JOURNAL OF CHEMICAL & ENGINEERING DATA

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High Solubility and Partial Molar Volume of 2,2′-Oxybis(*N*,*N*-bis(2-methoxyethyl)acetamide) in Supercritical Carbon Dioxide

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ABSTRACT: 2,2′-Oxybis(*N*,*N*-bis(2-methoxyethyl)acetamide) was synthesized and confirmed by IR, NMR, and elemental analysis. The solubility of this compound was measured at temperatures ranging from (313 to 333) K and pressures from (9.2 to 15.2) MPa in supercritical carbon dioxide. The synthesized compound showed high solubility in supercritical CO_2 at easily accessible temperatures and pressures (e.g., 1.84×10^{-3} mol·L^{-1} at 9.2 MPa and 313 K). To confirm the tested solubility, the density-based correlations proposed by Bartle and Chrastil were investigated for the synthesized compound. The results showed good self-consistency of the data calculated using the Bartle semiempirical equation, which differed from the measured values by between (0.96 and 41.22) %. Better agreement with the experimental solubility data was obtained with the Chrastil model, for which average absolute relative deviations of less than 6 % were observed. The solubility data were also used to estimate the partial molar volume $\overline{V}_2$ for the compound in the supercritical phase using the theory developed by Kumar and Johnston.

INTRODUCTION

Supercritical fluids (SCFs) have extensive applications in the dye, food, and pharmaceutical industries, separation processes, and catalytic and enzymatic reactions.[1−3] Unlike many conventional organic solvents, supercritical carbon dioxide ($scCO_2$) is nontoxic, nonflammable, inexpensive, recyclable, and abundant in nature. $scCO_2$ has received increasing attention for many applications as a reactant in the field of chemistry and chemical industry because of its unique properties, such as liquidlike density and solvent power, gaslike transport properties, sensitivity of the properties to the critical temperature (T_c = 31.3 °C) and pressure (P_c = 7.38 MPa), and its environmentally benign nature.[4,5]

However, the nonpolarity of CO_2 requires high CO_2 pressures to dissolve even small amounts of polar, silicone-functionalized amphiphilic, organometallic, or high-molecular-mass compounds.[6−9] Although compounds having perfluoroalkyl polyether (PFPE) tails show high solubilities in $scCO_2$, these types of compounds are very expensive and toxic.[10] According to the literature, the use of nonfluorous and non-silic compounds with β-carbonyl groups as CO_2-philes has been proposed for economic and environmental reasons.[11] The high solubilities of these β-carbonyl systems in $scCO_2$ have been attributed to Lewis acid−Lewis base interactions between the electron-donating carbonyl group and the carbon of CO_2 that could promote CO_2 solubility. The high CO_2 solubilities of hydrocarbons containing acetamide groups have been attributed to the accessibility of the carbonyl functionality to form a weak complex with CO_2.[12,13]

In our former works, we found that 2,2′-oxybis(*N*,*N*-dibutylacetamide) compounds showed good solubility in $scCO_2$.[14] Because we knew that oxygen atoms enhanced the solubility of that compound in $scCO_2$, in present work we introduced oxygen atoms into the alkyl groups of 2,2′-oxybis(*N*,*N*-dibutylacetamide) to obtain the new CO_2-philic compound 2,2′-oxybis(*N*,*N*-bis(2-methoxyethyl)acetamide) and investigated its solubility in $scCO_2$. The solubilities of the new compound in $scCO_2$ over the pressure range from (9.2 to 15.2) MPa at temperatures ranging from (313 to 333) K were determined, and the experimental results were correlated using the density-based correlation models proposed by Bartle and Chrastil. Furthermore, the solubility data were also employed to estimate the partial molar volume of the compound in $scCO_2$ according to the theory developed by Kumar and Johnston.

EXPERIMENTAL SECTION

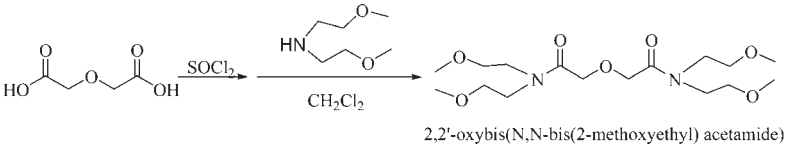
Chemicals and Apparatus. Diglycolic acid (mass fraction w = 0.98) and bis(2-methoxyethyl)amine (w = 0.99) were purchased from Fluka Chemical Co. and used as received without further purification. High-purity CO_2 (w = 0.9999) was obtained from Wuhan Steel Co. and used as the fluid.

