JOURNAL OF
CHEMICAL &
ENGINEERING
DATA

ARTICLE

pubs.acs.org/jced

Relative Permittivity Measurements of Carbon Dioxide + Ethanol Mixtures

Wayne Eltringham*

Industrial Research Limited, P.O. Box 31-310, Lower Hutt, New Zealand

ABSTRACT: The relative permittivities (ε_r) of carbon dioxide (CO_2) + ethanol mixtures (0.050, 0.100, 0.152, and 0.212 mass fractions of ethanol) were measured at (303 to 333) K in the pressure range (7.2 to 30.8) MPa using a direct capacitance method.

INTRODUCTION

Supercritical fluids have attracted a great deal of attention as alternatives to conventional organic solvents for a number of processes because of the ability to vary solvent properties by the simple manipulation of temperature and pressure. Density-dependent properties such as diffusivity, viscosity, and relative permittivity can be altered by up to an order of magnitude by varying the pressure at temperatures close to the critical temperature, T_c. This can offer several operational advantages for extraction,[1,2] chromatographic,[3,4] and reaction processes,[5] including control of reaction and extraction selectivity, enhanced reaction rates, and more rapid chromatographic separations. Supercritical fluid extraction in particular has received much attention because of enhanced mass transport properties compared to liquid solvent extraction, the ability to selectively extract and fractionate compounds of interest, the ability to easily recover solutes by pressure reduction, and because it is possible to produce solvent residue-free extracts.

Supercritical carbon dioxide (CO_2) has received the most attention for extraction applications because it has relatively low critical parameters (T_c = 304.18 K; P_c = 7.38 MPa),[6] is environmentally benign, and is available in high purity at low cost. Generally, processing with CO_2 alone is limited to the extraction of nonpolar, low-to-medium molecular weight compounds. The solvent capacity of CO_2 can be enhanced by the addition of cosolvents to enable extraction of a wider range of compounds. Ethanol is considered to be one of the most suitable cosolvents for many applications because it is widely accepted by the food industry as a processing fluid, generally does not degrade the compounds of interest, and is easily recovered from the extracts for reuse. Carbon dioxide + ethanol mixtures have been used to obtain a wide range of extracts from a range of feed materials including phospholipids from soybean,[7] canola,[8] eggs,[9] and fish roe;[10] seed oil lipids from jojoba,[11] sesame,[12] sunflower,[13] and peach;[14] and plant-derived bioactive compounds from rosemary,[15] guava seeds,[16] and grape pomace.[17]

Several research groups have reported thermodynamic and physical properties of CO_2 + ethanol mixtures including mixture densities,[18,19] excess volumes,[18] viscosities,[20] phase equilibria data,[21−23] surface tensions,[24] and critical parameters,[25] but few researchers have characterized the fundamental solvent properties of this mixture. Wesch et al.[26] have reported the relative permittivity of CO_2 + ethanol mixtures at 10.0 MPa and 313 K. This work reports the relative permittivities of CO_2 + ethanol mixtures over a wider range of conditions relevant to supercritical or near-critical processing using the as-received commercial grade solvents that may be encountered during such operations.

EXPERIMENTAL SECTION

The relative permittivity (ε_r) was measured using a direct capacitance method. The cell capacitance in air (C_o) and the capacitance of the fluid mixtures (C) were measured, and ε_r was given by

$$\varepsilon_r = \frac{C}{C_o} \tag{1}$$

Capacitances were measured with an applied potential of 1.0 V over the frequency range (40.0 to 80.0) kHz using a Hewlett-Packard 4284A precision LCR meter. The measurements are not affected by the electrode polarization effect in this frequency range, as evidenced by the excellent agreement with literature relative permittivity values for conducting liquids measured previously[27] using the same equipment and method reported here. The cell capacitance in air was measured to be 17.27 pF and was found to be independent of temperature. The pressure dependence of the cell constant was negligible over the pressure ranges studied ($< 7 \cdot 10^{-5}$ % variation in C_o). Pressure measurements have an associated uncertainty of ± 0.2 MPa, and the temperature was monitored using a type K ServoTech thermocouple (± 0.5 K). The general apparatus, experimental procedure, and equipment validation have been described in detail elsewhere.[27]

Each data point is the average of between two and four replicate measurements, with a maximum standard deviation (σ) for a given condition over all temperatures and pressures studied of 0.07. The replicate measurements were made by refilling the capacitance cell with the fluid mixture.

