0427$, and $h = -0.0480$. V^* is a pure-component characteristic volume generally within 1 to 4% of the critical volume; ω_{SRK} is the acentric factor that forces the Soave equation to give a best fit of existing vapor pressure data. β and c are obtained from

$$\frac{\beta}{P_{\mathrm{c}}} = -1 + a(1 - T_{\mathrm{r}})^{1/3} + b(1 - T_{\mathrm{r}})^{2/3} + d(1 - T_{\mathrm{r}}) + e(1 - T_{\mathrm{r}})^{4/3} \tag{22}$$

$$e = \exp(f + g\omega_{\mathrm{SRK}} + H\omega^2_{\mathrm{SRK}}) \tag{23}$$

$$c = j + k\omega_{\mathrm{SRK}} \tag{24}$$



(a)

(b)

Figure 3. Interfacial tension for the CO_2 + water system measured at (293.15, 298.15, 311.15, and 344.15) K: (a) interfacial tension vs pressure; (b) interfacial tension vs density of CO_2; ●, 293.15 K; ○, 298.15 K; ▲, 311.15 K; and △, 344.15 K.

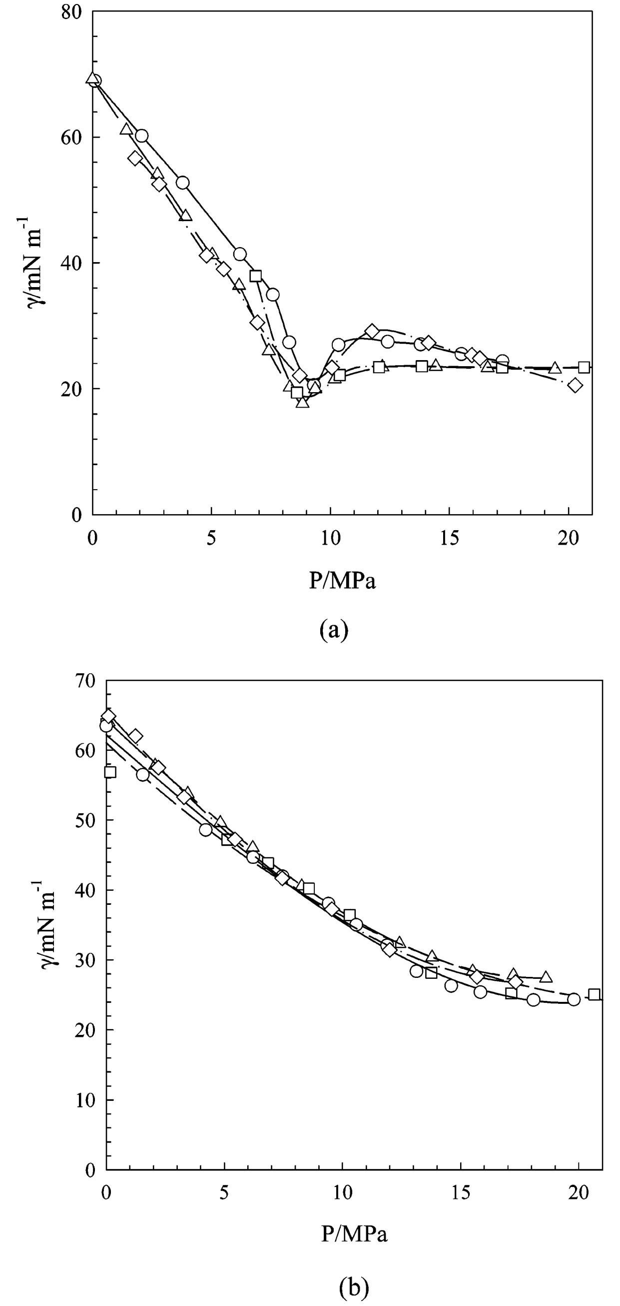
Constants *a* through *k* for eq (22 to 24) are $a = -9.0702$, $b = 62.4532$, $d = -135.1102$, $f = 4.7959$, $g = 0.2500$, $h = 1.1418$, $j = 0.0861$, and $k = 0.0344$. P_{vpm} for a mixture is calculated from

$$P_{vpm} = P_{cm} P_{rm} \tag{25}$$

P_{cm} is from eq 17, and P_{rm} is calculated from the generalized Reidel vapor pressure equation

$$\log_{10} P_{rm} = P^{(0)}{}_{rm} + \omega_{SRKm} P^{(1)}{}_{rm} \tag{26}$$

$$P^{(0)}{}_{rm} = 5.8031817 \log_{10} T_{rm} + 0.0760814\alpha \tag{27}$$



(a)

