Solubilities of Diglycolic Acid Esters at Temperatures Ranging from (343 to 363) K in Supercritical Carbon Dioxide

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The solubilities of four former-reported diglycolic acid esters were measured at high temperatures ranging from (343 to 363) K and pressures from (11.8 to 19.7) MPa in supercritical carbon dioxide. 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 (0.49 and 28.74) %.

Introduction

Supercritical carbon dioxide ($scCO_2$) is often used as a clean medium and has replaced traditional organic solvents for various industrial applications because it is inexpensive, nontoxic, nonflammable, and recyclable and has moderate critical constants (T_c = 304.15 K and P_c = 7.38 MPa).[1−4] In addition, $scCO_2$ is undoubtedly the most investigated and employed supercritical fluid in chemical reactions, natural product extraction, drying, and dyeing.[5−7] Experimental determinations of solubilities of various compounds in supercritical solvents continue to be a very important part in the fields of supercritical fluids. Solubility information of compounds is crucial for effectively designing and then building up any practical supercritical separation processes. However, the majority of experimental studies has dealt with solubilities of a wide variety of pure compounds under the low-temperature conditions in a supercritical fluid, while solubility data under the high temperature in supercritical carbon dioxide are less frequently reported.[8−11]

According to the literature and based on our research results,[10−14] 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. Our group has designed and synthesized an array of diglycolic acid ester derivatives, and the solubilities of these compounds were investigated under the temperatures of (313 to 333) K which have been reported in *J. Chem. Eng. Data.*[10] For practice use, the solubilities of compounds in higher temperature are necessary and interesting, so in this work, the solubilities of four diglycolic acid ester derivatives, which were synthesized before they were investigated at the high temperature of (343 to 363) K and over the pressure range of (11.8 to 19.7) MPa, were investigated.

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Table 1. List of Compounds 1 to 4

	compounds
1	dipentyl-2,2′-oxidiacetate
2	diheptyl-2,2′-oxidiacetate
3	dinonyl-2,2′-oxidiacetate
4	diundecyl-2,2′-oxidiacetate

Experimental Section

Chemicals and Experimental Apparatus. Carbon dioxide was purchased from Wuhan Steel Co. (99.99 %, mass fraction). An array of diglycolic acid ester derivatives (dipentyl-2,2′-oxidiacetate, diheptyl-2,2′-oxidiacetate, dinonyl-2,2′-oxidiacetate, diundecyl-2,2′-oxidiacetate, Table 1) were synthesized according to our former report.[10] 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.

Solubility Test. Solubility measurement was carried out in a stainless steel view cell (7.11 mL) with two sapphire windows, which permitted visual observation of the phase behavior. A suitable amount of solute was loaded into the high-pressure view cell, and the stainless steel cell was then sealed. The compounds in the cell were stirred by a magnetic stir bar, and the temperature was controlled using a temperature controller jacket with a circulator. A "BP-1580-81" back-pressure regulator was used to keep a stable and accurate pressure. The system was heated to the desired temperature and pressurized with CO_2 from a syringe pump (PU-1580-CO_2" CO_2 Delivery Pump). The pressure was increased gradually (fluid flow rate: 0.2 mL·min^{-1}) until the compound disappeared and the fluid in the cell became transparent single phase: this pressure was defined as 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.[15]

Results and Discussion

The solubilities of four diglycolic acid esters were investigated at the high temperature of (343 to 363) K and over the pressure