Carbon dioxide was supplied by BOC Limited (New Zealand) with a purity of 99.8 % by volume. Impurities for the CO_2 as stated by the certificate of analysis were: water, 80 $\mu L \cdot L^{-1}$; oxygen, 100 $\mu L \cdot L^{-1}$; the balance being other nonspecified constituents of air, including rare gases. Ethanol was supplied by Barwell Pacific with a stated purity of 99.8 % by volume, with the remaining 0.2 % being water. The CO_2 and ethanol were used as received without further purification to simulate conditions under which the chemicals would typically be used for extraction processes. The two fluids were

Received: March 28, 2011
Accepted: July 6, 2011
Published: July 15, 2011

Table 1. Relative Permittivity (ε_r) Values for CO_2 + Ethanol Mixtures, where ϕ_1 is the Mass Fraction of Ethanol in the Mixture

T/K = 303.4		T/K = 313.0		T/K = 322.5		T/K = 333.2	
P /MPa	ε_r	P /MPa	ε_r	P /MPa	ε_r	P /MPa	ε_r
			ϕ_1 = 0.050				
10.0	1.83	9.7	1.63	10.2	1.53	10.5	1.32
11.4	1.86	9.8	1.64	12.1	1.63	11.2	1.41
13.2	1.89	9.9	1.65	13.1	1.66	12.1	1.48
13.6	1.90	11.3	1.70	14.2	1.70	13.0	1.54
14.8	1.91	11.7	1.70	14.7	1.70	13.0	1.53
15.3	1.92	11.8	1.70	16.0	1.73	13.7	1.57
15.8	1.92	13.2	1.74	16.1	1.73	14.9	1.62
16.0	1.93	13.7	1.74	17.2	1.75	15.9	1.64
17.5	1.94	15.1	1.77	18.9	1.78	17.0	1.67
19.0	1.95	15.7	1.78	19.5	1.79	17.6	1.69
19.2	1.95	17.4	1.80	20.8	1.80	19.1	1.72
21.0	1.97	17.5	1.80	21.8	1.81	19.4	1.72
21.3	1.97	17.5	1.80	22.7	1.82	21.0	1.75
23.0	1.98	19.2	1.82	23.6	1.83	21.6	1.75
23.3	1.99	20.7	1.83	24.7	1.84	22.9	1.77
25.1	2.00	21.6	1.84	25.8	1.85	23.7	1.78
25.4	2.00	23.5	1.86	26.3	1.86	25.0	1.80
26.7	2.01	25.3	1.87	27.9	1.87	26.9	1.82
27.2	2.01	25.4	1.87	28.4	1.87	27.4	1.82
28.9	2.02	27.4	1.89	29.3	1.88	28.8	1.83
29.6	2.03	30.4	1.91	29.5	1.88	29.9	1.84
				30.3	1.89		

