Solubilities of Diglycolic Acid Esters in Supercritical Carbon Dioxide

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A series of new CO_2-soluble diglycolic acid esters were designed and synthesized, and their structures were confirmed by IR, NMR, and elemental analysis. The solubilities of compounds were measured at temperatures ranging from (313 to 333) K and pressures from (8.5 to 19.3) MPa in supercritical carbon dioxide. All of the newly synthesized esters showed good to high solubility (as high as 1.25 mol % for compound **1**) in supercritical CO_2 at easily accessible temperatures and pressures. The measured solubility data were correlated using a semiempirical model. Consequently, the calculated results showed satisfactory agreement with the experimental data and differed from the measured values by between (3.18 and 19.58) %.

Introduction

The use of supercritical fluid for industrial applications has been investigated widely—including chemical reactions, natural product extraction, cleaning, drying, and dyeing.[1−5] Carbon dioxide is undoubtedly the most investigated and employed supercritical fluid, mainly due to its relatively low critical temperature and critical pressure (T_c = 304.15 K, P_c = 7.38 MPa) as well as to other advantageous properties such as its mass and heat transfer properties, nontoxicity, nonflammability, and low cost.[6−8] Solubility data in supercritical fluids are among the most important thermophysical properties that are essential to the efficient design of supercritical processes, so an accurate solubility data test is necessary.

Many research groups have subsequently investigated the design of so-called "CO_2-philic"goups that are soluble in supercritical CO_2 at moderate pressure.[9−12] Compounds which have a perfluoroalkyl polyether (PFPE) tail are highly soluble in supercritical CO_2, but this type of compound is very expensive and toxic. Silicones are also generally considered to be CO_2-philic. However, silicone-functional amphiphiles require higher pressure to generate a single-phase solution in supercritical CO_2.

According to the literature and based on our research results,[11,12] hydrocarbons substituted with carbonyl groups as CO_2-philes have appeared economically, and the carbonyl group, ether group, and alkyl group with suitable length are so-called CO_2-philic groups. So in the present work, we have designed and synthesized an array of diglycolic acid ester derivatives. The alkyl, the carbonyl, and the ether groups were chosen as the CO_2-philic parts which are low cost, nonfluorous, and nonsilicone, and then the solubilities of these compounds were investigated in supercritical CO_2 over the pressure range of (8.5 to 19.3) MPa and at the temperature of (313 to 333) K. The tested results were correlated by a semiempirical model.

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Experimental Section

Chemicals and Experimental Apparatus. Carbon dioxide was purchased from Wuhan Steel Co. (99.99 %, mass fraction). 1-Pentanol (99+ %), 1-heptanol (99 %), 1-nonanol (98 %), 1-undecanol, 1-tridecanol (98 %), 1-pentadecanol (99 %), and diethylamine all were bought from Alfa Aesar Chem. Co. and used without further purification. Dichlorosulfoxide ($SOCl_2$) and dichloromethane (CH_2Cl_2) were obtained from Tianjin Kemel Co. LTD (China), and both of them were fresh distilled before use. NMR experiments were performed on a JEOL Al-400 MHz instrument using TMS as an internal standard. IR spectra were recorded on a Perkin-Elmer 2000 FT-IR spectrometer. Elemental analysis was conducted on a PE 2400 series II CHNS/O elemental analyzer. The apparatuses of supercritical carbon dioxide were bought from JASCO Corporation (Japan): "PU-1580-CO_2" CO_2 Delivery Pump, "PU-2080 Plus" intelligent HPLC Pump, and "BP-1580-81" Back Pressure Regulator.

General Procedure for the Synthesis of Compounds 1 to 6. Six compounds were synthesized according to the previously published similar procedure shown in Scheme 1.[12] To the best of our knowledge, all the compounds were new, and their structures were determined by IR, ^{1}H NMR, ^{13}C NMR, and elemental analysis.

Diglycolic acid (2.0 g, 15 mmol) was dissolved in $SOCl_2$ (40 mL, 0.55 mol) and refluxed for 8 h. After cooling to room temperature, excess thionyl chloride was evaporated under vacuum, then a CH_2Cl_2 solution (30 mL) of 1-alkylnol (30 mmol) and triethylamine (30 mmol) was added dropwise to the reaction system under an N_2 atmosphere. The mixture was stirred at room temperature for a whole night. Then, the reaction mixture was washed with 1 % HCl aq and saturated $NaHCO_3$ aq and then twice with water, and the organic phase was collected and dried over anhydrous Na_2SO_4. The residue was purified by silica gel column chromatography (ethyl acetate:petroleum ether = 1:2) to obtain the target compound.