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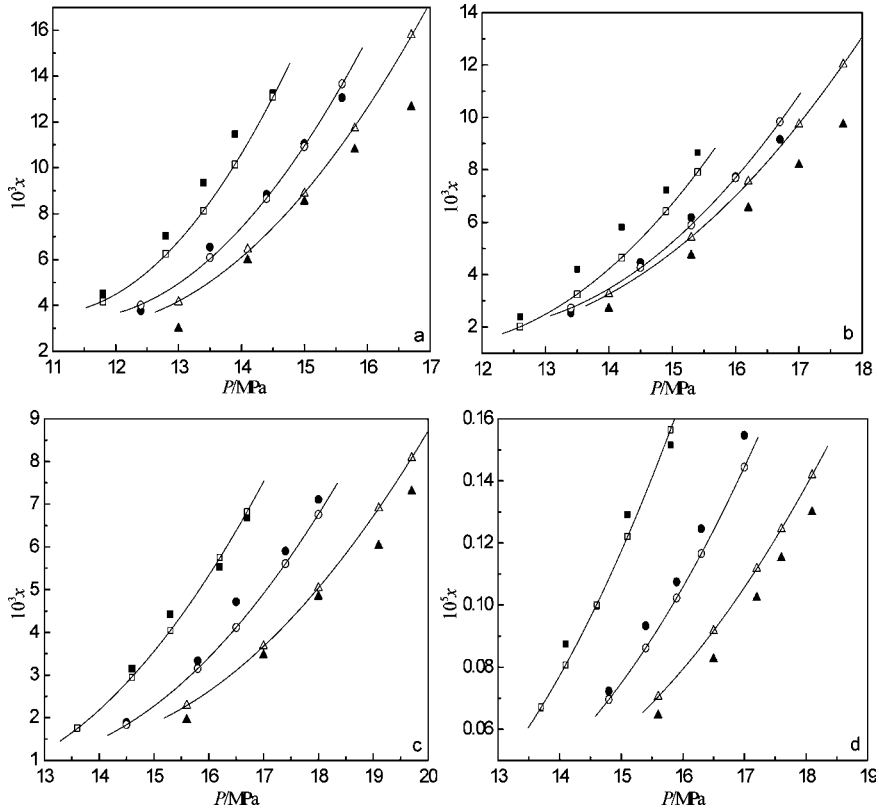

Figure 1. Comparison of experimental and calculated solubility values for compounds **1** to **4** in supercritical CO_2 at ■, □, 343 K; ●, ○, 353 K; and ▲, △, 363 K. (a) Compound **1** (dipentyl-2,2′-oxidiacetate). (b) Compound **2** (diheptyl-2,2′-oxidiacetate). (c) Compound **3** (dinonyl-2,2′-oxidiacetate). (d) Compound **4** (diundecyl-2,2′-oxidiacetate). ■, ●, ▲, exptl; □, ○, △, calcd. Lines represent the correlation by eq 1.

range of (11.8 to 19.7) MPa. The results were shown in Table 2 and Figure 1. The solubilities of all compounds represent the same character as the compounds at the low temperature as we expected.[10] Each reported data point was the average of at least three replicate samples. The mole fractions of the solutes were reproducible within ± 2 %. As shown in Figure 1, the

Table 2. Solubility at Temperature *T*, Density *ρ*, and Mole Fraction *x* for Compounds 1 to 4