T/K = 303.7		T/K = 313.1		T/K = 322.4		T/K = 333.3	
P /MPa	ε_r	P /MPa	ε_r	P /MPa	ε_r	P /MPa	ε_r
			ϕ_1 = 0.100				
9.8	2.24	9.7	1.98	10.5	1.86	11.9	1.74
11.3	2.27	10.2	2.00	11.9	1.94	12.9	1.81
11.4	2.28	11.0	2.03	11.9	1.94	13.7	1.86
13.1	2.30	12.0	2.05	12.2	1.96	14.8	1.90
14.0	2.32	12.7	2.08	13.7	2.01	15.7	1.94
14.9	2.34	13.1	2.09	13.9	2.02	16.7	1.96
16.0	2.36	13.7	2.11	15.7	2.06	17.8	2.00
16.9	2.37	14.8	2.13	15.7	2.06	18.5	2.01
17.8	2.38	15.8	2.15	15.8	2.07	19.4	2.03
19.1	2.40	17.0	2.17	16.7	2.09	19.6	2.03
19.1	2.40	17.7	2.18	17.1	2.09	20.6	2.06
19.9	2.41	18.8	2.19	17.6	2.11	21.7	2.08
20.4	2.42	19.8	2.20	18.6	2.13	22.6	2.09
21.4	2.43	21.9	2.23	19.6	2.14	23.9	2.11
21.9	2.43	22.1	2.23	20.6	2.16	24.8	2.12
23.1	2.45	22.4	2.24	21.6	2.18	25.2	2.13
24.1	2.46	24.1	2.26	21.7	2.18	25.6	2.14
24.2	2.46	24.4	2.26	22.6	2.19	25.6	2.13
25.3	2.47	25.8	2.28	23.6	2.21	26.5	2.15
25.5	2.48	26.4	2.28	24.5	2.22	26.6	2.15
25.5	2.48	27.7	2.30	25.5	2.23	27.2	2.16
26.5	2.48	27.8	2.30	26.5	2.24	27.5	2.16
27.4	2.49	28.3	2.30	27.5	2.26	27.9	2.16
28.0	2.50	29.3	2.31	28.4	2.27	28.5	2.17
28.4	2.50	29.5	2.32	29.9	2.28	29.2	2.18
29.4	2.51						

T/K = 304.9		T/K = 313.1		T/K = 323.3		T/K = 333.3	
P /MPa	ε_r	P /MPa	ε_r	P /MPa	ε_r	P /MPa	ε_r
			ϕ_1 = 0.152				
16.1	2.67	10.1	2.37	9.9	2.06	11.8	1.99
16.8	2.68	10.9	2.39	11.0	2.13	12.9	2.07
17.3	2.68	11.8	2.42	12.0	2.18	13.8	2.11
17.8	2.69	12.7	2.45	12.7	2.21	14.8	2.16
18.8	2.70	13.8	2.47	13.6	2.25	15.9	2.20
19.4	2.72	14.6	2.49	14.7	2.28	16.7	2.22
20.1	2.73	15.7	2.52	15.9	2.31	17.7	2.26
20.8	2.74	16.8	2.54	16.9	2.34	18.7	2.28
21.9	2.75	17.8	2.56	17.8	2.36	19.7	2.31
22.8	2.76	18.8	2.58	18.6	2.37	20.8	2.33
23.7	2.77	19.5	2.59	18.7	2.38	22.0	2.36
24.3	2.79	20.8	2.61	19.5	2.40	22.7	2.37
24.7	2.78	21.6	2.62	20.3	2.41	23.5	2.38
25.5	2.79	22.6	2.63	21.7	2.44	24.5	2.40
26.4	2.81	23.5	2.64	22.8	2.45	25.6	2.42
26.5	2.81	24.5	2.66	23.1	2.46	26.6	2.43
27.2	2.82	25.5	2.67	23.5	2.47	27.6	2.45
27.2	2.82	26.5	2.68	24.5	2.48	28.4	2.46
28.2	2.83	27.5	2.69	25.4	2.50	29.2	2.47
29.1	2.84	27.9	2.70	26.5	2.51	29.9	2.48
29.8	2.85	28.4	2.71	28.4	2.54		
		29.3	2.72	29.5	2.56		

