Solubilities of Amide Compounds in Supercritical Carbon Dioxide

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2,2′-Oxybis(*N*,*N*-diethylacetamide), 2,2′-oxybis(*N*,*N*-dibutylacetamide), and 2,2′-oxybis(*N*,*N*-dihexylacetamide) were 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 (8.7 to 16.4) MPa in supercritical carbon dioxide. The measured solubilities were correlated using a semiempirical model. The calculated results showed satisfactory agreement with the experimental data and differed from the measured values by between (4.54 and 30.84) %.

Introduction

In recent years, supercritical carbon dioxide (SC-CO_2) has attracted a tremendous amount of attention as a "green" solvent because it is inexpensive, nontoxic, nonflammable, and recyclable and has moderate critical constants ($T = 31.06$ °C and $P_c = 7.38$ MPa).[1,2] The properties of SC-CO_2 are between liquid and gas and have much higher diffusivity and lower viscosity than that of liquid and much stronger solvent power than gas. However, their practical use has been limited by the need for high CO_2 pressure to dissolve even small amounts of polar, amphiphilic, organometallic, or high-molecular-mass compounds.[3,4] So-called "CO_2-philes" can efficiently transport insoluble or poorly soluble materials into CO_2 solvents. As the most of effective CO_2-philes are expensive fluorocarbons, the commercialization of promising CO_2-based processes has only limited success.[5]

According to the literature,[5−9] hydrocarbons substituted with carbonyl groups as CO_2-philes have appeared economically. In SC-CO_2, the high solubility of these carbonyl systems was attributed to the electron-donating carbonyl group promoting Lewis acid−Lewis base interactions with the carbon of CO_2 that could promote CO_2 solubility.[4,5] Ab initio calculations on simple carbonyl systems revealed that the high degree of miscibility, melting point depression, and liquid swelling was attributed to a two-point interaction of the methyl acetate with CO_2, including the Lewis acid−Lewis base interaction and a weak cooperative hydrogen bond between a proton on the methyl group and an oxygen of the CO_2.[5] The high CO_2 solubility of hydrocarbons containing acetamide groups was attributed to the accessibility of the carbonyl functionality to form a weak complex with CO_2.

According to the literature and based on our research results,[1,6] the carbonyl group, ether group, and alky group with suitable length are so-called CO_2-philic groups, so in this work, we have designed and synthesized three new CO_2-philic compounds starting from diglycolic acid, which contains a carbonyl functional group and ether group, via a simple procedure with high yield. The solubilities of compounds in SC-CO_2 over the pressure range of (8.7 to 16.4) MPa and at temperatures of (313, 323, and 333) K were determined, and the measured solubilities were also correlated using a semiempirical model.

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Experimental Section

Chemicals and Apparatus. Diglycolic acid, diethylamine, dibutylamine, and dihexylamine were purchased from Aldrich Chem. Co. and used as received without further purification. Dichlorosulfoxide ($SOCl_2$) was freshly distilled before use. Dichloromethane (CH_2Cl_2) was distilled over calcium hydride under argon. 99.99 % purity CO_2 was bought from Wuhan Steel Co. NMR spectra were recorded on a JEOL Al-300 MHz instrument at ambient temperature using TMS as an internal standard. IR spectra were measured on a Perkin-Elmer 2000 FT-IR spectrometer. Elemental analysis was performed by using a PE 2400 series II CHNS/O elemental analyzer. 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 3. Three compounds were synthesized according to the methods shown in Scheme 1.

Diglycolic acid (2.0 g, 0.015 mol) was dissolved in $SOCl_2$ (40 mL, 0.55 mol) and refluxed for 8 h under nitrogen protection. After being cooled to room temperature, the excess of $SOCl_2$ was distilled under reduced pressure, and then a CH_2Cl_2 solution (20 mL) of dialkyl amine (0.045 mol) was added dropwise to the reaction system under nitrogen. The mixture was stirred at room temperature for a whole night. The reaction mixture was washed with 1 % HCl aq., saturated $NaHCO_3$ aq., and then twice with water, and the organic phase was collected and dried over anhydrous Na_2SO_4. After evaporation under vacuum, the residue was purified by silica gel column chromatography with petroleum ether/ethyl acetate (1:3 to 1:6) to get a yellow oil liquid.