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Table 1. Solubility at Temperature T, Density ρ, and Mole Fraction x for Compounds 1 to 6

	Compound **1**					Compound **2**				
T	P	ρ			AAD	P	ρ			AAD
K	MPa	kg·m^{-3}	10^4x	10^4x_{cal}	%	MPa	kg·m^{-3}	10^4x	10^4x_{cal}	%
T = 313 K	8.5	357.86	22.31	29.91	9.59	8.7	407.11	22.31	16.66	25.31
	8.7	407.11	39.03	49.18	15.45	8.9	465.37	39.03	28.79	26.24
	8.8	436.05	52.68	66.02	18.96	9.1	517.19	52.68	46.73	11.29
	8.9	465.37	67.49	88.98	12.57	9.2	538.22	67.49	56.77	15.88
	9.0	492.75	81.66	117.52	2.19	9.3	556.08	81.66	66.88	18.10
T = 323 K	9.7	352.29	33.61	35.86	6.69	10.2	411.27	22.08	19.15	13.29
	10.1	398.91	59.36	56.36	5.01	10.6	460.74	39.42	29.88	24.19
	10.4	436.22	81.43	81.19	0.30	11.0	505.69	53.88	44.69	17.04
	10.6	460.74	102.80	103.22	0.41	11.4	543.31	66.86	62.30	6.83
	10.8	484.05	122.31	129.60	6.00	11.7	566.85	80.11	76.41	4.61
T = 333 K	10.8	344.46	34.37	42.06	22.37	11.7	413.01	21.99	21.63	1.64
	11.4	389.65	60.78	64.24	5.70	12.6	480.50	37.80	38.85	2.78
	11.9	428.55	82.89	92.83	12.00	13.1	513.54	53.05	51.62	2.71
	12.2	451.44	104.91	115.33	9.92	13.5	537.09	67.64	63.06	6.77
	12.5	473.43	125.05	142.00	13.56	14.1	567.87	79.96	81.57	2.01

	Compound **3**					Compound **4**				
T	P	ρ			AAD	P	ρ			AAD
K	MPa	kg·m^{-3}	10^4x	10^4x_{cal}	%	MPa	kg·m^{-3}	10^4x	10^4x_{cal}	%
T = 313 K	9.1	517.19	14.86	14.89	0.21	9.2	538.22	7.92	6.69	15.52
	9.3	556.08	27.63	26.75	3.21	9.4	571.33	11.08	10.63	4.09
	9.4	571.33	40.35	33.58	16.76	9.5	584.52	13.46	12.76	5.26
	9.6	596.10	51.56	48.42	6.08	9.6	596.10	16.44	14.95	9.04
	9.8	615.65	62.40	64.37	3.16	9.7	606.40	20.52	17.20	16.14
T = 323 K	10.9	495.10	15.52	16.17	4.19	11.1	515.81	7.83	7.82	0.13
	11.2	525.44	29.24	25.28	13.65	11.4	543.31	12.94	11.39	12.00
	11.4	543.31	42.42	32.83	22.61	11.6	559.40	16.32	14.16	13.22
	11.9	580.66	52.93	56.37	6.51	12.0	587.07	19.52	20.52	5.09
	12.1	593.19	64.76	67.43	4.12	12.3	604.62	24.16	25.88	7.10
T = 333 K	12.6	480.50	15.99	19.72	23.33	13.0	507.26	7.44	11.08	48.92
	13.1	513.54	29.92	31.78	6.21	13.4	531.44	14.02	15.31	9.21
	13.6	542.58	42.48	48.19	13.44	13.6	542.58	16.56	17.75	7.18
	13.9	558.17	55.06	60.15	9.25	13.9	558.17	20.97	21.82	3.98
	14.2	572.52	67.10	73.68	9.80	14.5	585.74	24.34	31.31	28.62

