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Solubility Comparison of Bis(2-hydroxyethyl) Ether and Tetraethylene Glycol before and after End-Group Modification by Ethyl Oxalyl Chloride in Supercritical Carbon Dioxide

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The end groups of bis(2-hydroxyethyl) ether (compound **1**) and tetraethylene glycol (compound **2**) were modified by ethyl oxalyl chloride to produce two new compounds: oxalic acid 2-(2-ethoxy-oxalyloxy-ethoxy)-ethyl ester ethyl ester (compound **3**) and oxalic acid 2-{2-[2-(2-ethoxyoxalyloxyethoxy)-ethoxy]-ethoxy}-ethyl ester ethyl ester (compound **4**). Then, the solubility of compounds **1** to **4** were investigated and compared in supercritical carbon dioxide at a temperature range of (313 to 333) K and in the pressure range of (9.1 to 19.6) MPa. The effect of the end group and molecular weight for the solubility of the compounds were discussed. In addition, the tested solubility data were then calculated and correlated with the semiempirical model at different pressures and temperatures, which showed satisfactory agreement with each other, and the average absolute relative deviation was in the range of (0.07 to 13.82) %.

Introduction

The utilization of supercritical carbon dioxide (scCO_2) has attracted significant attention because of its nontoxicity, nonflammability, low cost, and abundance, and it has moderate critical constants ($T_c = 304.15$ K, $P_c = 7.38$ MPa).[1,2] In addition, scCO_2 is considered a clean medium and has replaced traditional organic solvents for various industrial applications because the CO_2 properties of the density, dielectric constant, diffusion coefficient, and solubility parameter can be continuously tuned by simply changing the pressure or temperature at the supercritical condition, especially in the near-critical region.[3] So, scCO_2 has become very popular in a rapidly developing field of environmentally friendly chemistry in the processes of food, pharmaceuticals, biochemical industries, cleaning systems, microelectronics development, and polymer processing.[4−12]

No matter what kind of applications for scCO_2, solubility data of compounds in scCO_2 are among the most important thermophysical properties that are essential to the efficient design of supercritical processes.[9−11] However, despite its inherent physical property advantages, CO_2 is a nonpolar molecule with a low dielectric constant and low polarizability per unit volume, which limits its ability to dissolve many polar compounds such as water, ureas, amides, ionic species, proteins, sugars, and so forth.[12] To overcome the drawbacks of lower solubility, a solution is to introduce CO_2-philic groups into compounds, which are nonsoluble or show lower solubility in scCO_2. Researchers observed that scCO_2 could be used to dissolve large quantities of some classes of compounds, including fluorinated materials, silicones, and certain Lewis bases. Therefore, modifying the high molecular weight polar compounds via the end group with fluoroether, fluoroalkyl, or silicone groups does greatly increase the solubility in CO_2.[13,14] So far, the most efficient CO_2-philic groups are fluoro-groups, but they are very expensive and toxic. Silicone-functional amphiphiles require higher pressure to generate a single-phase solution in scCO_2.[15−18] Obviously, the design and synthesis of highly CO_2-soluble compounds via end-group modification with low-cost, nonfluorous, and nonsilicone groups would greatly benefit the potential applications of CO_2 as a solvent.[19,20]

According to the literature and based on our research results,[18,21−25] hydrocarbons substituted with carbonyl groups as CO_2-philes showed good or excellent solubility in scCO_2, and carbonyl groups, ether groups, and alkyl groups with suitable length are so-called CO_2-philic groups. In the present study, the end group of tetraethylene glycol and bis(2-hydroxyethyl-)ether were modified by a reaction with ethyl oxalyl chloride to introduce more CO_2-philic carbonyl groups; then the solubility of all four compounds was determined and compared in supercritical CO_2 over the pressure range of (9.1 to 19.6) MPa and at temperatures of (313 to 333) K, and the relationship between the structure and the solubility was discussed. The tested results were correlated by a semiempirical model.