Compounds 1: 2,2′-Oxybis(N,N-diethylacetamide). Yield: 82%. IR (KBr) $\upsilon_{N-C=O}$: 1647.4 cm^{-1}. ^1H NMR ($CDCl_3$): $\delta =$ 4.31 (s, 4H, $CH_2C{=}O$), 3.28−3.41 (q, 8H, CH_2-N), 1.118−1.195 (t, $J = 6.8$, 12H, CH_3). ^{13}C NMR ($CDCl_3$): $\delta = 167.83, 69.21, 40.94, 12.70$. Elemental Anal.: $C_{12}H_{20}N_2O_3$. Found: C, 59.96; H, 8.42; N, 11.70; O, 19.96 %. Required: C, 59.98; H, 8.39; N, 11.66; O, 19.97 %.

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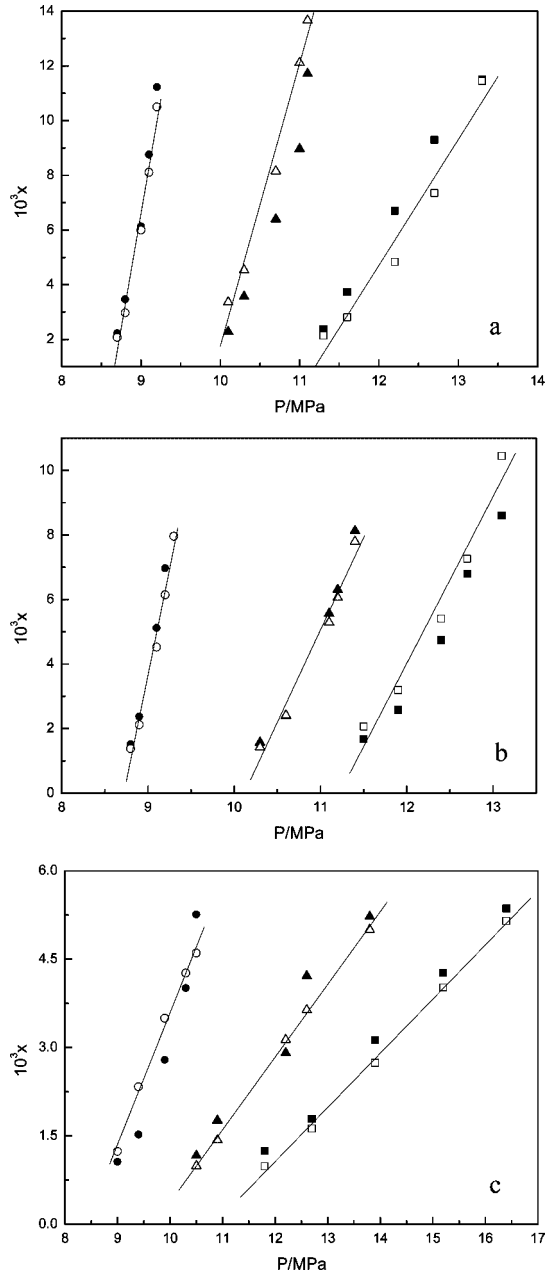
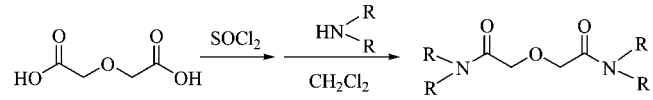


Figure 1. Comparison of solubility experiment and calculated value for compounds **1** to **3** in supercritical CO_2 at: ●,○, 313 K; ▲,△, 323 K; and ■,□, 333 K. (a) 2,2′-Oxybis(*N*,*N*-diethylacetamide) (compound **1**). (b) 2,2′-Oxybis(*N*,*N*-dibutylacetamide) (compound **2**). (c) 2,2′-Oxybis(*N*,*N*-dihexylacetamide) (compound **3**). ●,▲,■, exptl; ○,△,□, calcd. Lines represent correlation by eq 1.

Compounds 2: 2,2′-Oxybis(N,N-dibutylacetamide). Yield: 78%. IR (KBr) $\upsilon_{N-C=O}$: 1648.5 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 4.30 (s, 4H, $CH_2C{=}O$), 3.174−3.331 (t, J = 8, 8H, CH_2-N), 1.26−1.33 (m, 8H, CH_2), 1.48−1.55 (m, 8H, CH_2), 0.90−0.95 (t, J = 4.4, 12H, CH_3). ^{13}C NMR ($CDCl_3$): δ = 168.28, 68.94, 46.50, 30.85, 20.01, 13.60. Elemental Anal.: $C_{20}H_{40}N_2O_3$. Found: C, 67.34; H, 11.33; N, 7.90; O, 13.46 %. Required: C, 67.37; H, 11.31; N, 7.86; O, 13.46 %.