	Compound **5**					Compound **6**				
T	P	ρ			AAD	P	ρ			AAD
K	MPa	kg·m^{-3}	10^4x	10^4x_{cal}	%	MPa	kg·m^{-3}	10^4x	10^4x_{cal}	%
T = 313 K	9.90	624.05	6.08	5.00	17.81	11.0	685.58	6.77	6.75	0.19
	10.3	651.49	9.35	7.89	15.60	11.7	710.44	9.15	8.82	3.66
	10.7	672.50	12.03	11.10	7.68	12.4	730.15	10.49	10.79	2.85
	11.2	693.38	15.32	15.47	1.02	13.5	754.92	11.82	13.75	16.32
	11.5	703.98	18.12	18.25	0.74	14.3	769.81	13.26	15.80	19.18
T = 323 K	12.4	609.97	6.65	7.58	14.00	13.8	667.36	6.77	7.10	4.92
	12.9	633.72	9.75	11.19	14.83	14.4	685.43	8.31	8.64	3.90
	13.1	642.06	12.03	12.82	6.48	15.0	701.08	10.34	10.20	1.38
	13.4	653.57	14.62	15.43	5.55	15.9	721.23	12.08	12.55	3.93
	13.8	667.36	18.22	19.22	5.50	16.4	731.10	13.56	13.86	2.22
T = 333 K	14.0	563.09	5.57	6.68	19.86	16.0	638.84	5.39	6.84	26.72
	14.7	593.99	9.77	11.12	13.79	16.2	644.66	6.66	7.29	9.46
	15.0	605.60	11.90	13.44	12.96	17.3	672.95	10.77	9.92	7.92
	15.2	612.88	13.60	15.13	11.26	18.0	688.34	12.52	11.68	6.74
	15.6	626.44	16.95	18.84	11.14	19.3	713.00	14.03	15.08	7.52

Compounds 1: Dipentyl-2,2′-oxidiacetate. A light yellow oil with 85 % yield. FT-IR (KBr, cm^{-1}) 1754.7 (C═O), 1206.4, 1143.7, 1050.1 (C−O); ^{1}H NMR ($CDCl_3$) δ = 4.27 (s, 4H, 2×O═CCH_2O), 4.15−4.17 (t, 4H, J = 7.2, 2×CH_2O), 1.65−1.68 (m, 4H, 2×CH_2), 1.22−1.34 (m, 8H, 4×CH_2), 0.90−0.92 (t, 6H, J = 6.6, 2×CH_3); ^{13}C NMR ($CDCl_3$) δ_C = 169.62 (2C, s), 67.86 (2C, s), 64.91 (2C, s), 27.99 (2C, s), 27.73 (2C, s), 22.04 (2C, s), 13.68 (2C, s). Elemental Anal.: $C_{14}H_{26}O_5$. Found: C, 61.25; H, 9.44; O, 29.08 %. Required: C, 61.29; H, 9.55; O, 29.16 %.

Compounds 2: Diheptyl-2,2′-oxidiacetate. A light yellow oil with 81 % yield. FT-IR (KBr, cm^{-1}) 1754.3 (C═O), 1207.2, 1143.0, 1054.9 (C−O); ^{1}H NMR ($CDCl_3$) δ_H = 4.24 (s, 4H, 2×O═CCH_2O), 4.14−4.18 (t, 4H, J = 6.8, 2×CH_2O), 1.63−1.66 (m, 4H, 2×CH_2), 1.28−1.32 (m, 16H, 8×CH_2), 0.87−0.90 (t, 6H, J = 6.8, 2×CH_3); ^{13}C NMR ($CDCl_3$) δ_C = 169.67 (2C, s), 67.91 (2C, s), 64.98 (2C, s), 31.49 (2C, s), 28.68 (2C, s), 28.34 (2C, s), 25.59 (2C, s), 22.37 (2C, s), 13.84 (2C, s). Elemental Anal.: $C_{18}H_{34}O_5$. Found: C, 65.34; H, 10.25; O, 24.13 %. Required: C, 65.42; H, 10.37; O, 24.21 %.

Compounds 3: Dinonyl-2,2′-oxidiacetate. A light yellow oil with 83 % yield. FT-IR (KBr, cm^{-1}): 1753.5 (C═O), 1205.3, 1141.1, 1053.9 (C−O); ^{1}H NMR ($CDCl_3$) δ_H = 4.24 (s, 4H, 2×O═CCH_2O), 4.14−4.18 (t, 4H, J = 6.8, 2×CH_2O),