A JASCO PU-CO_2 CO_2 delivery pump was used to cool and deliver CO_2 fluid, and a JASCO BP-1580-81 back-pressure regulator was used to keep the pressure in the (0−30.0) MPa range. The temperature was controlled using a temperature controller jacket with an accuracy of ± 0.01 K. IR spectra were measured on a PerkinElmer 2000 FT-IR spectrometer. NMR experiments were performed on a JEOL Al-600 MHz instrument

Special Issue: John M. Prausnitz Festschrift

Received: October 26, 2010
Accepted: March 5, 2011
Published: March 16, 2011

Scheme 1. Synthesis of 2,2′-Oxybis(*N*,*N*-bis(2-methoxyethyl)acetamide)



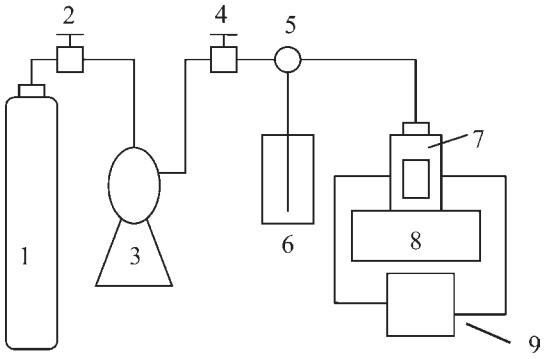


Figure 1. Schematic diagram of the experimental apparatus for solubility tests in supercritical CO_2. 1, CO_2; 2 and 4, two-way valves; 3, JASCO PU-CO_2 CO_2 delivery pump; 5, three-way valve; 6, JASCO BP-1580-81 back-pressure regulator; 7, view cell with two sapphire windows and a water jacket; 8, magnetic stirrer; 9, water circulator for temperature control.

using TMS as an internal standard. Elemental analysis was performed using a PE 2400 series II CHNS/O elemental analyzer.

Synthesis of 2,2′-Oxybis(*N*,*N*-bis(2-methoxyethyl) acetamide). The target compound 2,2′-oxybis(*N*,*N*-bis(2-methoxyethyl)acetamide) was synthesized according to the method shown in Scheme 1. Diglycolic acid (2.20 g, 0.016 mol) was dissolved in $SOCl_2$ (40 mL, 0.55 mol) and refluxed for 8 h under nitrogen protection. After the reaction mixture was cooled to room temperature, the excess $SOCl_2$ was distilled under reduced pressure, and then a CH_2Cl_2 solution (20 mL) of bis(2-methoxyethyl)amine (4.8 mL, 0.033 mol) was added dropwise to the reaction system under nitrogen. The mixture was stirred at room temperature overnight. The reaction mixture was washed with aqueous HCl (0.05 mol·L^{-1}), saturated aqueous $NaHCO_3$, and twice with water, after which the organic phase was collected and dried over anhydrous Na_2SO_4. After filtration and evaporation under vacuum, the residue was purified by silica gel column chromatography with 1:3 petroleum ether/ethanol as the eluent to give a yellow oil (w = 0.995 by GC). Yield: 80%. IR (KBr) $\nu_{N-C=O}$: 1638.5 cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.378(s, 4H, $CH_2C{=}O$), 3.574−3.540 (t, J = 5.4 Hz, 8H, CH_2O), 3.488−3.533 (t, J = 5.4 Hz, 8H, CH_2N), 3.325 (s, 12H, CH_3). ^{13}C NMR ($CDCl_3$): δ 169.574, 70.822, 69.211, 58.685, 47.819. Anal. Calcd for $C_{16}H_{32}N_2O_7$: C, 52.73; H, 8.85; N, 7.69; O, 30.73. Found: C, 52.75; H, 8.86; N, 7.67; O, 30.72.