T / K	*P* / MPa	*ρ* / kg·m^{-3}	10^3x	10^3x_{cal}	AARD %	*P* / MPa	*ρ* / kg·m^{-3}	10^3x	10^3x_{cal}	AARD %
			Compound **1**					Compound **2**		
T = 343 K	11.8	335.9	3.53	3.18	9.7	12.6	380.32	2.39	2.02	15.6
	12.8	391.64	6.05	5.25	13.16	13.5	430.94	4.21	3.26	22.72
	13.4	425.4	8.35	7.14	14.55	14.2	468.38	5.82	4.65	20.09
	13.9	452.67	10.46	9.14	12.6	14.9	502.65	7.23	6.42	11.11
	14.5	483.5	12.24	12.09	1.23	15.4	524.86	8.65	7.91	8.58
T = 353 K	12.4	314.05	3.77	4.02	6.5	13.4	357.57	2.54	2.72	7.28
	13.5	362.01	6.54	6.09	6.98	14.5	406.4	4.47	4.28	4.32
	14.4	402	8.84	8.66	1.98	15.3	440.9	6.18	5.89	4.65
	15	428.15	11.06	10.92	1.24	16	469.49	7.74	7.68	0.7
	15.6	453.37	13.06	13.67	4.67	16.7	496.16	9.15	9.83	7.41
T = 363 K	13	296.19	3.99	5.15	28.74	14	335.68	2.71	3.26	20.48
	14.1	339.33	6.98	7.44	6.68	15.3	383.4	4.74	5.42	14.39
	15	372.4	9.54	9.88	3.62	16.2	415.92	6.55	7.55	15.28
	15.8	401.59	11.79	12.73	7.91	17	443.76	8.19	9.73	18.89
	16.7	433.47	13.65	16.8	22.97	17.7	466.96	9.72	12.02	23.64
			Compound **3**					Compound **4**		
T = 343 K	13.6	436.44	1.76	1.75	0.64	13.7	441.9	0.068	0.067	0.65
	14.6	488.4	3.15	2.94	6.51	14.1	463.21	0.088	0.081	7.82
	15.3	520.57	4.43	4.05	8.61	14.6	488.4	0.099	0.10	0.49
	16.2	556.56	5.52	5.75	4.21	15.1	511.76	0.129	0.122	5.51
	16.7	574.17	6.69	6.82	1.92	15.8	541.29	0.152	0.156	3.23
T = 353 K	14.5	406.4	1.89	1.83	2.94	14.8	419.51	0.072	0.069	3.8
	15.8	461.51	3.33	3.15	5.36	15.4	445.09	0.093	0.086	7.58
	16.5	488.75	4.72	4.11	12.79	15.9	465.52	0.107	0.102	4.83
	17.4	520.72	5.90	5.61	4.95	16.3	481.17	0.125	0.117	6.45
	18	540.11	7.11	6.76	4.95	17	506.95	0.155	0.144	6.61
T = 363 K	15.6	394.34	1.95	2.28	17.15	15.6	394.34	0.065	0.07	9.27
	17	443.76	3.46	3.67	6.08	16.5	426.51	0.083	0.092	11.11
	18	476.52	4.84	5.04	4.10	17.2	450.51	0.102	0.111	9.15
	19.1	509.51	6.03	6.91	14.49	17.6	463.72	0.115	0.124	8.16
	19.7	526.1	7.30	8.09	10.72	18.1	479.66	0.129	0.142	9.18

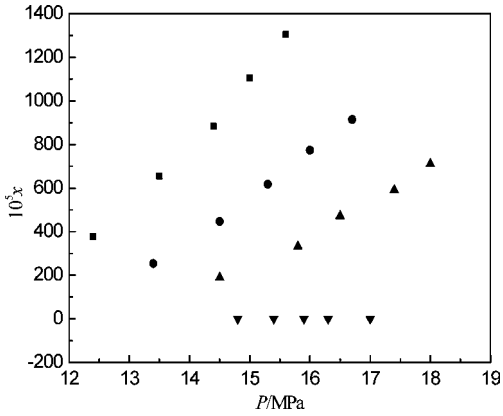

Figure 2. Solubility comparison of compounds **1** to **4** in supercritical CO_2 at 353 K. ■, compound **1** (dipentyl-2,2′-oxidiacetate); ●, compound **2** (diheptyl-2,2′-oxidiacetate); ▲, compound **3** (dinonyl-2,2′-oxidiacetate); ▼, compound **4** (diundecyl-2,2′-oxidiacetate).

solubilities of all compounds increased with the increase of pressure at the same temperature, and at the same pressure, the solubilities decreased with the increase of temperature. The solubilities of compounds decreased (**1** > **2** > **3** > **4**) with the increase of molecular weight at the same pressure and temperature (Figure 2). This phenomenon was consistent with Shen's[16] and Chang's[17] description.

The experimental solubility data for the four 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·m^{-3}; and C, a, and b were constants.

Table 3. Solubility Contants *a*, *b*, and *C* from the Data Correlation Procedure

compounds	*a*	*b*/k	*C*/m^3·kg^{-1}
dipentyl-2,2′-oxidiacetate	20.8256	−6175.24	0.01044
diheptyl-2,2′-oxidiacetate	23.62396	−7383.77	0.010846667
dinonyl-2,2′-oxidiacetate	17.5704	−5491.33	0.01137
diundecyl-2,2′-oxidiacetate	5.0877	−4052.47	0.009943333

The first step was the plots of $\ln(xP/P_{ref})$ values versus $(\rho - \rho_{ref})$ (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 3). When 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 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 3. 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

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

where n was the number of experimental points and $x_{i,cal}$ and $x_{i,exp}$ were the calculated and experimental data, respectively. The values of AARD were in the range of (0.49 and 28.74) %.