Compounds 3: 2,2′-Oxybis(N,N-dihexylacetamide). Yield: 70%. IR (KBr) $\upsilon_{N-C=O}$: 1644.7 cm^{-1}. ^1H NMR ($CDCl_3$): 4.30 (s, 4H, $CH_2C{=}O$), 3.16−3.31 (t, J = 7.6, 8H, CH_2-N), 1.52−1.53 (m, 8H, CH_2), 1.29 (m, 24H, CH_2), 0.86−0.90 (t, J = 6.8, 12H, CH_3). ^{13}C NMR ($CDCl_3$): δ = 168.39, 69.04, 46.86, 31.42−31.49, 28.83, 26.50−26.58, 22.46, 13.89. Elemental Anal: $C_{28}H_{56}N_2O_3$. Found: C, 71.75; H, 12.03; N, 5.61; O, 10.31 %. Required: C, 71.74; H, 12.04; N, 5.98; O, 10.24 %.

Scheme 1. Synthesis of CO_2-Philic Compounds 1 to 3



Compounds 1-3

Compounds	R
1	CH_2CH_3
2	$CH_2CH_2CH_2CH_3$
3	$CH_2CH_2CH_2CH_2CH_2CH_3$

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.[6,7] A suitable amount of solute was charged 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. Carbon dioxide was poured and heated to the experimental temperature. The fluid was stirred at a fixed pressure to obtain almost an equilibrium state. Stirring was stopped for observation. The pressure was increased gradually (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 dissolution pressure and temperature were recorded to obtain the density of CO_2 in terms of IUPAC international thermodynamic tables.[8−10] The uncertainty of the dissolution pressure and temperature was ± 0.5 MPa and ± 0.1 °C, respectively.[11−13]

Results and Discussion

The solubilities of 2,2′-oxybis(*N*,*N*-diethylacetamide), 2,2′-oxybis(*N*,*N*-dibutylacetamide), and 2,2′-oxybis(*N*,*N*-dihexylacetamide) in supercritical CO_2 were studied at different conditions of pressures (8.2 MPa∼16.4 MPa) and temperatures (313 K, 323 K, and 333 K). The resulting solubilities in terms of mole fraction, x, of the solute were shown in Table 1. Each reported data point was the average of at least three replicate samples. The

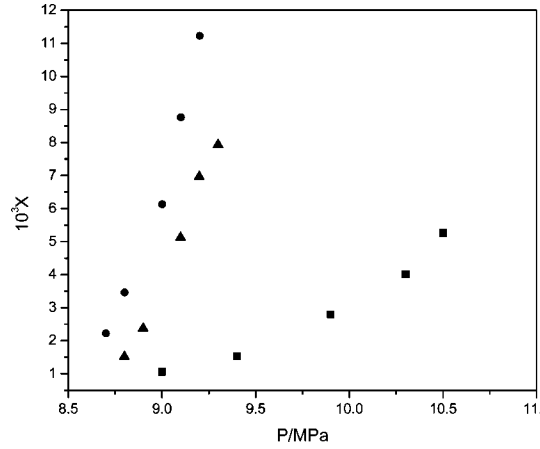


Figure 2. Solubility comparison of compounds **1** to **3** in supercritical CO_2 at 313 K: ●, 2,2′-oxybis(*N*,*N*-diethylacetamide) (compound **1**); ▲, 2,2′-oxybis(*N*,*N*-dibutylacetamide) (compound **2**); ■, 2,2′-oxybis(*N*,*N*-dihexylacetamide) (compound **3**).