Procedure for Solubility Tests in Supercritical CO_2. Solubility tests in $scCO_2$ were carried out using a modification of the method reported by Aiba and Ohkawa.[15] A schematic diagram of the apparatus is shown in Figure 1. A suitable amount of compound and a magnetic stirring bar were placed into the cell (7.11 mL). The cell was then purged with CO_2 to remove the air and sealed. The system was heated to the desired temperature using a temperature circulating bath jacket, and the solution was allowed to equilibrate while being stirred. The pressure was increased gradually until the system became a homogeneous transparent single phase. When the pressure remained constant for a period of time (0.33 h), the pressure was recorded and defined as the dissolution pressure. Under each set of conditions, the experiment was repeated at least three times. The dissolution pressure and temperature were recorded and used to obtain the density of CO_2 from the NIST Web site.[16] The uncertainties in the dissolution pressure and temperature were ± 0.5 MPa and ± 0.1 °C, respectively.

Table 1. Experimental and Calculated Solubilities of 2,2′-Oxybis(*N*,*N*-bis(2-methoxyethyl)acetamide) at Temperatures T, Densities ρ, and Mole Fractions x in Supercritical CO_2 (the Condensed Phase Is Liquid)

P	ρ	10^3x		AARD
MPa	kg·m^{-3}	exptl	calcd	%
	T = 313 K			
9.2	538.22	1.84	1.52	17.27
9.7	606.4	3.27	2.81	14.19
10.3	651.49	4.57	4.1	10.24
11.2	693.38	5.72	5.67	0.96
12.4	730.15	6.8	7.32	7.78
	T = 323 K			
11.1	515.81	1.92	1.98	3.04
11.7	566.85	3.5	3.09	11.74
12.3	604.62	4.92	4.24	13.79
13	637.96	5.29	5.55	5.04
13.4	653.57	6.07	6.27	3.3
	T = 333 K			
12.8	494.19	2.01	2.83	41.22
13.8	553.12	3.59	4.66	30.06
14.2	572.52	4.5	5.47	21.55
14.5	585.74	5.08	6.1	20.03
15.2	612.88	6.47	7.57	17.01

RESULTS AND DISCUSSION

Solubility Results. Solubility data for 2,2′-oxybis(*N*,*N*-bis(2-methoxyethyl)acetamide) were measured at various pressures [(9.2 to 15.2) MPa] and temperatures [(313 to 333) K] in $scCO_2$, and the results are listed in Table 1. Each data point was obtained from an arithmetic average of several measurements (at least three times) at each pressure. The mole fractions of the solutes were reproducible within ± 3 %. As shown in Figure 2, the solubility of the compound increased with increasing

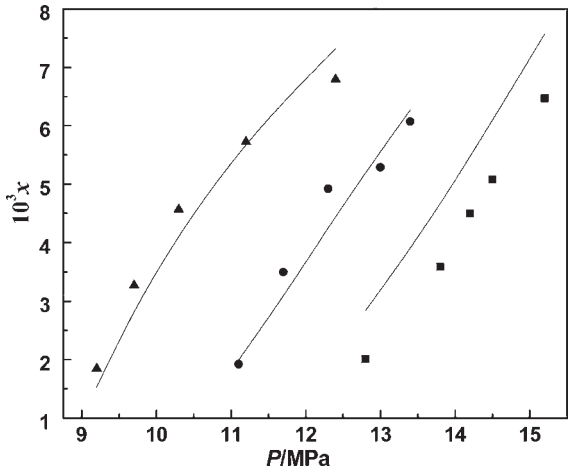


Figure 2. Comparison of experimental and calculated solubilities for 2,2′-oxybis(*N*,*N*-bis(2-methoxyethyl)acetamide) in supercritical CO_2, Experimental data: ▲, 313 K; ●, 323 K; ■, 333 K. Solid curves were calculated using Bartle's model (eq 1).