T/K = 303.7		T/K = 312.8		T/K = 323.4		T/K = 333.2	
P /MPa	ε_r	P /MPa	ε_r	P /MPa	ε_r	P /MPa	ε_r
			ϕ_1 = 0.212				
7.2	3.15	8.0	2.80	9.8	2.59	11.9	2.38
7.9	3.18	9.3	2.86	10.6	2.61	12.9	2.45
8.8	3.22	11.2	2.94	11.5	2.67	13.2	2.47
9.8	3.25	11.5	2.94	12.4	2.71	14.1	2.52
11.0	3.29	14.2	3.00	13.1	2.75	14.7	2.54
13.0	3.35	14.3	3.01	14.1	2.79	15.8	2.59
14.9	3.40	14.9	3.03	15.8	2.85	16.2	2.61
15.0	3.40	15.8	3.05	16.6	2.87	16.9	2.62
16.5	3.44	17.4	3.11	17.8	2.90	17.3	2.64
16.7	3.45	18.0	3.14	18.8	2.93	18.5	2.68
17.3	3.46	20.0	3.17	19.6	2.95	19.1	2.70
18.0	3.47	20.6	3.18	19.7	2.95	19.2	2.70
18.8	3.49	22.2	3.22	21.1	2.98	21.2	2.75
20.2	3.52	22.8	3.23	22.9	3.03	21.2	2.75
21.6	3.54	23.7	3.25	23.1	3.03	21.2	2.75
21.8	3.55	26.3	3.30	23.2	3.03	21.3	2.75
23.3	3.57	28.1	3.32	24.7	3.06	23.0	2.79
23.9	3.58	28.4	3.34	26.0	3.08	23.1	2.79
25.4	3.61	30.8	3.37	26.7	3.10	24.9	2.83
26.2	3.62			27.9	3.12	25.0	2.83
27.2	3.64			29.5	3.14	25.2	2.83
28.4	3.66			30.6	3.15	25.5	2.85
30.2	3.68					26.8	2.86
						27.0	2.87
						28.4	2.90
						30.6	2.94

premixed in a 1 L stainless steel pressure cylinder before being used for the ε_r measurements.

A 1 L cylinder was evacuated and then weighed. A known mass of ethanol was drawn into the cylinder under vacuum, followed by the addition of a known mass of CO_2 to give the desired overall composition. For all compositions studied, sufficient quantities of ethanol and CO_2 were added to the cylinder so that the liquid phase filled greater than 95 % of the cylinder volume. By keeping the gas phase volume in the cylinder small, the initial composition of the liquid phase will closely resemble the overall mixture composition. The change in mixture composition due to removal of liquid from the cylinder during the ε_r measurements is discussed in more detail in the Results section.

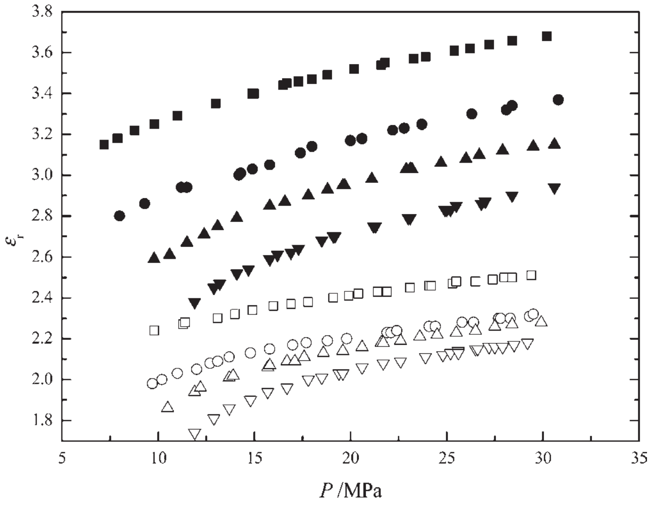

Figure 1. Pressure dependence of the relative permittivity (ε_r) of CO_2 + ethanol mixtures, where ϕ_1 is the mass fraction of ethanol in the mixture: ■, $\phi_1 = 0.212$ at 303.7 K; ●, $\phi_1 = 0.212$ at 312.8 K; ▲, $\phi_1 = 0.212$ at 323.4 K; ▼, $\phi_1 = 0.212$ at 333.2 K; □, $\phi_1 = 0.100$ at 303.7 K; ○, $\phi_1 = 0.100$ at 313.1 K; △, $\phi_1 = 0.100$ at 322.4 K; ▽, $\phi_1 = 0.100$ at 333.3 K.