Experimental Section

Chemicals and Experimental Apparatus. Carbon dioxide was purchased from Wuhan Steel Co. ($w = 0.9999$, mass fraction). Ethyl oxalyl chloride ($w = 0.98$, CAS Registry No.: 4755-77-5) was bought from Alfa Aesar Chem. Co. Tetraethylene glycol ($w = 0.995$, CAS Registry No.: 112-60-7), bis(2-hydroxyethyl) ether ($w = 0.99$, CAS Registry No.: 111-46-6), and triethylamine ($w = 0.99$, CAS Registry No.: 121-44-8) were bought from J&K Chem. Co. and used without further purification. Dichloromethane (CH_2Cl_2) was obtained from Tianjin Kemel Co. Ltd. (China) and distilled before use. NMR experiments were performed on a JEOL Al-400 MHz instrument using tetramethylsilane (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

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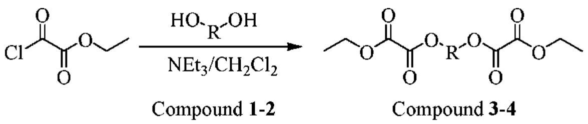
Scheme 1. Synthesis of Compounds 3 and 4



Compound	R	Full name
1	$-CH_2CH_2OCH_2CH_2-$	bis(2-hydroxyehyl)ether
2	$-CH_2CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2-$	tetraethylene glycol
3	$-CH_2CH_2OCH_2CH_2-$	oxalic acid 2-(2-ethoxy-oxalyloxy-ethoxy)-ethyl ester ethyl ester
4	$-CH_2CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2-$	oxalic acid 2-{2-[2-(2-ethoxy-oxalyloxy-ethoxy)-ethoxy]-ethoxy}-ethyl ester ethyl ester

Jasco Corp. (Japan): a PU-1580-CO_2 CO_2 delivery pump, a PU-2080 Plus intelligent high-performance liquid chromatography (HPLC) pump, and a BP-1580-81 back pressure regulator.

Modification. The ethyl oxalyl chloride was used to modify the end group of tetraethylene glycol and bis(2-hydroxyethyl) ether. The synthesis procedure was shown in Scheme 1. To the best of our knowledge, compounds **3** and **4** are new, and their structures were determined by IR, ^{1}H NMR, ^{13}C NMR, and elemental analysis.

The synthesis of oxalic acid 2-(2-ethoxy-oxalyloxy-ethoxy)-ethyl ester ethyl ester (compound **3**) was as follows. The reagent of bis(2-hydroxyethyl) ether (1.56 mL, 8.98 mmol) was added into the flask under N_2 atmosphere, and then a CH_2Cl_2 solution (30 mL) of ethyl oxalyl chloride (2 mL, 17.96 mmol) and triethylamine (17.96 mmol) was added dropwise to the flask under the protection of 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 **3**.

Compound* 3*: Oxalic Acid 2-(2-Ethoxy-oxalyloxy-ethoxy)-ethyl Ester Ethyl Ester. A light yellow oil with 89 % yield. FT-IR (KBr, cm^{-1}) 1647.6 (O=C—C=O), 1050.0, 1089.0 (C—O—C). ^{1}H NMR ($CDCl_3$): δ_H = 4.42 to 4.45 (t, 4H, J = 4.4, $2CH_2$), 4.33 to 4.39 (m, 4H, $2CH_2$), 3.81 to 3.82 (t, 4H, J = 4.8, $2CH_2$), 1.36 to 1.4 (t, 6H, J = 7.2, $2CH_3$). ^{13}C NMR ($CDCl_3$): δ_C = 157.99 (2C, s), 157.68 (2C, s), 68.61 (2C, s), 65.86 (2C, s), 63.45 (2C, s), 14.08 (2C, s). Element anal.: $C_{12}H_{18}O_9$. Found: C, w = 0.4702; H, w = 0.59; O, w = 0.4708. Required: C, w = 0.4706; H, w = 0.592; O, w = 0.4702.

The compound **4** was obtained as a light yellow oil using the same procedure.