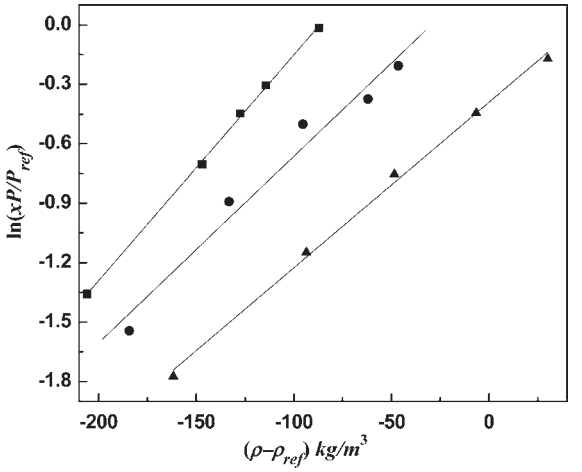


Figure 3. Plots of ln (xP/P_{ref}) vs $(\rho - \rho_{ref})$/kg·m^{-3} (based on the Bartle model, eq 1) for 2,2′-oxybis(*N*,*N*-bis(2-methoxyethyl)acetamide) at various temperatures: ▲, 313 K; ●, 323 K; ■, 333 K. Definitions: *x*, mole fraction of the compound; *P*, CO_2 pressure; P_{ref}, 0.1 MPa; ρ, density of pure CO_2; ρ_{ref}, 700 kg·m^{-3}.

pressure at a given temperature. At a given pressure, the solubility decreased with increasing temperature. The main reason for this behavior is that the solvent power of CO_2 varies as the CO_2 density changes with pressure or temperature.

Correlation of Experimental Solubility Data Using Density-Based Models. In order to correlate the solubility data, the density-based correlations proposed by Bartle and Chrastil were investigated for the compound. The literature has already provided many examples in which these models were investigated.[17−20]

Bartle Model. Bartle and co-workers[20] proposed a simple density-based semiempirical model to correlate the solubilities of solids in SCFs. The experimental solubility data for the compound were correlated using the following equation:

$$\ln\left(\frac{xP}{P_{ref}}\right) = A + C(\rho - \rho_{ref}) \qquad (1)$$

Table 2. Results of the Correlation of the Solubility Data for 2,2′-Oxybis(*N*,*N*-bis(2-methoxyethyl)acetamide) Using the Bartle Model[a]

		b	*C*	$\Delta_{sub}H$	AARD
n	*a*	K	m^3·kg^{-1}	kJ·mol^{-1}	%
15	22.5375	−7180.74	0.00973	59.7	14.48

[a] Definitions: *n*, number of data points used in the correlation; *a*, *b*, and *C*, parameters in the Bartle model; AARD, average absolute relative deviation; $\Delta_{sub}H$, enthalpy of sublimation of the solid solute.

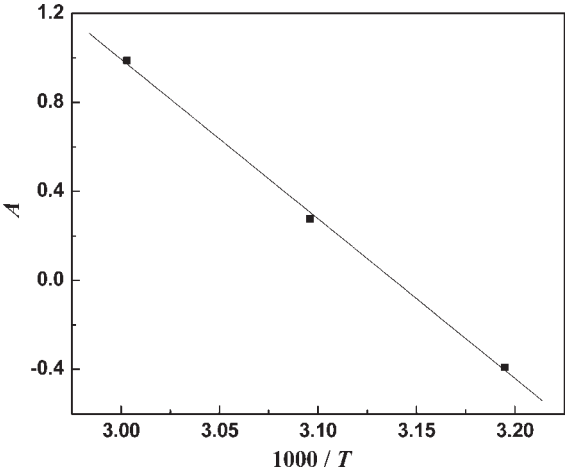


Figure 4. Plot of *A* vs 1000/*T* for 2,2′-oxybis(*N*,*N*-bis(2-methoxyethyl)acetamide).

in which

$$A = a + \frac{b}{T} \qquad (2)$$

where *x* is the mole fraction of the solute, *P* is the pressure, P_{ref} = 0.1 MPa, ρ is the density of pure CO_2 at the experimental temperature and pressure, ρ_{ref} = 700 kg·m^{-3}, and *A*, *C*, *a*, and *b* are constants. In the initial stage, values of $\ln(xP/P_{ref})$ were plotted against $(\rho - \rho_{ref})$ (Figure 3), and the values were fitted to straight lines 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 (Table 2). With *C* held at its average value, the experimental solubility data were then used to evaluate the *A* values at various temperatures. The plot of *A* versus 1/*T* was 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 the compound are shown in Table 2. The values of *a*, *b*, and *C* were used along with eqs 1 and eq 2 to predict the solubility; the calculated data and the experimental data are compared in Figure 2. In the Bartle model, the parameter *b* is related to the enthalpy of sublimation of the solute, $\Delta_{sub}H$, by the expression $\Delta_{sub}H = -Rb$, where *R* is the gas constant.