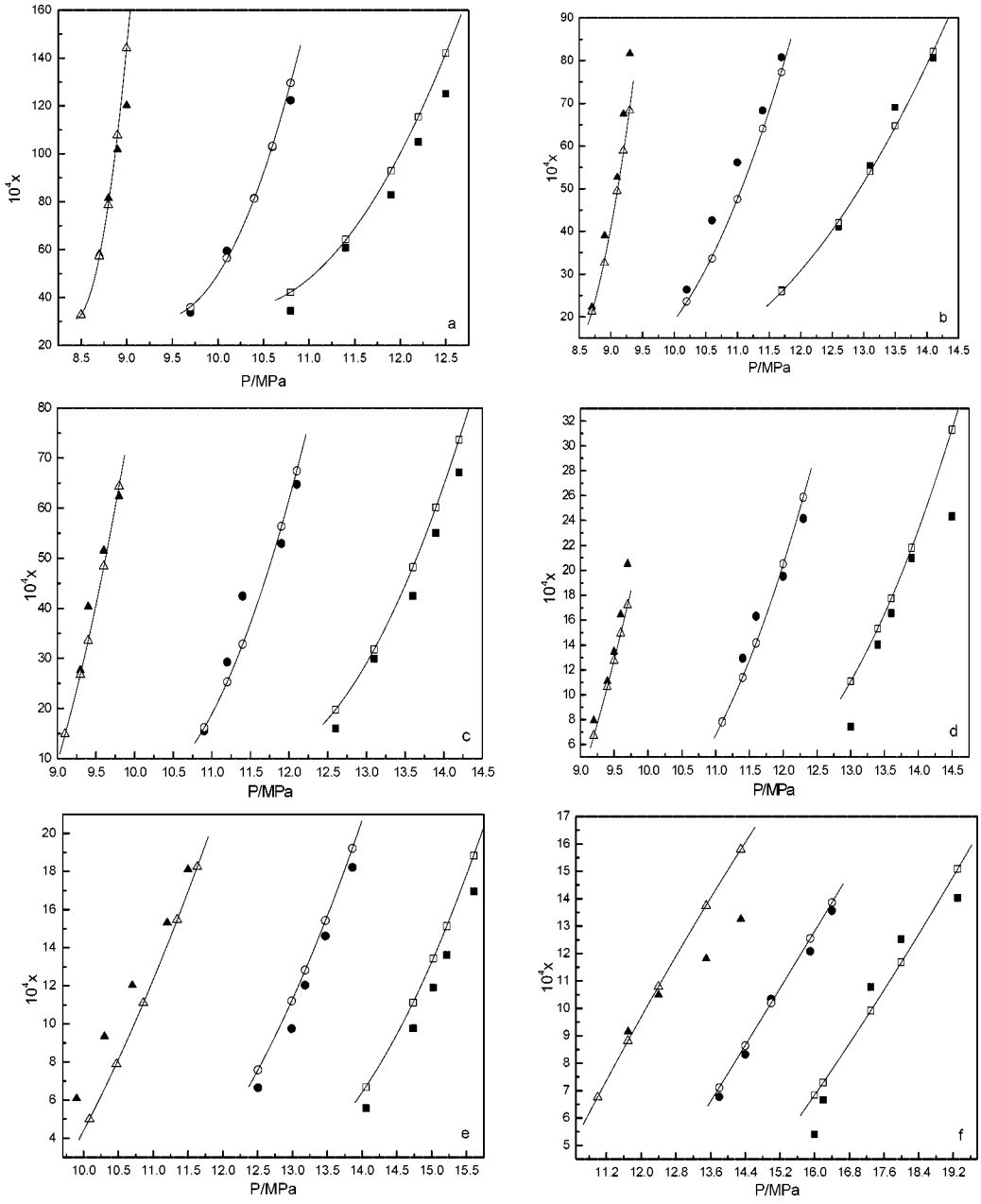


Figure 1. Comparison of solubility experimental and calculated values for compounds in supercritical CO_2 at ▲,△, 313 K; ●,○, 323 K; and ■,□, 333 K. (a) Compound **1** (dipentyl-2,2'-oxydiacetate). (b) Compound **2** (diheptyl-2,2'-oxydiacetate). (c) Compound **3** (dinonyl-2,2'-oxydiacetate). (d) Compound **4** (diundecyl-2,2'-oxydiacetate). (e) Compound **5** (ditridecyl-2,2'-oxydiacetate). (f) Compound **6** (dipentadecyl-2,2'-oxydiacetate). ●,▲,■, exptl; ○,△,□, calcd. Lines represent correlation by eq 1.