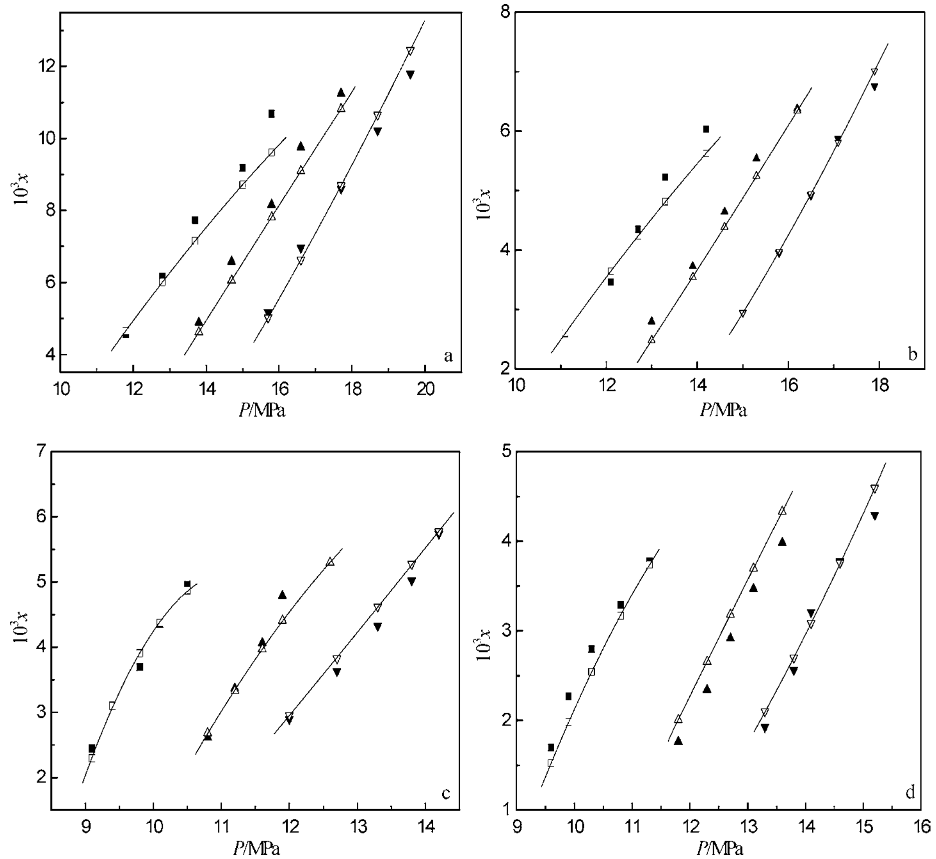


Figure 1. Comparison of solubility experimental and calculated values for compounds **1** to **4** in supercritical CO_2 at ■, □, 313 K; ▲, △, 323 K; and ▼, ▽, 333 K. (a) Compound **1** (bis(2-hydroxyethyl)ether). (b) Compound **2** (tetraethylene glycol). (c) Compound **3** (oxalic acid 2-(2-ethoxy-oxalyloxy-ethoxy)-ethyl ester ethyl ester). (d) Compound **4** (oxalic acid 2-{2-[2-(2-ethoxyoxalyloxyethoxy)-ethoxy]-ethoxy}-ethyl ester ethyl ester). x, mole fraction of compounds; P, CO_2 pressure; ■, ▲, ▼, experimental; □, △, ▽, calculated. Lines represent the correlation by eq 1.