(b)

Figure 4. Comparison of interfacial tension for the CO_2 + water system measured at (a) 311.15 K and (b) 344.15 K: ○, Hough;[9] △, Chun;[10] □, Da Rocha;[11] ◇, this work.

$$P^{(1)}{}_{rm} = 4.86601 \log_{10} T_{rm} + 0.0372175\alpha \tag{28}$$

$$\alpha = 35.0 - \frac{36.0}{T_{rm}} - 96.736 \log_{10} T_{rm} + T^{6}{}_{rm} \tag{29}$$

$$T_{rm} = \frac{T}{T_{cm}} \tag{30}$$

Thermodynamic properties of ethanol + water mixtures and parameters obtained by these equations are given in Table 3.

Apparatus and Procedures. The schematic diagram of the experimental apparatus for the interfacial tension measurement is shown in Figure 1. The equilibrium cell is a 316 stainless steel vessel, and a pair of Pyrex glass windows of 20-mm thickness were installed so that the liquid level and capillary rise behavior could be observed

Table 6. Comparison of Our Interfacial Tension Data with Literature Data[9–11] for the Water + CO_2 System Measured at (311.15 and 344.15) K

T/K = 311.15								T/K = 344.15							
this work		Hough[9]		Chun[10]		Da Rocha[11]		this work		Hough[9]		Chun[10]		Da Rocha[11]	
P/MPa	γ/mN·m^{-1}	P/MPa	γ/mN·m^{-1}	P/MPa	γ/mN·m^{-1}	P/MPa	γ/mN·m^{-1}	P/MPa	γ/mN·m^{-1}	P/MPa	γ/mN·m^{-1}	P/MPa	γ/mN·m^{-1}	P/MPa	γ/mN·m^{-1}
0.10	69.05	0.10	69.20	0.10	68.91	6.85	37.90	0.10	64.84	0.10	63.45	0.10	64.00	0.00	63.71
1.79	56.61	1.42	61.04	2.07	60.18	8.59	19.38	1.23	62.00	1.55	56.45	2.07	57.79	0.16	56.86
2.80	52.50	2.73	54.04	3.79	52.72	10.39	22.17	2.20	57.49	4.20	48.58	3.45	53.75	5.12	47.20
4.79	41.17	3.91	47.34	6.20	41.36	12.04	23.42	3.29	53.27	6.21	44.67	4.83	49.58	6.84	43.84
5.52	39.00	5.04	41.28	7.58	34.92	13.84	23.55	5.44	47.23	7.45	41.96	6.20	46.05	8.57	40.20
6.93	30.53	6.16	36.39	8.27	27.37	17.21	23.40	7.45	41.68	9.40	38.04	8.27	40.53	10.30	36.42
8.71	22.09	7.41	26.02	9.31	20.56	20.66	23.39	9.54	37.25	10.58	35.02	10.34	36.18	12.03	31.94
10.06	23.36	8.29	20.22	10.34	26.95	24.03	24.07	12.00	31.42	11.88	32.08	12.41	32.34	13.76	28.16
11.74	29.15	8.82	17.63	12.41	27.47			15.69	27.57	13.12	28.37	13.79	30.38	17.13	25.22
14.12	27.28	9.36	19.95	13.79	27.06			17.32	26.83	14.60	26.28	15.51	28.37	20.65	25.06
15.94	25.34	10.18	21.52	15.51	25.51					15.84	25.40	17.23	27.81	24.03	25.05
16.28	24.85	12.18	23.43	17.23	24.36					18.08	24.26	18.61	27.37	27.55	24.90
20.28	20.55	14.42	23.51							19.78	24.33			31.07	24.88
		16.61	23.29												
		19.44	23.09												