1.63−1.66 (m, 4H, 2×CH_2), 1.27−1.30 (m, 24H, 12×CH_2), 0.86−0.91 (t, 6H, J = 7.2, 2×CH_3); ^{13}C NMR ($CDCl_3$) δ_C = 169.65 (2C, s), 67.89 (2C, s), 64.93 (2C, s), 31.68 (2C, s), 29.29 (2C, s), 29.05 (4C, s), 28.38 (2C, s), 25.66 (2C, s), 22.49 (2C, s), 13.91 (2C, s). Elemental Anal.: $C_{22}H_{42}O_5$. Found: C, 68.27; H, 10.96; O, 20.87 %. Required: C, 68.35; H, 10.95; O, 20.69 %.

Compounds 4: Diundecyl-2,2′-oxidiacetate. A light yellow solid with 73 % yield. FT-IR (KBr, cm^{-1}): 1752.5 (C═O), 1210.9, 1143.4, 1052.7 (C−O); ^{1}H NMR ($CDCl_3$) δ_H = 4.24 (s, 4H, 2×O═CCH_2O), 4.14−4.18 (t, 4H, J = 6.4, 2×CH_2O), 1.63−1.66 (m, 4H, 2×CH_2), 1.26−1.30 (m, 32H, 16×CH_2), 0.86−0.90 (t, 6H, J = 6.8, 2×CH_3); ^{13}C NMR ($CDCl_3$) δ_C = 169.64 (2C, s), 67.92 (2C, s), 64.97 (2C, s), 31.76 (2C, s), 29.44 (4C, s), 29.34 (2C, s), 29.18 (2C, s), 29.06 (2C, s), 28.40 (2C, s), 25.68 (2C, s), 22.53 (2C, s), 13.93 (2C, s). Elemental Anal.: $C_{26}H_{50}O_5$. Found: C, 70.53; H, 11.25; O, 18.08 %. Required: C, 70.54; H, 11.38; O, 18.07 %.

Compounds 5: Ditridecyl-2,2′-oxidiacetate. A light yellow solid with 75 % yield. FT-IR (KBr, cm^{-1}) 1747.4 (C═O), 1217.8, 1157.9, 1062.2 (C−O); ^{1}H NMR ($CDCl_3$) δ_H = 4.24 (s, 4H, 2×O═CCH_2O), 4.14−4.18 (t, 4H, J = 6.8, 2×CH_2O), 1.63−1.64 (m, 4H, 2×CH_2), 1.26−1.30 (m, 40H, 20×CH_2), 0.86−0.90 (t, 6H, J = 6.8, 2×CH_3); ^{13}C NMR ($CDCl_3$) δ_C = 169.73 (2C, s), 68.02 (2C, s), 65.09 (2C, s), 31.84 (2C, s), 29.57 (4C, s), 29.49 (2C, s), 29.42 (2C, s), 29.28 (4C, s), 29.13 (2C, s), 28.46 (2C, s), 25.75 (2C, s), 22.61 (2C, s), 14.02 (2C, s).

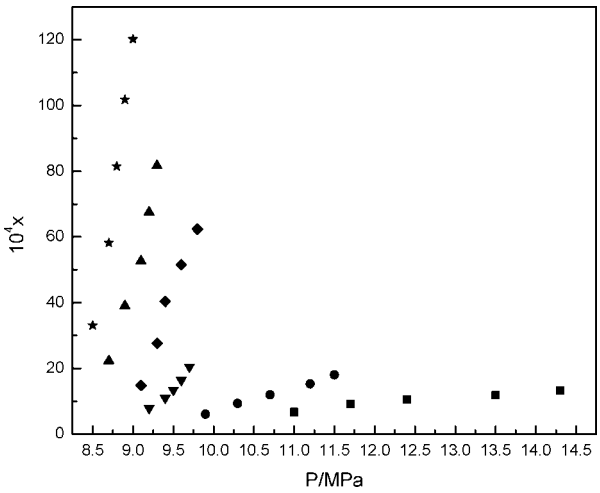
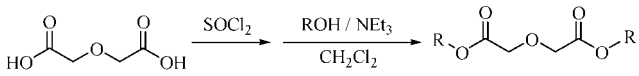


Figure 2. Solubility comparison of compounds **1** to **6** in supercritical CO_2 at 313 K. ★, compound **1** (dipentyl-2,2'-oxydiacetate); ▲, compound **2** (diheptyl-2,2'-oxydiacetate); ◆, compound **3** (dinonyl-2,2'-oxydiacetate); ▼, compound **4** (diundecyl-2,2'-oxydiacetate); ●, compound **5** (ditridecyl-2,2'-oxydiacetate); ■, compound **6** (dipentadecyl-2,2'-oxydiacetate).