Finally, the average absolute relative deviation (AARD) was used to test the correlation results. It was calculated according to eq 3:

$$\text{AARD} = \frac{1}{n}\sum_i \left|\frac{x_{i,\,\text{calcd}} - x_{i,\,\text{exptl}}}{x_{i,\,\text{exptl}}}\right| \cdot 100\ \% \qquad (3)$$

dx.doi.org/10.1021/je101104m |*J. Chem. Eng. Data* 2011, 56, 1191–1196

Table 3. Results of the Correlation of the Solubility Data for 2,2′-Oxybis(*N*,*N*-bis(2-methoxyethyl)acetamide) Using the Chrastil Model[a]

		α			ΔH	AARD
n	*k*	K	*β*	σ^2	kJ·mol^{-1}	%
15	5.6865	−3178.6	−23.515	0.98	26.43	5.48

[a] Definitions: *n*, number of data points used in the correlation; k, α, and *β*, parameters of Chrastil model; AARD, average absolute relative deviation; σ^2, regression coefficient; ΔH, sum of the enthalpies of vaporization and solvation of the solute.

where *n* is the number of experimental points and $x_{i,\mathrm{calcd}}$ and $x_{i,\mathrm{exptl}}$ are the calculated and experimental data values, respectively. The AARD values were in the range (0.96 to 41.22) % for the Bartle model.

Chrastil Model. The model proposed by Chrastil relates the solubility of the solute to the density of the supercritical solvent on the assumption that one molecule of solute (A) associates with *k* molecules of the solvent (B) to form a solvate complex AB_k in equilibrium with the system.[21−24] For this model, the experimental solubility data for the compound were correlated according to eq 4:

$$\ln S = k \ln \rho + \frac{\alpha}{T} + \beta \tag{4}$$

in which ρ (kg·m^{-3}) is the density of pure $scCO_2$, *S* (kg·m^{-3}) is the solubility of the solid in the supercritical phase, *T* (K) is the temperature, and *k*, α, and *β* are the adjustable parameters of the model. The solubility, *S*, is calculated by means of eq 5:

$$S = \frac{\rho M_2 x}{M_1(1-x)} \tag{5}$$

where *x* is the mole fraction of the solute and M_1 and M_2 are the molecular weights of CO_2 and the solute, respectively. In the Chrastil model, the constant *k* is the association number, α is a constant defined as $\alpha = -\Delta H/R$, where ΔH is the sum of the enthalpies of vaporization and solvation of the solute, and *β* depends on the molecular weights of the solute and solvent. This model suggests that plots of ln *S* versus ln ρ at various temperatures should be straight lines whose slopes are identical and equal to *k*. The parameters *k*, α, and *β* are obtained performing a multiple linear regression on the experimental solubility data.

The values of the calculated constants for the 2,2′-oxybis(*N*,*N*-bis(2-methoxyethyl)acetamide) + $scCO_2$ system are presented in Table 3. The quality of the correlation is expressed in terms of σ^2 and the AARD between experimental and calculated values of *S*. The consistency of the model with the measured data can be seen from Figure 5 and the AARD values at different temperatures, which are less than 6 %. The results exhibited the good agreement between the tested and calculated data.

Estimation of the Partial Molar Volumes of the Solute. The partial molar volumes of the solutes are very important parameters for the evaluation of the solubilities of solutes in SCF. Although the compound reported compound is new and corresponding data for partial molar volumes are not available in the literature, it will be useful and interesting for other scientists to refer to such data in the future. Therefore, the partial molar volumes of the new compound were calculated as follows.

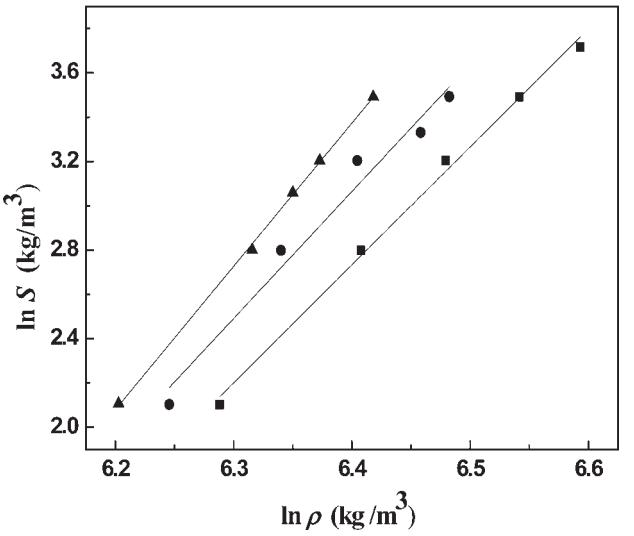


Figure 5. Plots of ln *S* vs ln ρ (based on the Chrastil model, eq 4) for 2,2′-oxybis(*N*,*N*-bis(2-methoxyethyl)acetamide): ■, 313 K; ●, 323 K ; ▲, 333 K.