Table 7. Point-to-Point Comparison of Our Correlated Interfacial Tension Data with Literature Data[9–11] for the Water + CO_2 System Measured at 344.15 K

this work		Hough[9]			Chun[10]			Da Rocha[11]		
P/MPa	γ/mN·m^{-1}	γ/mN·m^{-1}	deviation[a]	absolute deviation[b]	γ/mN·m^{-1}	deviation[a]	absolute deviation[b]	γ/mN·m^{-1}	deviation[a]	absolute deviation[b]
0.1	65.20	61.90	0.05	0.05	63.98	0.02	0.02	60.73	0.07	0.07
1.0	61.90	59.27	0.04	0.04	61.16	0.01	0.01	57.93	0.06	0.06
2.0	58.35	56.37	0.03	0.03	58.06	0.00	0.00	54.96	0.06	0.06
3.0	54.94	53.49	0.03	0.03	55.03	0.00	0.00	52.13	0.05	0.05
4.0	51.67	50.65	0.02	0.02	52.07	−0.01	0.01	49.44	0.04	0.04
5.0	48.56	47.88	0.01	0.01	49.20	−0.01	0.01	46.90	0.03	0.03
6.0	45.61	45.17	0.01	0.01	46.44	−0.02	0.02	44.49	0.02	0.02
7.0	42.84	42.56	0.01	0.01	43.80	−0.02	0.02	42.23	0.01	0.01
8.0	40.25	40.05	0.00	0.00	41.30	−0.03	0.03	40.10	0.00	0.00
9.0	37.85	37.66	0.01	0.01	38.95	−0.03	0.03	38.11	−0.01	0.01
10.0	35.66	35.41	0.01	0.01	36.78	−0.03	0.03	36.25	−0.02	0.02
11.0	33.68	33.31	0.01	0.01	34.78	−0.03	0.03	34.53	−0.03	0.03
12.0	31.93	31.38	0.02	0.02	33.00	−0.03	0.03	32.93	−0.03	0.03
13.0	30.41	29.64	0.03	0.03	31.43	−0.03	0.03	31.47	−0.03	0.03
14.0	29.14	28.09	0.04	0.04	30.09	−0.03	0.03	30.14	−0.03	0.03
15.0	28.12	26.76	0.05	0.05	29.01	−0.03	0.03	28.93	−0.03	0.03
16.0	27.36	25.67	0.06	0.06	28.19	−0.03	0.03	27.85	−0.02	0.02
17.0	26.88	24.82	0.08	0.08	27.65	−0.03	0.03	26.89	0.00	0.00
18.0	26.71	24.41	0.09	0.09	27.46	−0.03	0.03	26.34	0.01	0.01
19.0	26.77	23.92	0.11	0.11	27.49	−0.03	0.03	25.35	0.05	0.05
20.0	27.17	23.91	0.12	0.12	27.90	−0.03	0.03	24.76	0.09	0.09
				av = 0.04			av = 0.02			av = 0.03

[a] Deviation = [exp(1) − exp(2)]/exp(1). [b] Absolute deviation = |exp(1) − exp(2)|/exp(1).

during operation. In its middle part, the capillary tube (i.d., 1.1 mm; wall, 0.2 ± 0.02 mm; length, 75 mm) was fixed in the cover of the high-pressure cell. The whole system was evacuated with a vacuum pump to remove all materials in the cell, and a proper amount of water (or Ni-plating solution) was introduced into the cell. The temperature of the entire system was maintained at a constant value by controlling the temperature of the air bath to within ±0.1 K. The temperature in the reactor was measured with a K-type thermocouple and a digital indicator (Omega Co.) that was calibrated by KRISS (Korea Institute of Standards and Science) with an uncertainty of ±0.1 K. After the desired temperature was attained, CO_2 was supplied to the cell to pressurize the system. A pressure generator (High-Pressure Equipment Co., model 376-30, pressure rating 30 000 psi) was used to pressurize the water, Ni-plating solution, and CO_2. The pressure in the reactor was measured with a pressure transducer (Sensotec model TJE TJE0743-06TJA) and a digital indicator (Sensotec model L20000WM1) that was calibrated with a dead-weight gauge (Nagano Keiki PD12) with a measuring accuracy of ±0.17 MPa. At equilibrium, water was drained from the cell to form a clear meniscus. A visual observation of the inside of the cell through the sapphire window installed for the capillary rise phenomena is made with a microscope (Leica, magnification 350×). The equilibration time was (5 to 7) s, after which the interfacial tension was measured. The time dependency of the interfacial tension between the solution and carbon dioxide is negligible because of the fast mass transfer of carbon dioxide into the solution for the equilibration time.[19] After completing the test at a given temperature, we stabilized the cell temperature at a new value and repeated the experimental procedure.