Scheme 1. Synthesis of CO_2-Philic Compounds 1 to 6



Compounds 1-6

Compounds	R	Compounds	R
1	$CH_2(CH_2)_3CH_3$	**4**	$CH_2(CH_2)_9CH_3$
2	$CH_2(CH_2)_5CH_3$	**5**	$CH_2(CH_2)_{11}CH_3$
3	$CH_2(CH_2)_7CH_3$	**6**	$CH_2(CH_2)_{13}CH_3$

Table 2. Solubility Constants *a*, *b*, and *C* Obtained from the Data Correlation Procedure

compounds	*a*	*b*/K	$C/m^3 \cdot kg^{-1}$
dipentyl-2,2′-oxidiacetate	14.26627	−3762.33	0.010567
diheptyl-2,2′-oxidiacetate	9.24873	−2603.06	0.00916
dinonyl-2,2′-oxidiacetate	20.49936	−6148.02	0.015623
diundecyl-2,2′-oxidiacetate	21.27185	−6789.97	0.014627
ditridecyl-2,2′-oxidiacetate	27.30772	−9058.51	0.018073
dipentadecyl-2,2′-oxidiacetate	14.30383	−5231.23	0.013203

Elemental Anal.: $C_{30}H_{58}O_5$. Found: C, 72.11; H, 11.63; O, 16.06 %. Required: C, 72.24; H, 11.72; O, 16.04 %.

Compounds 6: Dipentadecyl-2,2′-oxidiacetate. A light yellow solid with 72 % yield. FT-IR (KBr, cm^{-1}) 1752.9 (C═O), 1217.5, 1157.2, 1043.5 (C−O); ^1H NMR ($CDCl_3$) $\delta_H = 4.23$ (s, 4H, 2×O═CCH_2O), 4.14−4.18 (t, 4H, $J = 6.8$, 2×CH_2O), 1.63−1.65 (m, 4H, 2×CH_2), 1.23−1.30 (m, 48H, 24×CH_2), 0.86−0.90 (t, 6H, $J = 6.8$, 2×CH_3); ^{13}C NMR ($CDCl_3$) δ_C =169.68 (2C, s), 67.97 (2C, s), 65.02 (2C, s), 31.84 (2C, s), 29.60 (8C, s), 29.48 (2C, s), 29.42 (2C, s), 29.29 (4C, s), 29.13 (2C, s), 28.46 (2C, s), 25.74 (2C, s), 22.60 (2C, s), 14.00 (2C, s). Elemental Anal.: $C_{34}H_{66}O_5$. Found: C, 73.53; H, 11.95; O, 14.39 %. Required: C, 73.59; H, 11.99; O, 14.42 %.

Solubility Test. A variable-volume view cell (7.11 mL) with two sapphire windows was used to determine the solubility of each compound at various conditions. A suitable amount of compounds and a stirring bar were loaded into the cell using a micropipette or weighing paper, and the cell was sealed tightly. The system was heated to the desired temperature and pressurized with CO_2 from a syringe pump. The pressure increased gradually until the system became a homogeneous transparent single phase. When the pressure kept constant for a period of time of 20 min, the pressure was recorded and confined as the dissolution pressure. At each condition, the experiment was repeated at least three times. The uncertainty of the dissolution pressure and temperature was ± 0.5 MPa and ± 0.1 °C. The dissolution pressure and temperature were recorded to obtain the density of CO_2 on the Web site page.[13]

Results and Discussion

The solubility of the CO_2-philic compounds in supercritical CO_2 was determined at 313 K, 323 K, and 333 K and the pressure range of (8.5 to 19.3) MPa. The experimental results were shown in Table 1 and Figure 1, and the mole fraction of the solutes were reproducible within ± 3 %. As expected, at the same temperature, the solubilities of all the compounds increased with the increase of pressure, and at the same pressure, the solubilities of all the compounds decreased with the increase of temperature.[14,15] As shown in Table 1, the mole fraction of dipentyl-2,2′-oxidiacetate (compound **1**) in supercritical CO_2 could reach as high as 1.25 % at 12.5 MPa and 333 K. The other compounds also showed good solubilities in supercritical CO_2 at easily accessible temperatures and pressures. It seems that the high solubility of compounds (**1** to **6**) in supercritical CO_2 can be attributed to the presence of CO_2-philic hydrocarbon, carbonyl, and ether groups in these compounds.[11,12]

As we expected, the solubility sequence was observed as **1** > **2** > **3** > **4** > **5** > **6** (Figure 2). The solubility of the compounds decreased with the increase of the length of hydrocarbon chain at the same temperature and pressure. This phenomenon was consisted with Shen's[16] and Chang's[17] description.