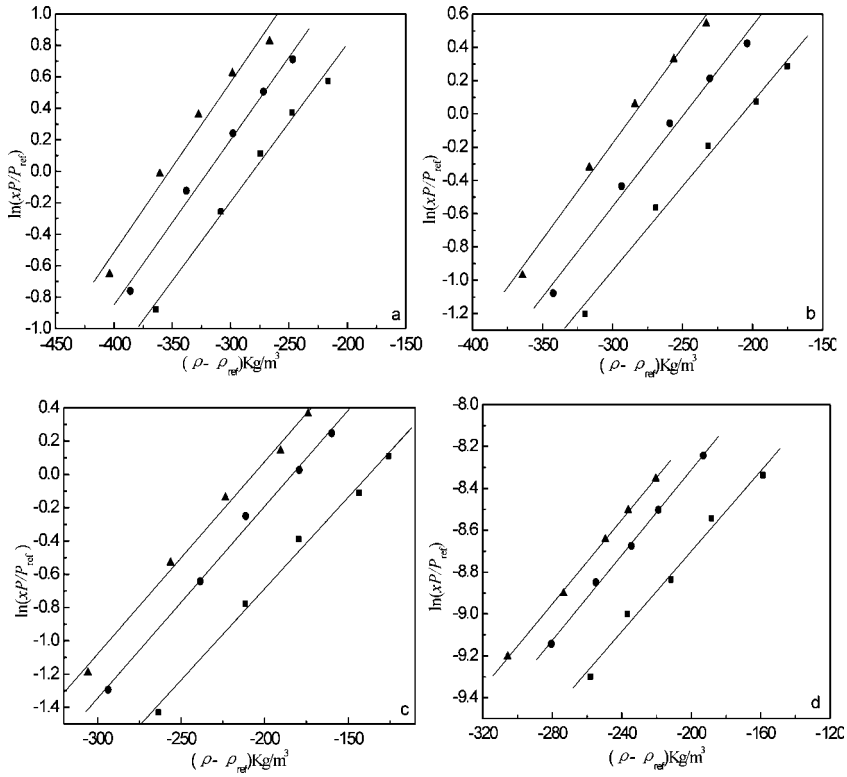

Figure 3. Plots of $\ln(xP/P_{ref})$ vs $(\rho - \rho_{ref})$/kg·m^{-3} for compounds **1** to **4** at various temperatures. (a) Compound **1** (dipentyl-2,2′-oxidiacetate). (b) Compound **2** (diheptyl-2,2′-oxidiacetate). (c) Compound **3** (dinonyl-2,2′-oxidiacetate). (d) Compound **4** (diundecyl-2,2′-oxidiacetate). ■, 343 K; ●, 353 K; ▲, 363 K.

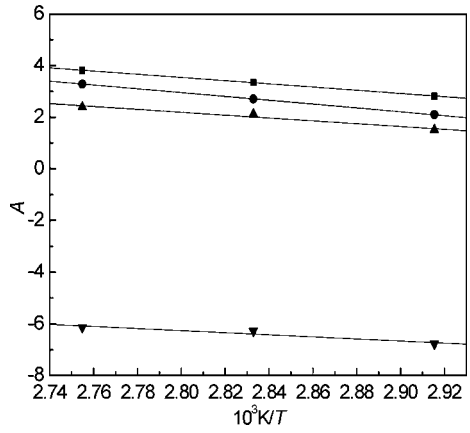

Figure 4. Plots of A vs $1/T$ for compounds **1** to **4**. ■, compound **1** (dipentyl-2,2′-oxidiacetate); ●, compound **2** (diheptyl-2,2′-oxidiacetate); ▲, compound **3** (dinonyl-2,2′-oxidiacetate); ▼, compound **4** (diundecyl-2,2′-oxidiacetate).

Conclusion

The solubilities of four diglycolic acid esters were measured at higher temperatures from (343 to 363) K and in the pressure range of (11.8 to 19.7) MPa. As we expected, this type of compound still showed good solubility at high temperature in supercritical CO_2 and represents the same character as the compounds at the low temperature. The solubilities of compounds increased with increasing pressure (at constant T) and decreased with increasing temperature (at constant P). The solubilities of compounds decreased with increasing length of the hydrocarbon chain at the same temperature and pressure. 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 that diglycolic acid esters were good nonfluorous CO_2-philic compounds.

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