Reproducibility and Accuracy. To determine the reproducibility (or precision) of our experiment, we measured the interfacial tension of the CO_2 + water system at 344.15 K in the pressure range from 0.1 MPa to about 17.65 MPa two times. This result is shown in Table 4 and Figure 2. On the basis of the correlated equation of these experimental data, a comparison between these two data was made point to point at every same pressure in the range from (0.1 to 17.65) MPa. As a result, the average absolute deviation (AAD) was 0.02. To determine the accuracy of our experimental data, we measured the interfacial tension

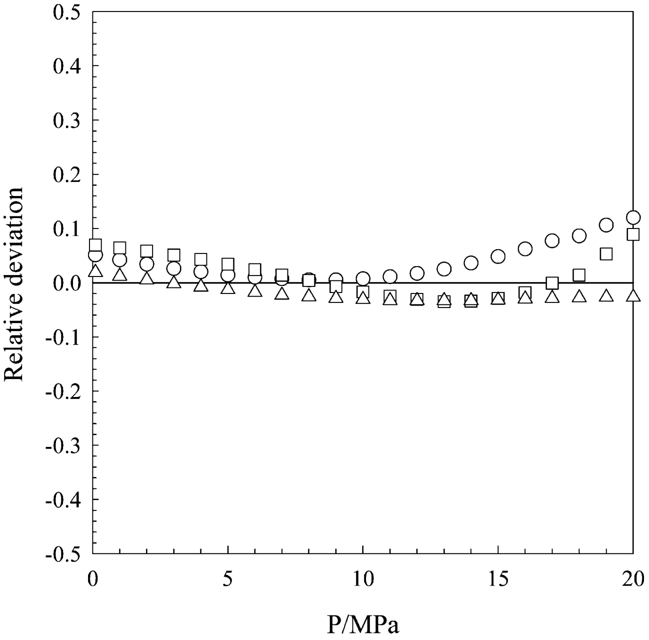


Figure 5. Relative deviations obtained by the correlated curves for the data here presented and those taken from ○, Hough;[9] △, Chun;[10] and □, Da Rocha.[11]

Table 8. Interfacial Tension Data for the Ni-Plating Solution + CO_2 System Measured at (313.15, 328.15, and 344.15) K

T/K = 313.15		T/K = 328.15		T/K = 344.15	
P/MPa	γ/mN·m^{-1}	P/MPa	γ/mN·m^{-1}	P/MPa	γ/mN·m^{-1}
0.10	41.51	0.10	41.51	1.16	35.59
1.29	39.45	1.29	39.45	2.99	31.86
3.45	34.84	3.45	34.84	5.17	29.98
6.06	30.73	6.06	30.73	6.53	28.42
8.47	25.51	8.47	25.51	8.86	25.55
10.31	22.26	10.31	22.26	10.86	23.00
12.94	17.14	12.94	17.14	15.12	19.44
14.79	14.26	14.79	14.26	19.56	13.78
16.14	12.39	16.14	12.39		
19.18	9.89	19.18	9.89		

of the air + water system five times, and the averaged value was compared with the recommended values supported by the *CRC Handbook of Chemistry and Physics*.[20] The average absolute deviation between our experimental data and the literature data was within 0.012.