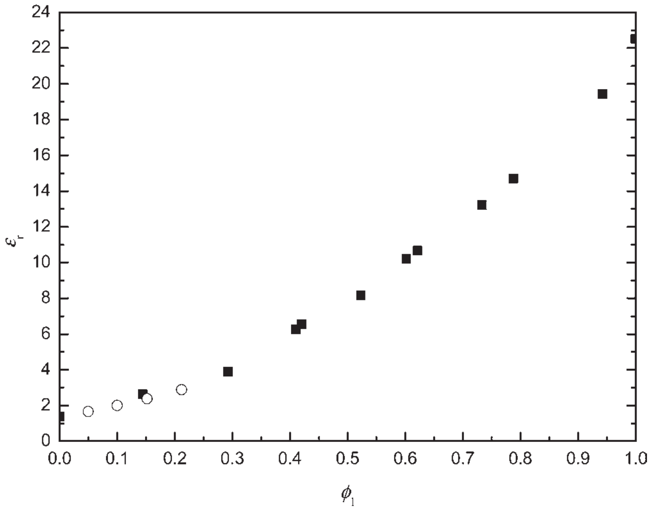

Figure 2. Comparison of the interpolated CO_2 + ethanol mixture relative permittivities from this work with literature values at 10.0 MPa and 313 K: ■, Wesch et al.;[26] ○, this work.

■ RESULTS

The measured ε_r values of CO_2 + ethanol mixtures are given in Table 1. The mixture compositions are reported as mass fractions, since mass measurements are the most common methods of monitoring cosolvent usage during extraction processes. Figure 1 shows the variation of ε_r as a function of temperature, pressure, and mass fraction of ethanol for two of the mixture compositions measured in this work. The ε_r increases with increasing pressure, increasing mass fraction of ethanol, and decreasing temperature. The ε_r values at 10.0 MPa and 313 K were interpolated from the data in Table 1 and are shown in Figure 2 to be in good agreement with the values reported by Wesch et al.[26] The volume fractions reported by Wesch et al. were converted to mass fractions using literature density data for CO_2[28] and ethanol.[29]

The ε_r measurements have an associated absolute uncertainty of ± 0.20 at the 95 % confidence level. The reported uncertainty takes into account the maximum absolute variation in the CO_2 + ethanol mixture liquid phase composition as liquid is withdrawn from the supply cylinder. Since CO_2 has a higher vapor pressure than ethanol, the CO_2 will preferentially migrate to the gas phase as liquid is withdrawn from the cylinder. This means that the liquid phase will become slightly more enriched in ethanol compared to the overall mixture composition as the cylinder is drawn down.

To calculate the uncertainty of the ε_r values due to the change in liquid phase composition during cylinder draw-down, four sets of repeat measurements were carried out starting with a cylinder filled to at least 95 % of its volume with liquid. The 95 % full cylinder was used to measure the ε_r values of a CO_2 + ethanol mixture containing 0.212 mass fraction of ethanol at 312.8 K in the pressure range (8.0 to 30.8) MPa. After the first isotherm had been measured the mixture in the capacitance cell was discarded. The capacitance cell was refilled from the partially drawn-down cylinder, and the measurement was repeated. This was repeated a further two times, and the absolute maximum variation in the ε_r values was determined to be 0.08. The variation of the ε_r values due to liquid withdrawal was always positive due to increased ethanol concentration in the liquid phase as the gas phase volume in the supply cylinder increased. The mixture containing the greatest mass fraction of ethanol was used since the mass fraction composition of the liquid phase changes most rapidly during cylinder draw-down when the concentration of the less volatile component (ethanol) is highest. A period of at least 1 h elapsed between each draw-down, and it is assumed that the mixture in the cylinder returned to equilibrium before each measurement.

The absolute maximum variation of 0.08 was used in the overall uncertainty calculation, since for all other ε_r measurements reported in Table 1, the volume of liquid withdrawn from the cylinder was less than that for the four repeat measurements used to determine the effect of change in composition of the liquid phase.