Table 1. Solubility at Temperature T, Density ρ, and Mole Fraction x for Compounds 1 to 4

T	P	ρ			AARD	P	ρ			AARD
K	MPa	$kg \cdot m^{-3}$	$10^3\ x$	$10^3\ x_{cal}$	%	MPa	$kg \cdot m^{-3}$	$10^3\ x$	$10^3\ x_{cal}$	%
		Compound **1**					Compound **3**			
313	11.8	713.51	4.57	4.66	1.92	9.1	517.19	2.44	2.29	5.93
	13.2	739.88	6.17	6.01	2.54	9.4	571.33	3.09	3.10	0.24
	14.9	758.85	7.73	7.16	7.46	9.8	615.65	3.69	3.91	5.84
	16.7	781.32	9.17	8.71	5.13	10.1	638.82	4.35	4.37	0.54
	19.0	793.14	10.69	9.61	10.03	10.5	662.60	4.96	4.87	1.76
323	13.8	667.36	4.88	4.62	5.37	10.8	484.05	2.60	2.68	2.68
	14.7	693.52	6.58	6.06	7.90	11.2	525.44	3.36	3.33	0.97
	15.8	719.15	8.16	7.82	4.13	11.6	559.40	4.06	3.97	2.43
	16.6	734.83	9.76	9.09	6.80	11.9	580.66	4.78	4.41	7.95
	17.7	753.49	11.25	10.82	3.76	12.6	620.03	5.29	5.30	0.07
333	15.7	629.64	5.18	5.02	2.94	12.0	436.26	2.89	2.96	2.06
	16.6	655.62	6.96	6.62	4.86	12.7	487.42	3.63	3.83	5.42
	17.7	681.96	8.60	8.69	1.05	13.3	525.64	4.33	4.62	6.81
	18.7	702.17	10.21	10.65	4.30	13.8	553.12	5.02	5.27	4.94
	19.6	718.11	11.80	12.45	5.55	14.2	572.52	5.74	5.77	0.64
		Compound **2**					Compound **4**			
313	11.1	689.56	2.59	2.60	0.62	9.6	596.10	1.69	1.52	10.25
	12.1	722.18	3.46	3.65	5.41	9.9	624.05	2.27	1.98	12.73
	12.7	737.53	4.35	4.24	2.66	10.3	651.49	2.80	2.54	9.14
	13.3	750.85	5.23	4.81	7.98	10.8	677.07	3.29	3.17	3.62
	14.2	768.06	6.04	5.63	6.75	11.3	697.04	3.78	3.73	1.04
323	13.0	637.96	2.80	2.48	11.23	11.8	573.93	1.76	2.01	13.82
	13.9	670.57	3.73	3.54	4.86	12.3	604.62	2.34	2.66	13.40
	14.6	690.88	4.65	4.39	5.54	12.7	624.77	2.92	3.18	9.07
	15.3	708.19	5.54	5.24	5.38	13.1	642.06	3.47	3.70	6.61
	16.2	727.25	6.38	6.34	0.59	13.6	660.67	3.98	4.33	8.70
333	15.0	605.60	2.95	2.94	0.11	13.3	525.64	1.93	2.10	9.04
	15.8	632.77	3.95	3.97	0.66	13.8	553.12	2.56	2.70	5.40
	16.5	652.96	4.91	4.94	0.52	14.1	567.87	3.21	3.09	3.83
	17.1	668.22	5.87	5.82	1.01	14.6	589.92	3.77	3.76	0.48
	17.9	686.25	6.76	7.02	3.81	15.2	612.88	4.29	4.59	6.93

Compound* 4*: Oxalic Acid 2-{2-[2-(2-Ethoxyoxalyloxyethoxy)-ethoxy]ethoxy}-ethyl Ester Ethyl Ester. A light yellow oil with 85 % yield. FT-IR (KBr, cm^{-1}) 1643.7 (O=C—C=O), 1049.9, 1088.9 (C—O—C). ^1H NMR ($CDCl_3$): $\delta_H = 4.42$ to 4.44 (t, 4H, $J = 4.8$, $2CH_2$), 4.32 to 4.38 (m, 4H, $2CH_2$), 3.78 to 3.8 (t, 4H, $J = 4.8$, $2CH_2$), 3.64 to 3.68 (m, 8H, $4CH_2$), 1.35 to 1.39 (t, 6H, $J = 7.2$, $2CH_3$). ^{13}C NMR ($CDCl_3$): $\delta_C = 158.05$ (2C, s), 157.78 (2C, s), 70.86 (2C, s), 70.81 (2C, s), 68.58 (2C, s), 66.05 (2C, s), 63.37 (2C, s), 14.13 (2C, s). Element anal.: $C_{16}H_{26}O_{11}$. Found: C, $w = 0.4869$; H, $w = 0.653$; O, $w = 0.4478$. Required: C, $w = 0.4873$; H, $w = 0.665$; O, $w = 0.4463$.