3. Results and Discussion

The density of the ethanol and water mixture was calculated by the modified Rackett−Hankinson equation, and the thermodynamic properties of chemicals and parameters of pure components and mixtures for this equation are listed in Tables 2 and 3. Interfacial tensions were measured for various systems in order to quantify the effect of the surfactant in the formation of CO_2 + Ni-plating solution macroemulsions in the near-critical and supercritical states. The systems studied were CO_2 + water, CO_2 + Ni-plating solution, CO_2 + Ni-plating solution + surfactant, CO_2 + Ni-plating solution + ethanol, and CO_2 + Ni-plating solution + surfactant + ethanol. The effects of temperature, surfactant, and ethanol on the interface between CO_2 and water and the Ni-plating solution in supercritical CO_2 were considered.

Table 5 and Figure 3a show the interfacial tension data of the CO_2 + water system measured at (293.15, 298.15, 311.15, and 344.15) K. At (293.15, 298.15, and 311.15) K, the minimum values appeared. The minimum interfacial

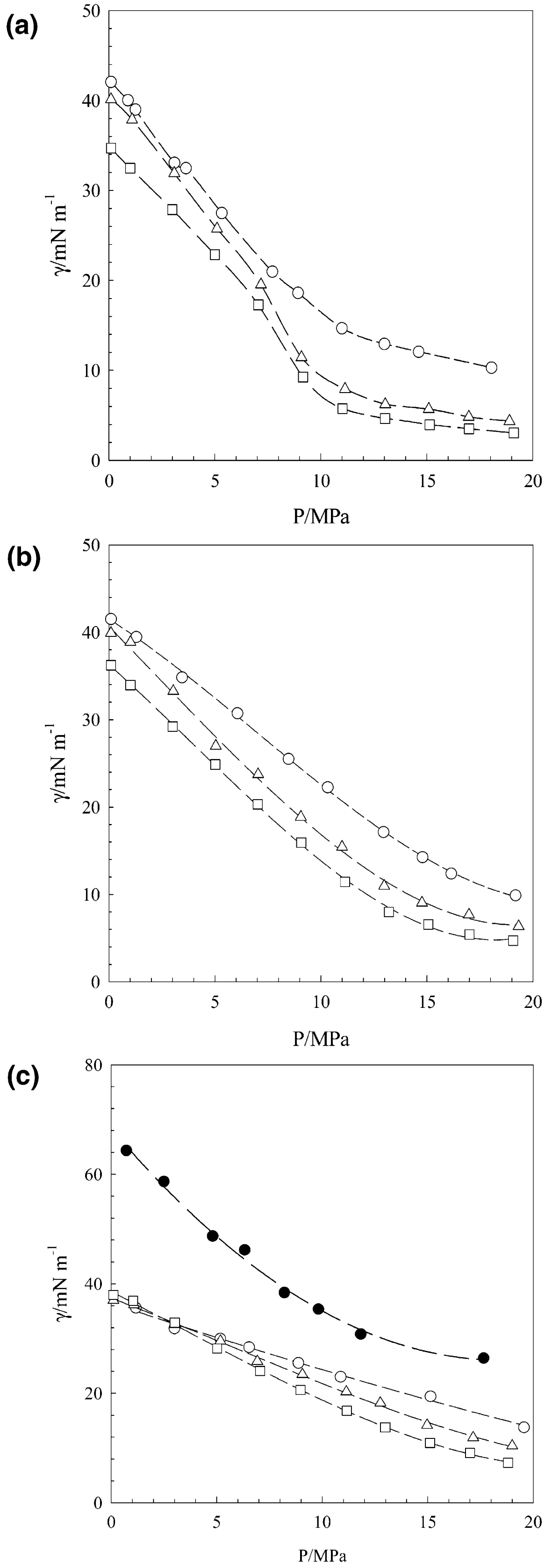


Figure 6. (a) Interfacial tension of the CO_2 + Ni-plating solution measured at 313.15 K: ○, no addition; △, + 0.1 mass % surfactant; □, + 0.3 mass % surfactant. (b) Interfacial tension of the CO_2 + Ni-plating solution measured at 328.15 K: ○, no addition; △; + 0.1 mass % surfactant; □, + 0.3 mass % surfactant. (c) Interfacial tension of the CO_2 + Ni-plating solution measured at 344.15 K: ○, no addition; △, + 0.1 mass % surfactant; □, + 0.3 mass % surfactant; ●, CO_2 + pure water.