According to Kumar and Johnston,[18] the dependence of the solubility of the solute (expressed as its mole fraction, *x*) on its partial molar volume $\overline{V}_2$ in the vicinity of the critical density ρ_c of the SCF can be expressed by the following equation:

$$\ln x = -C_2 + \ln\left(\frac{P_2^s}{\rho_c RT}\right) + \frac{PV_2^s}{RT} - \left(\frac{\overline{V}_2}{RT\kappa_T}\right)_{\rho_r=1} \ln \rho_r \tag{6}$$

where P_2^s and V_2^s are the vapor pressure and molar volume of the solid solute, respectively, $\kappa_T = (1/\rho)(\partial\rho/\partial P)_{T,x}$ is the isothermal compressibility, $\rho_r = \rho/\rho_c$ is the reduced density of the phase, and *T* and *P* are the operating temperature and pressure, respectively.

The partial molar volume of the solute in the SCF phase, $\overline{V}_2$, is much larger than the molar volume of the solute, V_2^s. Thus, the third term in eq 6 was considered to be a constant in the region of interest, allowing eq 6 to be simplified to the following:

$$\ln x = C_0 - \left(\frac{\overline{V}_2}{RT\kappa_T}\right)_{\rho_r=1} \ln \rho_r \tag{7}$$

Equation 7 implies that in the approximate reduced density interval $0.5 \le \rho_r \le 2.0$, the logarithm of the mole fraction of the solubility of the solute in an SCF varies linearly with the logarithm of the reduced density of the SCF phase. The slope of this line is the ratio of the partial molar volume of the solute in the SCF phase, $\overline{V}_2$, to *RT* times the isothermal compressibility of the fluid phase, κ_T. This ratio can be considered as independent of ρ_r, so knowledge of the value of κ_T and the slope of the plot of ln *x* versus ln ρ_r at a given temperature permits the estimation of $\overline{V}_2$ under these conditions. As demonstrated in Figure 6, the investigated system displayed linear plots of ln *x* versus ln ρ_r. This linearity was not observed when values of ln *x* were plotted versus ρ_r. The slopes of the ln *x* versus ln ρ_r lines were computed by linear least-squares fits for the 2,2′-oxybis(*N*,*N*-bis(2-methoxyethyl)acetamide) + $scCO_2$ system at different temperatures. The quality of the linear correlations are expressed in terms of σ^2. The partial molar volumes were then deduced from the determined slopes and the values of κ_T for CO_2 under the appropriate *P*−*T* conditions.

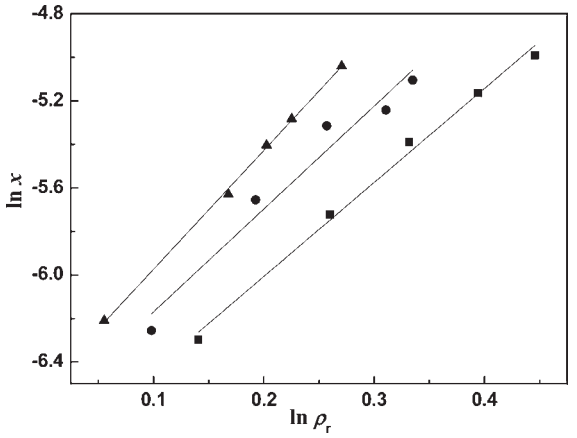


Figure 6. Plots of ln x vs ln ρ_r (based on eq 7) for 2,2′-oxybis(*N*,*N*-bis(2-methoxyethyl)acetamide): ■, 313 K; ●, 323 K ; ▲, 333 K.