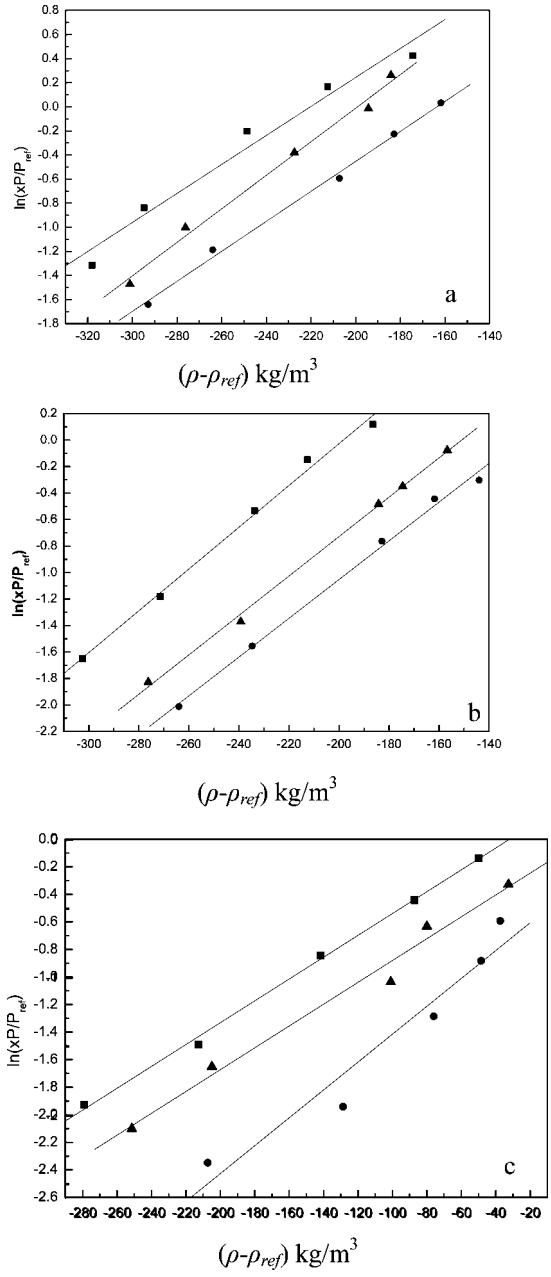


Figure 3. Plots of $\ln(xP/P_{ref})$ vs $(\rho - \rho_{ref})$/kg·m^{-3} for compounds at various temperatures. (a) 2,2′-Oxybis(*N*,*N*-diethylacetamide) (compound **1**). (b) 2,2′-Oxybis(*N*,*N*-dibutylacetamide) (compound **2**). (c) 2,2′-Oxybis(*N*,*N*-dihexylacetamide) (compound **3**). ●, 313 K; ▲, 323 K; ■, 333 K.

mole fractions of the solutes were reproducible within ± 5 %. As shown in Figure 1 and Figure 2, the solubilities of all three compounds increased with the increase of pressure at the same temperature, and at the same pressure, the solubilities decreased with the increase of temperature and molecular weight.

The experimental solubility data for the three compounds **1** to **3** were correlated using the following equation[14−17]

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

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 A, C, a, and b were constants. The first step was plots of $\ln(xP/P_{ref})$ versus density for compounds (Figure 3) and fitting the plots to a straight line by least-squares regression to obtain the A and C parameters. The values of C, obtained from the

Table 1. Solubility at Temperature *T*, Density ρ, and Mole Fraction *x* for Compounds 1 to 3