Table 9. Interfacial Tension Data for the Ni-Plating Solution + CO_2 + F-AOT Surfactant (0.1 mass % and 0.3 mass %) System Measured at (313.15, 328.15, and 344.15) K

surfactant concentration = 0.1 mass %[a]						surfactant concentration = 0.3 mass %[a]					
T/K = 313.15		T/K = 328.15		T/K = 344.15		T/K = 313.15		T/K = 328.15		T/K = 344.15	
P/MPa	γ/mN·m^{-1}	P/MPa	γ/mN·m^{-1}	P/MPa	γ/mN·m^{-1}	P/MPa	γ/mN·m^{-1}	P/MPa	γ/mN·m^{-1}	P/MPa	γ/mN·m^{-1}
0.10	40.12	0.10	39.91	0.10	37.01	0.10	34.70	0.10	36.22	0.10	37.96
1.09	37.87	1.01	38.87	1.06	36.19	1.00	32.47	1.01	33.95	1.02	36.90
3.08	31.91	3.03	33.26	3.04	32.58	2.99	27.87	3.00	29.21	3.00	32.89
5.10	25.74	5.04	26.99	5.17	29.57	4.99	22.87	5.01	24.89	5.01	28.19
7.17	19.53	7.04	23.74	6.92	25.85	7.05	17.28	7.01	20.32	7.05	24.09
9.08	11.44	9.05	18.86	9.05	23.47	9.16	9.24	9.07	15.93	8.97	20.61
11.13	7.92	10.99	15.44	11.13	20.27	11.02	5.74	11.13	11.44	11.16	16.80
13.03	6.22	12.98	10.97	12.75	18.24	13.02	4.64	13.21	7.99	12.98	13.78
15.08	5.68	14.76	9.04	14.96	14.16	15.13	3.96	15.06	6.56	15.10	10.93
16.98	4.82	16.97	7.68	17.15	11.91	16.98	3.50	17.00	5.40	16.99	9.10
18.89	4.35	19.32	6.34	19.00	10.43	19.09	3.04	19.06	4.72	18.80	7.29

[a] Surfactant concentration (mass %) = 100 × [(mass of surfactant)/(mass of Ni-plating solution)].

tensions measured at these temperatures were 10.22 mN/m at 5.66 MPa and 293.15 K, 12.94 mN/m at 6.37 MPa and 298.15 K, and 21.8 mN/m at 9.35 MPa and 311.15 K. The data under these conditions showed a concave curve. The interfacial tension decreased markedly as the CO_2 phase approached the dew point and increased as the bubble point was passed. These phenomena were most obvious at low temperature, which became less so as the temperature rose and disappeared at (311.15 and 344.15) K. The interfacial tension curve measured at 344.15 K did not show the concave phenomenon and the minimum value and decreased monotonically with increasing pressure. Figure 3b shows the interfacial tension as a quadratic function of CO_2 density. Decreasing interfacial tension was seen with increasing CO_2 density at all temperatures.

Figure 4 shows the results compared with previous studies[9−11] on the interfacial tension of CO_2 + water at (311.15 and 344.15) K. As can be seen in this Figure, all of the interfacial tension curves that have been reported by Hough,[9] Chun,[10] and Da Rocha[11] including this work show the dip and concave curve at 311.15 K, which decreases monotonically with increasing pressure at 344.15 K. These data are listed in Table 6. On the basis of the correlated equation of interfacial tension data measured in the CO_2 + water system, a point-to-point comparison was made between this work and the published data of Hough,[9] Chun,[10] and Da Rocha[11] in the pressure range of (0.1 to 20.0) MPa. In Table 7, the results of the comparison are summarized. The average absolute deviations (AADs) between this work and literature were 0.04 with Hough's data, 0.02 with Chun's data, and 0.03 with Da Rocha's data. These results are shown in Figures 4 and 5 and are listed in Table 7.