Table 4. Slopes Computed Using Equation 7 and the Corresponding Partial Molar Volumes $\overline{V}_2$ of the Solute for the 2,2′-Oxybis(*N*,*N*-bis(2-methoxyethyl)acetamide) + scCO$_2$ System at Different Temperatures

T/K	slope at $\rho_r = 1$	σ^2	$\overline{V}_2$/cm^3·mol^{-1}
313	4.32043	0.92379	−6448.50
323	4.72949	0.98296	−3066.67
333	5.46199	0.9088	−2247.35

The results obtained are recapitulated in Table 4. As shown in Table 4, the partial molar volume for the solute decreases as the temperature increases. The partial molar volumes $\overline{V}_2$ of 2,2′-oxybis(*N*,*N*-bis(2-methoxyethyl)acetamide) in the vicinity of the critical point of the solvent, which are difficult to measure experimentally, were estimated using the theory developed by Kumar and Johnston. As reported by these authors,[25] the data calculated for naphthalene + CO_2 and naphthalene + ethylene systems according to this theory were in good agreement with experimental data. However, the calculated results in this work necessitate a confrontation with experimental measurements by other scientists.

CONCLUSION

In this work, new CO_2-philic compound 2,2′-oxybis(*N*,*N*-bis(2-methoxyethyl)acetamide) was designed and synthesized via simple procedures with high yield. The solubilities of the compound in scCO$_2$ were determined. The compound showed high solubility in scCO$_2$ at easily accessible temperatures and pressures. The measured data were correlated with two density-based models (the Bartle and Chrastil models), and the results showed good agreement between the correlated results and the experimental data. Better agreement with experimental solubility data was obtained with Chrastil model, for which AARD values of less than 6% were observed. The solubility data were also used to estimate the partial molar volume $\overline{V}_2$ for the compound in the supercritical phase using the theory developed by Kumar and Johnston. This work might provide basic information for designing and synthesizing new low-cost, non-fluorous CO_2-philic compounds.

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ACKNOWLEDGMENT

We are grateful to the National Natural Science Foundation of China (51073175). H.-J.Y. also appreciates the finacial support of the Beijing National Laboratory for Molecular Sciences (BNLMS) and the valuable help of Prof. Buxing Han. Z.Y. and J.T. thank the Innovative Foundation Project for Students of South-Central University for Nationalities (KYCX090210Z) for financial support.

REFERENCES

(1) Porto, C. D.; Decorti, D.; Kikic, I. Flavour Compounds of *Lavandula angustifolia* L. To Use in Food Manufacturing: Comparison of Three Different Extraction Methods. *Food Chem.* **2009**, *112*, 1072–1078.

(2) Yang, H.-J.; Tian, J.; Kim, H. New Highly CO_2-Philic Diglycolic Acid Esters: Synthesis and Solubility in Supercritical Carbon Dioxide. *J. Chem. Eng. Data* **2010**, *55*, 4130–4139.

(3) Liu, Z.; Han, B. Synthesis of Carbon Nanotube Composites Using Supercritical Fluids and Their Potential Applications. *Adv. Mater.* **2009**, *21*, 825–829.

(4) Du, Y.; Cai, F.; Kong, D. L.; He, L. N. Organic Solvent-Free Process for the Synthesis of Propylene Carbonate from Supercritical Carbon Dioxide and Propylene Oxide Catalyzed by Insoluble Ion Exchange Resins. *Green Chem.* **2005**, *7*, 518–523.

(5) Wang, W.; Yang, H.-J.; Hu, J.; Guo, C.-Y. Solubilities of Diglycolic Acid Esters at Temperatures Ranging from (343 to 363) K in Supercritical Carbon Dioxide. *J. Chem. Eng. Data* **2010**, *55*, 694–697.

(6) Zhang, Y.; Cangul, B.; Garrabos, Y.; Erkey, C. Thermodynamics and kinetics of adsorption of bis(2,2,6,6-tetramethyl-3,5-heptanedionato)(1,5-cyclooctadiene)ruthenium(II) on carbon aerogel from supercritical CO_2 solution. *J. Supercrit. Fluids* **2008**, *44*, 71–77.

(7) Yang, H.-J.; Kim, H.; Guo, C.-Y. Metal Ion Extraction with Bipyridine Derivatives as Chelating Ligands in Supercritical Carbon Dioxide. *Clean* **2010**, *38*, 159–166.

(8) Chang, F.; Kim, H.; Joo, B.; Park, K.; Kim, H. Novel CO_2-Soluble Pyridine Derivatives and the Extraction of Heavy Metals into SC-CO_2. *J. Supercrit. Fluids* **2008**, *45*, 43–50.