■ CONCLUSION

The relative permittivities of CO_2 + ethanol mixtures (0.050, 0.100, 0.152, and 0.212 mass fraction of ethanol) have been measured at (303 to 333) K in the pressure range (7.2 to 30.8) MPa. Under these conditions the isothermal pressure dependence of the relative permittivity is always positive, and the isobaric temperature dependence is always negative. Relative permittivity increases with increasing mass fraction of ethanol in the mixture.

■ AUTHOR INFORMATION

Corresponding Author

*Telephone: +64-4-9313318. Fax: +64-4-9313055. E-mail: w.eltringham@irl.cri.nz.

Funding Sources

This work was supported by the Foundation for Research Science and Technology, New Zealand, under Grant No. CO8X0305.

■ REFERENCES

(1) McHugh, M.; Krukonis, V. J. *Supercritical Fluid Extraction*, 2nd ed.; Butterworth-Heinemann: Boston, 1994.

(2) Taylor, L. T. *Supercritical Fluid Extraction*; John Wiley & Sons: New York, 1996.

(3) Combs, M. T.; Ashraf-Khorassani, M.; Taylor, L. T. Packed column supercritical fluid chromatography mass spectroscopy: A review. *J. Chromatogr., A* **1997**, *785*, 85–100.

(4) Smith, R. M. Supercritical fluids in separation science — the dreams, the reality and the future. *J. Chromatogr., A* **1999**, *856*, 83–115.

(5) *Chemical Synthesis using Supercritical Fluids*; Jessop, P. G., Leitner, W., Eds.; Wiley-VCH: Weinheim, 1999.

(6) Suehiro, Y.; Nakajima, M.; Yamada, K.; Uematsu, M. Critical parameters of $\{x\mathrm{CO_2} + (1-x)\mathrm{CHF_3}\}$ for $x = 1.0000$, 0.7496, 0.5013, and 0.2522. *J. Chem. Thermodyn.* **1996**, *28*, 1153–1164.

(7) Montanari, L.; King, J. W.; List, G. R.; Rennick, K. A. Selective extraction of phospholipid mixtures by supercritical carbon dioxide and cosolvents. *J. Food. Sci.* **1996**, *61*, 1230–1233.

(8) Dunford, N. T.; Temelli, F. Extraction of phospholipids from canola with supercritical carbon dioxide and ethanol. *J. Am. Oil Chem. Soc.* **1995**, *72*, 1009–1015.

(9) Shah, A.; Akoh, C. C.; Toledo, R. T.; Corredig, M. Isolation of phospholipid fraction from inedible egg. *J. Supercrit. Fluids* **2004**, *30*, 303–313.

(10) Tanaka, Y.; Sakaki, I.; Ohkubo, T. Extraction of phospholipids from salmon roe with supercritical carbon dioxide and an entrainer. *J. Oleo Sci.* **2004**, *53*, 417–424.

(11) Salgin, U. Extraction of jojoba seed oil using supercritical $\mathrm{CO_2}$ + ethanol mixture in green and high-tech separation process. *J. Supercrit. Fluids* **2007**, *39*, 330–337.

(12) Adabasi, A. Z.; Balaban, M. O. Supercritical $\mathrm{CO_2}$ extraction of sesame oil from raw seeds. *J. Food Sci. Technol.* **2002**, *39*, 496–501.

(13) Cocero, M. J.; Calvo, L. Supercritical fluid extraction of sunflower seed oil with $\mathrm{CO_2}$-ethanol mixtures. *J. Am. Oil Chem. Soc.* **1996**, *73*, 1573–1578.

(14) Sánchez-Vicente, Y.; Cabañas, A.; Renuncio, J. A. R.; Pando, C. Supercritical fluid extraction of peach (Prunus persica) seed oil using carbon dioxide and ethanol. *J. Supercrit. Fluids* **2009**, *49*, 167–173.