Figure 6a−c shows the interfacial tension of the CO_2 + Ni-plating solution system and the CO_2 + Ni-plating solution + surfactant system measured at (313.15, 328.15, and 344.15) K. At first, the investigation of the effect of the F-AOT surfactant concentration on the interfacial tension of the CO_2 + Ni-plating solution + F-AOT surfactant system was performed. F-AOT surfactant was added (0.1 mass % and 0.3 mass %) to the Ni-plating solution. The Ni-plating solution + CO_2 system was not interfacially active because it did not contain F-AOT surfactant. On the contrary, the CO_2 + Ni-plating solution + surfactant system was interfacially active. The interfacial tension of the CO_2 + Ni-plating solution + surfactant system became lower than that of the CO_2 + Ni-plating solution system and decreased monotonically and showed reduced interfacial tension at higher surfactant concentration. This trend is explained by the strong interactions of the surfactant tail with CO_2 and the surfactant headgroup with the Ni-plating solution; higher F-AOT surfactant concentration means a greater driving force for these interactions. As shown in Figure 6, interfacial tension decreased with increasing pressure for a given surfactant concentration. These results are listed in Tables 8 and 9.

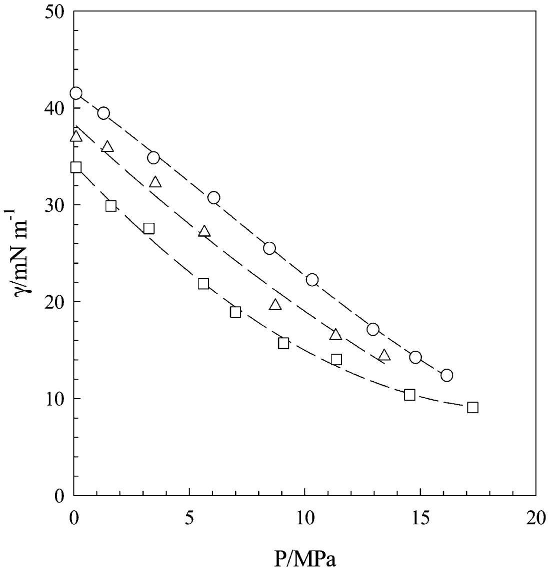


Figure 7. Interfacial tension of the CO_2 + Ni-plating solution measured at 328.15 K: ○, no addition; △, + 10 vol % ethanol; □, + 20 vol % ethanol.

It was reported by Chun et al.[10] that the interfacial tension of the CO_2 + water system was reduced by adding alcohols such as isopropyl alcohol, ethanol, methanol, and butanol. Therefore, ethanol was adopted to reduce the interfacial tension of the CO_2 + Ni-plating solution. Figure 7 shows the change in interfacial tension brought about by adding ethanol (10 and 20 vol %) to the CO_2 + Ni-plating solution system at 328.15 K. In this work, the interfacial tension decreased with increasing amounts of ethanol added to the CO_2 + Ni-plating solution system at constant temperature and was lower than that of the equivalent system without ethanol. These results are listed in Table 10.

From these results, ethanol was considered to be an additive for reducing the interfacial tension of the CO_2 + Ni-plating solution. Figure 8 shows the interfacial tension of the CO_2 + Ni-plating solution + surfactant + ethanol system measured at (313.15, 328.15, and 344.15) K. The concentration of surfactant was 0.1 mass %, and the volume

Table 10. Interfacial Tension Data for the Ni-Plating Solution + CO_2 + Ethanol System Measured at 328.15 K

ethanol concentration = 10 vol %[a]		ethanol concentration = 20 vol %[a]	
P/MPa	γ/mN·m^{-1}	P/MPa	γ/mN·m^{-1}
0.10	36.95	0.10	33.88
1.45	35.89	1.61	29.89
3.53	32.23	3.25	27.57
5.65	27.16	5.61	21.85
8.72	19.57	7.00	18.93
11.33	16.48	9.07	15.71
13.43	14.37	11.36	14.04
		14.54	10.40
		17.26	9.09

[a] Ethanol concentration (vol %) = 100 × [(volume of Ni-plating solution)/(volume of ethanol)].