Solubility Measurement. 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, and then 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 was 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 ± 0.2 MPa and ± 0.1 °C. The dissolution pressure and temperature were recorded to obtain the density of CO_2 on the Web site page.[26]

Results and Discussion

Solubility Results. The solubility of all four compounds was determined at the temperature range from (313 to 333) K and the pressure range of (9.1 to 19.6) MPa for compounds. The mole fractions of the solutes were reproducible within ± 2 %. As shown in Figure 1 and Table 1, the solubility increased with increasing pressure at a constant temperature as expected. It was mainly due to the fact that the density of CO_2 increased with the increase of pressure, and thus the solvent power of $scCO_2$ was stronger at higher pressures.

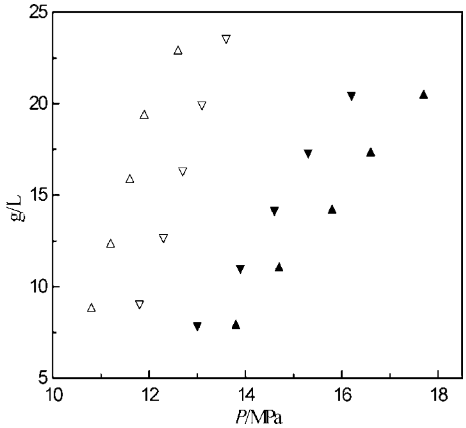


Figure 2. Solubility comparison of compounds **1** to **4** in supercritical CO_2 at 323K. $g \cdot L^{-1}$, weight solubility of compounds in supercritical CO_2; P, CO_2 pressure; ▲, compound **1** (bis(2-hydroxyethyl)ether); ▼, compound **2** (tetraethylene glycol); △, compound **3** (oxalic acid 2-(2-ethoxy-oxalyloxy-ethoxy)-ethyl ester ethyl ester); ▽, compound **4** (oxalic acid 2-{2-[2-(2-ethoxyoxalyloxyethoxy)-ethoxy]-ethoxy}-ethyl ester ethyl ester).

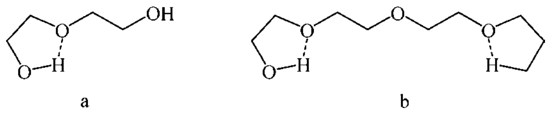


Figure 3. Proposed intramolecular hydrogen bonds existing in solute. (a) Compound **1** (bis(2-hydroxyethyl)ether). (b) Compound **2** (tetraethylene glycol).

As shown in Figure 2, the solubility sequence was observed as compound **3** > **4** > **2** > **1**. It is obvious that end-group modification can enhance the solubility of compound in $scCO_2$.

Before end-group modification, although the molecular weight of compound **2** is much bigger than compound **1**, compound **2** is more soluble than compound **1** in $scCO_2$. We assumed that there are two main forces affecting the solubility of the compound in $scCO_2$: self-interaction between compounds (solute−solute) and specific intermolecular interaction between compounds and the CO_2 molecule (solute−solvent). As shown in Figure 3, the short chain makes compound **1** to form only one intramolecular hydrogen bond with one isolated OH group, and the isolated OH group will tend to form a intermolecular hydrogen bond and strong self-interaction, which accordingly elevates the cloud-point pressure of solubility in CO_2. However, compound **2** with a longer chain could form two intramolecular hydrogen bonds, which is helpful to enhance the intermolecular solute−solvent interaction. Furthermore, more CO_2-philic ether groups are also helpful for solute−solvent interaction. Both intense specific intermolecular solute−solvent interactions contrarily resulted in the higher CO_2 solubility of the compound **2**.