(9) Wang, W.; Yang, H.-J.; Hu, J.; Guo, C.-Y. Extraction of Metal Ions with Non-fluorous Bipyridine Derivatives as Chelating Ligands in Supercritical Carbon Dioxide. *J. Supercrit. Fluids* **2009**, *51*, 181–187.

(10) Eastoe, J.; Dupont, A.; Steytler, D. C. Fluorinated Surfactants in Supercritical CO_2. *Curr. Opin. Colloid Interface Sci.* **2003**, *8*, 267–273.

(11) Sarbu, T.; Styranec, T.; Beckman, E. J. Non-fluorous Polymers with Very High Solubility in Supercritical CO_2 Down to Low Pressures. *Nature* **2000**, *405*, 165–168.

(12) Beckman, E. J. A Challenge for Green Chemistry: Designing Molecules That Readily Dissolve in Carbon Dioxide. *Chem. Commun.* **2004**, 1885–1888.

(13) Xie, Y.; Yang, H. J.; Wang, W.; Chen, R. Solubilities of Diglycolic Acid Esters in Supercritical Carbon Dioxide. *J. Chem. Eng. Data* **2009**, *54*, 102–107.

(14) Liu, J. F.; Yang, H. J.; Wang, W.; Li, Z. Solubilities of Amide Compounds in Supercritical Carbon Dioxide. *J. Chem. Eng. Data* **2008**, *53*, 2189–2192.

(15) Kawakami, T.; Saito, N.; Aiba, K.; Ohkawa, T. Highly-Soluble Fluorocarbon Surfactant in Supercritical Carbon Dioxide: Effect of Counter Cation on Solubility. *Chem. Lett.* **2000**, *29*, 402–403.

(16) http://www.nist.gov/srd/fluids.htm (accessed May 20, 2010).
(17) Miller, D. J.; Hawthrone, S. B.; Clifford, A. A.; Zhu, S. Solubility of Polycyclic Aromatic Hydrocarbons in Supercritical Carbon Dioxide from 313 K to 523 K and Pressures from 100 bar to 450 bar. *J. Chem. Eng. Data* **1996**, *41*, 779–786.
(18) Huang, Z.; Yang, X.-W.; Sun, G.-B.; Song, S.-W.; Kawi, S. The Solubilities of Xanthone and Xanthene in Supercritical Carbon Dioxide. Structure Effect. *J. Supercrit. Fluids* **2005**, *36*, 91–97.
(19) Bai, Y.; Yang, H. J.; Quan, C.; Guo, C. Y. Solubilities of 2,2′-Bipyridine and 4,4′-Dimethyl-2,2′-bipyridine in Supercritical Carbon Dioxide. *J. Chem. Eng. Data* **2007**, *52*, 2074–2076.
(20) Bartle, K. D.; Clifford, A. A.; Jafar, S. A.; Shilstone, G. F. Solubilities of Solids and Liquids of Low Volatility in Supercritical Carbon Dioxide. *J. Phys. Chem. Ref. Data* **1991**, *20*, 713–756.
(21) Coimbra, P.; Fernandes, D.; Ferreira, P.; Gil, M. H.; Sousa, H. C. Solubility of Irgacure® 2959 Photoinitiator in Supercritical Carbon Dioxide: Experimental Determination and Correlation. *J. Supercrit. Fluids* **2008**, *45*, 272–281.
(22) Li, W.; Jin, J.; Tian, G.; Zhang, Z. Single-Component and Mixture Solubilities of Ethyl *p*-Hydroxybenzoate and Ethyl *p*-Aminobenzoate in Supercritical CO_2. *Fluid Phase Equilib.* **2008**, *264*, 93–98.
(23) Khimeche, K.; Alessi, P.; Kikic, I.; Dahmani, A. Solubility of Diamines in Supercritical Carbon Dioxide: Experimental Determination and Correlation. *J. Supercrit. Fluids* **2007**, *41*, 10–19.
(24) Chrastil, J. Solubility of Solids and Liquids in Supercritical Gases. *J. Phys. Chem.* **1982**, *86*, 3016–3021.
(25) Kumar, S. K.; Johnston, K. P. Modeling the Solubility of Solids in Supercritical Fluids with Density as the Independent Variable. *J. Supercrit. Fluids* **1988**, *1*, 15–22.