The experimental solubility data for the six CO_2-philic compounds were correlated using the following equation[18,19]

$$\ln(xP/P_{ref}) = A + C(\rho - \rho_{ref}) \quad (1)$$

where

$$A = a + b/T \quad (2)$$

where x was the mole fraction of the solutes; P was the pressure; P_{ref} was 0.1 MPa; ρ was the density of pure CO_2 at the experimental temperature and pressure; ρ_{ref} was 700 $kg \cdot m^{-3}$; and A, C, a, and b were constants. The initial stage, $\ln(xP/P_{ref})$ values were plotted against $(\rho - \rho_{ref})$ (Figure 3), and the values were fitted with a straight line by least-squares regression to estimate the C and A parameters. The values of C, obtained from the slopes of the corresponding plots, were then averaged for each compound (Table 2). When the C was held at its average value, the experimental solubility data was then used to evaluate the A values at various temperatures for each compound. The plots of A versus $1/T$ for each compound were fitted to a straight line (Figure 4) from which the intercept and the slope (a and b) were obtained. The resulting a and b values for compounds were also shown in Table 2.

The values of a, b, and C were used to predict solubility using eq 1 and eq 2. The calculated data and the experimental data were compared in Figure 1. Finally, the average absolute relative

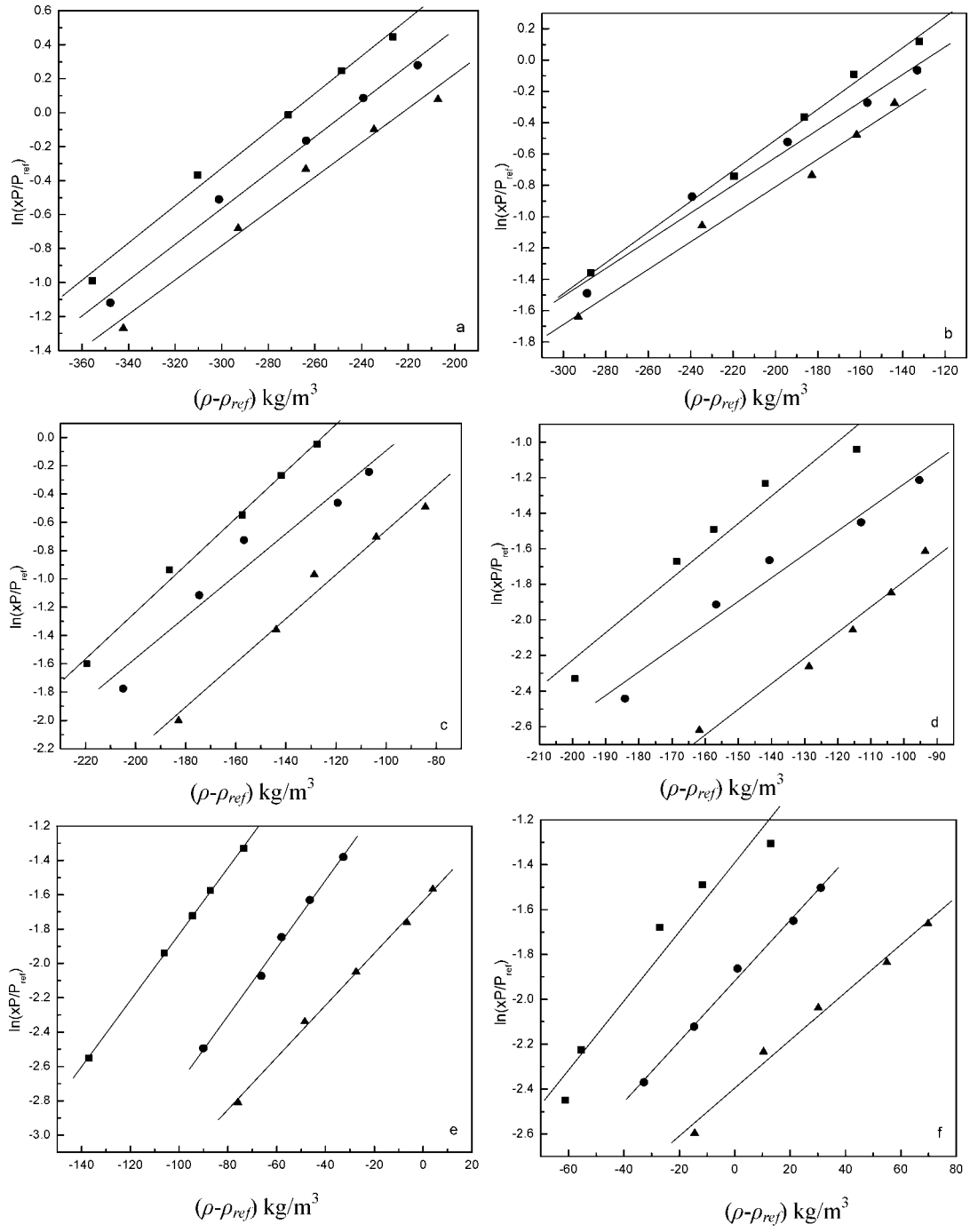


Figure 3. Plots of $\ln(xP/P_{ref})$ vs $(\rho - \rho_{ref})/\mathrm{kg \cdot m^{-3}}$ for compounds at various temperatures. (a) Compound **1** (dipentyl-2,2'-oxydiacetate). (b) Compound **2** (diheptyl-2,2'-oxydiacetate). (c) Compound **3** (dinonyl-2,2'-oxydiacetate). (d) Compound **4** (diundecyl-2,2'-oxydiacetate). (e) Compound **5** (ditridecyl-2,2'-oxydiacetate). (f) Compound **6** (dipentadecyl-2,2'-oxydiacetate). ●, 313 K; ▲, 323 K; ■, 333 K.