The solubility of compound **3** [22.86 $g \cdot L^{-1}$ (12.6 MPa)] was much higher than that of compound **1** [7.86 $g \cdot L^{-1}$ (13.8 MPa)], and the solubility of compound **4** [16.32 $g \cdot L^{-1}$ (12.7 MPa)] was much higher than that of compound **2** [11.03 $g \cdot L^{-1}$ (13.9 MPa)] at 323 K after end-group modification via using the ethyl oxalyl group to take place of hydroxyl group. Ethyl oxalyl group is more CO_2-philic than the hydroxyl group and can reduce the intermolecular attraction of the compound (solute−solute) and enhance the interaction of the solute and solvent. We proposed that the influence of molecular weight on the solubility of

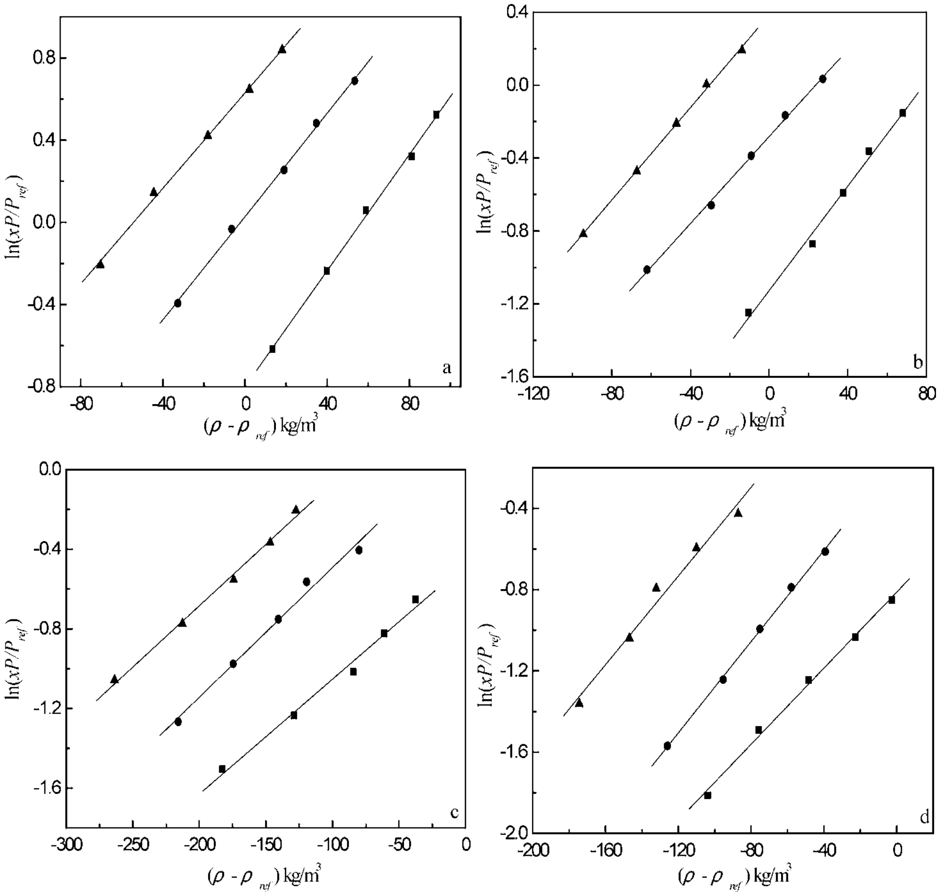


Figure 4. Plots of $\ln(xP/P_{ref})$ vs $(\rho - \rho_{ref})$ via eq 1 for compounds **1** to **4** at various temperatures. x, mole fraction of compounds; P, CO_2 pressure; P_{ref}, 0.1 MPa; ρ, density of pure CO_2; ρ_{ref}, 700 kg·m^{-3}. (a) Compound **1** (bis(2-hydroxyethyl)ether). (b) Compound **2** (tetraethylene glycol). (c) Compound **3** (oxalic acid 2-(2-ethoxy-oxalyloxy-ethoxy)-ethyl ester ethyl ester). (d) Compound **4** (oxalic acid 2-{2-[2-(2-ethoxyoxalyloxyethoxy)-ethoxy]-ethoxy}-ethyl ester ethyl ester). ■, 313 K; ●, 323 K; ▲, 333 K.