(15) Herrero, M.; Plaza, M.; Cifuentes, A.; Ibáñez, E. Green processes for the extraction of bioactives from rosemary: Chemical and functional characterization via ultra-performance liquid chromatography-tandem mass spectrometry and in-vitro assays. *J. Chromatogr., A* **2010**, *1217*, 2512–2520.

(16) Castro-Vargasa, H. I.; Rodríguez-Varelab, L. I.; Ferreirac, S. R. S.; Parada-Alfonsoa, F. Extraction of phenolic fraction from guava seeds (Psidium guajava L.) using supercritical carbon dioxide and co-solvents. *J. Supercrit. Fluids* **2010**, *51*, 319–324.

(17) Pinelo, M.; Ruiz-Rodríguez, A.; Sineiro, J.; Señoráns, F. J.; Reglero, G.; Núñez, M. J. Supercritical fluid and solid-liquid extraction of phenolic antioxidants from grape pomace: A comparative study. *Eur. Food Sci. Technol.* **2007**, *226*, 199–205.

(18) Pöhler, H.; Kiran, E. Volumetric properties of carbon dioxide + ethanol at high pressures. *J. Chem. Eng. Data* **1997**, *42*, 384–388.

(19) Kato, M.; Kodama, D.; Ono, T.; Kokubo, M. Volumetric properties of carbon dioxide + ethanol at 313.15 K. *J. Chem. Eng. Data* **2009**, *54*, 2953–2956.

(20) Tilly, K. D.; Foster, N. R.; Macnaughton, S. J.; Tomasko, D. L. Viscosity correlations for binary supercritical fluids. *Ind. Eng. Chem. Res.* **1994**, *33*, 681–688.

(21) Kato, M.; Kodama, D. High-pressure phase equilibrium for carbon dioxide + ethanol at 291.15 K. *J. Chem. Eng. Data* **2005**, *50*, 16–17.

(22) Day, C. Y.; Chang, C. J.; Chen, C. Y. Phase equilibrium of ethanol + $\mathrm{CO_2}$ and acetone + $\mathrm{CO_2}$ at elevated pressures. *J. Chem. Eng. Data* **1996**, *41*, 839–843.

(23) Suzuki, K.; Sue, H. Isothermal vapor-liquid equilibrium data for binary systems at high pressures: carbon dioxide-methanol, carbon dioxide-ethanol, carbon dioxide-1-propanol, methane-ethanol, methane-1-propanol, ethane-ethanol, and ethane-1-propanol systems. *J. Chem. Eng. Data* **1990**, *35*, 63–66.

(24) Sun, Y.; Shekunov, B. Y. Surface tension of ethanol in supercritical $\mathrm{CO_2}$. *J. Supercrit. Fluids* **2003**, *27*, 73–83.

(25) Yeo, S. D.; Park, S. J.; Kim, J. W.; Kim, J. C. Critical properties of carbon dioxide + methanol, + ethanol, + 1-propanol, and 1-butanol. *J. Chem. Eng. Data* **2000**, *45*, 932–935.

(26) Wesch, A.; Dahmen, N.; Ebert, K. H. Measuring the static dielectric constants of pure carbon dioxide and carbon dioxide mixed with ethanol and toluene at elevated pressures. *Ber. Bunsenges. Phys. Chem.* **1996**, *100*, 1368–1371.

(27) Eltringham, W.; Catchpole, O. J. Relative permittivity measurements of gaseous, liquid and supercritical dimethyl ether. *J. Chem. Eng. Data* **2007**, *52*, 363–367.

(28) Lemmon, E. W.; McLinden, M. O.; Friend, D. G. *Thermophysical Properties of Fluid Systems in NIST Chemistry WebBook*, NIST Standard Reference Database Number 69; Linstrom, P. J., Mallard, W. G., Eds.; National Institute of Standards and Technology: Gaithersburg, MD, 2008. http://webbook.nist.gov/chemistry/.

(29) Takiguchi, Y.; Uematsu, M. PVT measurements of liquid ethanol in the temperature range from 310 to 363 K at pressures up to 200 MPa. *Int. J. Thermophys.* **1995**, *16*, 205–214.