compound **1**				
P/MPa	ρ/kg·m^{-3}	10^3x	10^3x_{calcd}	AAD/%
		T = 313 K		
8.7	407.11	2.23	2.07	6.98
8.8	436.05	3.46	2.97	14.38
9.0	492.75	6.13	5.99	2.23
9.1	517.19	8.76	8.11	7.47
9.2	538.22	11.23	10.50	6.49
		T = 323 K		
10.1	398.91	2.27	3.36	47.90
10.3	423.74	3.56	4.53	27.04
10.7	472.58	6.39	8.15	27.46
11.0	505.69	8.96	12.11	35.16
11.1	515.81	11.71	13.66	16.65
		T = 333 K		
11.3	381.93	2.37	2.14	9.84
11.6	405.21	3.73	2.81	24.67
12.2	451.44	6.69	4.83	27.87
12.7	487.42	9.30	7.35	20.94
13.3	525.64	11.49	11.45	0.38
compound **2**				
P/MPa	ρ/kg·m^{-3}	10^3x	10^3x_{calcd}	AAD/%
		T = 313 K		
8.8	436.05	1.52	1.37	9.52
8.9	465.37	2.37	2.12	10.81
9.1	517.19	5.12	4.52	11.68
9.2	538.22	6.97	6.15	11.85
9.3	556.08	7.94	7.96	0.28
		T = 323 K		
10.3	423.74	1.56	1.42	9.20
10.6	460.74	2.40	2.41	0.63
11.1	515.81	5.56	5.29	4.98
11.2	525.44	6.30	6.06	3.85
11.4	543.31	8.12	7.80	4.06
		T = 333 K		
11.5	397.42	1.67	2.06	23.73
11.9	428.55	2.58	3.19	23.77
12.4	466.23	4.73	5.40	14.12
12.7	487.42	6.79	7.26	6.94
13.1	513.54	8.60	10.45	21.52
compound **3**				
P/MPa	ρ/kg·m^{-3}	10^3x	10^3x_{calcd}	AAD/%
		T = 313 K		
9.0	492.75	1.06	1.24	16.39
9.4	571.33	1.52	2.33	53.06
9.9	624.05	2.79	3.50	25.27
10.3	651.49	4.01	4.26	6.27
10.5	662.60	5.26	4.60	12.45
		T = 323 K		
10.5	448.59	1.17	0.99	15.09
10.9	495.10	1.76	1.43	18.99
12.2	599.03	2.91	3.13	7.66
12.6	620.03	4.22	3.64	13.72
13.8	667.36	5.22	5.00	4.21
		T = 333 K		
11.8	420.80	1.24	0.98	20.99
12.7	487.42	1.79	1.62	9.17
13.9	558.17	3.12	2.74	12.33
15.2	612.88	4.26	4.02	5.77
16.4	650.25	5.36	5.15	3.96

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

compounds	*a*	*b*/K	$C/m^3 \cdot kg^{-1}$
2,2′-oxybis(*N*,*N*-diethylacetamide)	12.58336	−3258.49	0.012807
2,2′-oxybis(*N*,*N*-dibutylacetamide)	22.61084	−6518.76	0.015079
2,2′-oxybis(*N*,*N*-dihexylacetamide)	10.63849	−3458.75	0.008657

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* against 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 are also listed 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

$$\mathrm{AARD} = 1/n\Sigma|(x_{i,\mathrm{calcd}} - x_{i,\mathrm{exptl}})/x_{i,\mathrm{exptl}}| \cdot 100\ \% \qquad (3)$$

where *n* was the number of experimental points and $x_{i,\mathrm{calcd}}$ and $x_{i,\mathrm{exptl}}$ were the calculated and experimental data ($kg \cdot m^{-3}$), respectively. The values of AARD were in the range of (4.54 to 30.84) %.

Conclusion

A series of CO_2-philic compounds were designed and synthesized via a simple procedure with good yield. The solubilities of compounds were tested in SC-CO_2. The solubilities of compounds increased with increasing pressure (at constant *T*) and decreased with increasing temperature, molecular weight (at constant *P*) over the pressure range from (8.2∼16.4) MPa, and at temperatures ranging from (313 to 333) K in SC-CO_2. The measured data were correlated with the semiempirical model, and good agreement was obtained 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.

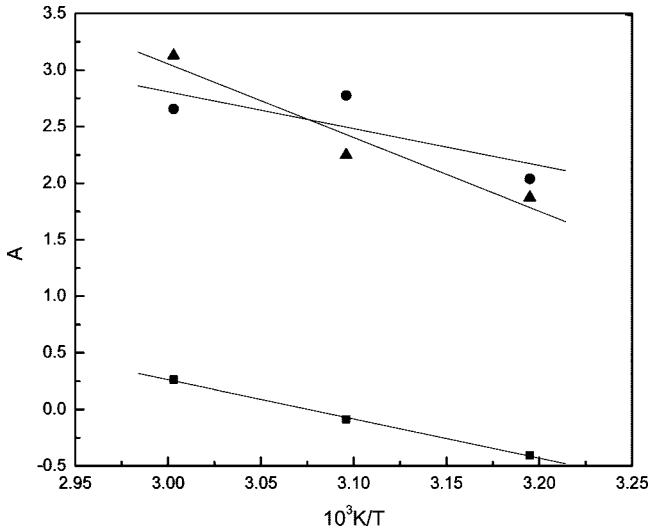


Figure 4. Plots of *A* vs 1/*T* for compounds **1** to **3**: ●, 2,2′-oxybis(*N*,*N*-diethylacetamide) (compound **1**); ▲, 2,2′-oxybis(*N*,*N*-dibutylacetamide) (compound **2**); ■, 2,2′-oxybis(*N*,*N*-dihexylacetamide) (compound **3**).

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