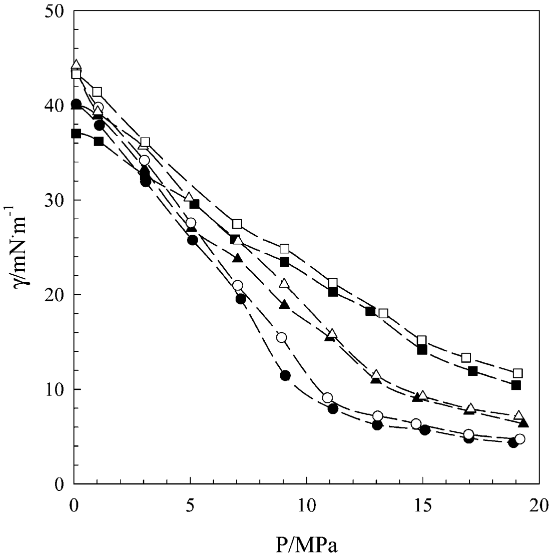


Figure 8. Interfacial tension of the CO_2 + Ni-plating solution + 0.1 mass % surfactant system at ●, 313.15 K; ▲, 328.15 K; and ■, 344.15 K and that of the CO_2 + Ni-plating solution + 0.1 mass % surfactant + 10 vol % ethanol system at ○, 313.15 K; △, 328.15 K; and □, 344.15 K.

Table 11. Interfacial Tension Data for the Ni-Plating Solution + CO_2 + F-AOT Surfactant (0.1 mass %) + Ethanol (10 vol %) System Measured at (313.15, 328.15, and 344.15) K

T/K = 313.15		T/K = 328.15		T/K = 344.15	
P/MPa	γ/mN·m^{-1}	P/MPa	γ/mN·m^{-1}	P/MPa	γ/mN·m^{-1}
0.10	43.61	0.10	44.22	0.10	43.28
1.14	39.78	1.10	39.33	1.08	41.41
3.12	34.17	3.06	35.70	3.15	36.11
5.12	27.57	5.03	30.20	5.06	33.72
7.13	20.95	7.14	25.66	7.10	27.46
9.02	15.45	9.12	21.11	9.14	24.84
10.99	9.08	11.18	15.79	11.21	21.24
13.15	7.16	13.08	11.47	13.39	18.02
14.80	6.33	15.08	9.26	15.03	15.18
17.06	5.22	17.14	7.92	16.94	13.34
19.27	4.73	19.21	7.15	19.16	11.68

of ethanol was 10 vol % in the Ni-plating solution. One would therefore predict a reduction of interfacial tension upon the addition of ethanol and surfactant to the CO_2 + Ni-plating solution system. However, the interfacial tension of this system was observed to increase monotonically for the CO_2 + Ni-plating solution + F-AOT surfactant + ethanol system when measured at (313.15, 328.15, and 344.15) K. These phenomena can be explained by a driving force to absorb ethanol into the interfacial region of the Ni-plating solution rather than partitioning it toward one of the bulk phases. These results are listed in Table 11. When measuring the interfacial tension of these systems, the effect of ethanol was measured. Measuring the interfacial tension is useful in selecting the additives used to investigate the relation of surfactant and solvent in microemulsions and macroemulsions. Both the surfactant interaction and absorption can be explained by measuring the interfacial tension between the surfactant and rich-phase solvent. This study is significant for its adequate description of interfacial characteristics. What is more, this research on interfacial tension at high pressure is helpful for selecting additives in the emulsion process.

Conclusions

A fluorinated F-AOT analogue surfactant with two CO_2-philic tails and a hydrophilic headgroup was synthesized, and the interfacial tension of the CO_2 + water and CO_2 + Ni-plating solution systems was measured with and without this surfactant. In measuring the interfacial tension, we investigated the effects of surfactant and ethanol. This research is pertinent to selecting useful additives and understanding the interface phenomena between supercritical CO_2 and polar chemicals such as water or Ni-plating solution.

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