compounds **3** and **4** is the main force. Although compound **4** has more CO_2-philic groups, the much higher molecular weight resulted in less solubility in comparison with compound **3**. These were consistent with the descriptions of Chang et al.[18] and Shen et al.[27]

The experimental solubility data for the four compounds were correlated using the following equation:[28,29]

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

where

$$A = a + b/T \tag{2}$$

where x is the mole fraction of solute, P is pressure, P_{ref} is 0.1 MPa, and ρ is the density of pure CO_2 at the experimental temperature and pressure.[24] The ρ_{ref} is 700 kg·m^{-3}, and C, a, and b are constants.

The first step was the plots of $\ln(xP/P_{ref})$ values versus $(\rho - \rho_{ref})$ (Figure 4), 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 were 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 5) from which the intercept and the slope (a and b) were obtained. The resulting a and b values for compounds are also shown in Table 2. Then, the values of a, b, and C were used to predict solubility using eqs 1 and 2. The calculated data and the experimental data were compared (Figure 1). Finally, the average absolute relative deviation from experimental date (AARD) was used to test the correlation results and calculated with the following eq 3

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

		b	C
compound	a	k	m^3·kg^{-1}
1	23.08488	−7467.00007	0.01277
2	24.07392	−7881.29912	0.012966667
3	16.6445	−5347.68853	0.00615
4	22.25073	−7224.66909	0.0105

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

where n is the number of experimental points and $x_{i,\mathrm{cal}}$ and $x_{i,\mathrm{exp}}$ are the calculated and experimental data, respectively. The values of AARD were in the range of (0.07 to 13.82) %.

Conclusion

In summary, the solubility of compounds **1** to **4** were measured at temperatures from (313 to 333) K and the pressure range of (9.1 to 19.6) MPa. The solubility of compounds is influenced by the end groups and their molecular weight. The modified compounds showed better solubility than the unmodified compounds in supercritical CO_2. The solubility of the compounds increased with increasing pressure (at constant T) and decreased with increasing temperature (at constant P). In

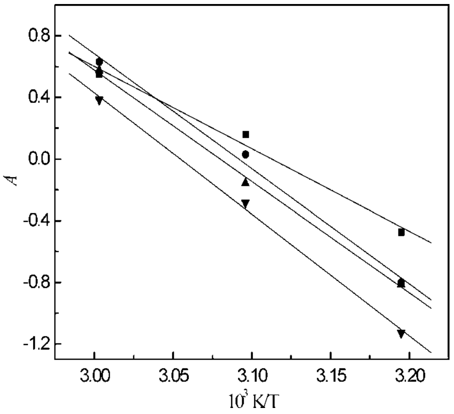


Figure 5. Plot of A vs $1/T$ via eq 2 for compounds **1** to **4**. T, temperature; A, constant. ●, Compound **1** (bis(2-hydroxyethyl)ether); ▼, compound **2** (tetraethylene glycol); ■, compound **3** (oxalic acid 2-(2-ethoxy-oxalyloxy-ethoxy)-ethyl ester ethyl ester); ▲, compound **4** (oxalic acid 2-{2-[2-(2-ethoxyoxalyloxyethoxy)-ethoxy]-ethoxy}-ethyl ester ethyl ester).

addition, the solubility of the compound was mainly affected by the self-interaction (solute−solute) and intermolecular interaction between the solute and the CO_2 molecule (solute−solvent). The measured data were correlated with the semiempirical model and showed good agreement between the correlated results and the experimental data.

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