deviation (AARD) was used to test the correlation results. It was calculated with the following equation

$$\mathrm{AARD} = 1/n \sum (x_{i,\mathrm{cal}} - x_{i,\mathrm{exp}})/x_{i,\mathrm{exp}} \cdot 100\ \% \qquad (3)$$

where n was the number of experimental points, and $x_{i,\mathrm{cal}}$ and $x_{i,\mathrm{exp}}$ were the calculated and experimental data, respectively. The values of AARD were in the range of (3.18 to 19.58) %.

Conclusions

The solubilities of the six diglycolic acid esters were measured at the temperatures from (313 to 333) K and in the pressure range of (8.5 to 19.3) MPa. The results manifested that this type of compound showed good solubility in supercritical CO_2. The measured data were correlated with the semiempirical model and showed good agreement between the correlated results and the experimental data. This work might provide basic information for designing and synthesizing new low-cost, nonfluorous CO_2-philic compounds. Furthermore, this series of compounds which contain two carbonyl groups and one ether group could provide the lone pairs of electrons for chelating with metal ions. Therefore, compounds **1** to **6** might be used as chelating agents for extracting metal ions, and this part will be reported in our future work.

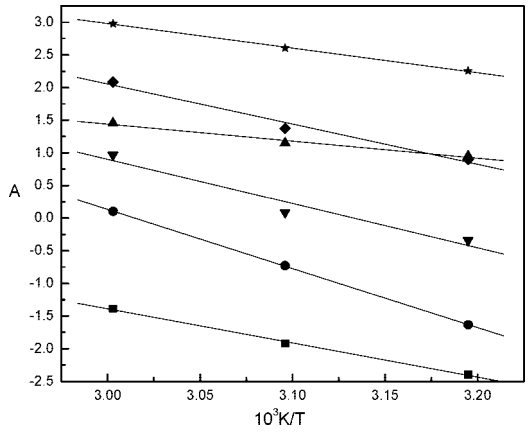


Figure 4. Plots of *A* vs 1/*T* for compounds. ★, compound **1** (dipentyl-2,2'-oxydiacetate); ▲, compound **2** (diheptyl-2,2'-oxydiacetate); ◆, compound **3** (dinonyl-2,2'-oxydiacetate); ▼, compound **4** (diundecyl-2,2'-oxydiacetate); ●, compound **5** (ditridecyl-2,2'-oxydiacetate); ■, compound **6** (dipentadecyl-2,2'-oxydiacetate).

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