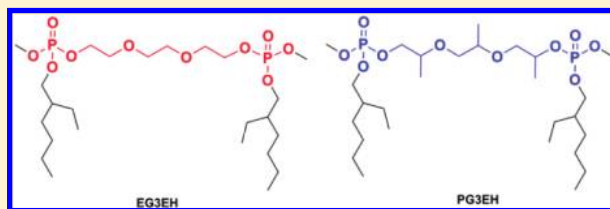


Solubilities of the Triethylene Glycol and Tripropylene Glycol Derivatives Terminated with Phosphoryl Groups in Supercritical CO₂

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ABSTRACT: The triethylene glycol and tripropylene glycol derivatives terminated with the CO₂-philic phosphoryl groups, named 2-(2-(2-((2-ethylhexoxy(methoxy)phosphoryl)oxy)ethoxy)ethoxy)ethyl 2-ethylhexyl methyl phosphate (EG3EH) and 2-(2-(2-((2-ethylhexoxy(methoxy)phosphoryl)oxy)propoxy)propoxy)propyl 2-ethylhexyl methyl phosphate (PG3EH), were synthesized and characterized. The solubilities of EG3EH and PG3EH in scCO₂ were determined by a static method at temperatures from (313 to 333) K and over a pressure range of (10 to 19) MPa. The values calculated by the Bartle semiempirical model exhibited good agreement with the experimental data.



INTRODUCTION

Supercritical CO₂ (scCO₂) has many advantageous properties over conventional solvents, such as high diffusivity, easy operation, recyclability, nontoxicity, low cost, and so forth. As a consequence, scCO₂ has been used as a promising alternative solvent in a variety of realms, for example, in the processing of pharmaceuticals,¹ development of advanced materials,² and decontamination of heavy metal ion pollution.^{3,4} However, high polar species are sparingly soluble in neat scCO₂, probably due to its nonpolarity and low dielectric constant (ca. 1.5), which, to a great extent, limits the scCO₂ technology for further application.^{5,6}

To address this problem, the use of CO₂-philic agents, that is, surfactants, chelating agents, and so forth, has become a general strategy to decrease the miscible pressures and increase the efficiency of scCO₂. Currently, the F-based species, for example, fluoroether and fluoroalkyl compounds, have proved to be the most CO₂ soluble and efficient.^{7–10} However, in view of the high cost and toxicity, the practical use of fluorinated agents in scCO₂ was restricted. Simultaneously, quantum calculations and phase behavior tests demonstrated that molecules bearing non-fluorinated carbonyl, ether, or ester groups are also able to enhance the efficiency of scCO₂.^{7,11–18}

Recently, the results of ab initio calculations demonstrated that the phosphoryl functional group showed stronger interactions with CO₂ than that of carbonyl or ether groups.¹⁹ The Lewis acid/Lewis base interaction energy between CO₂ and the P=O group was 15.1 kJ·mol⁻¹ for trimethylphosphate including zero-point energy, which was much larger than 12.1 kJ·mol⁻¹ for the CO₂-methylacetate complex. Therefore, we herein attempted to prepare new CO₂-philic agents as the potential chelating ligands by incorporation phosphoryl groups into oligo(ethylene glycol) (OEG) and oligo(propylene glycol) (OPG), respectively, resulting in 2-(2-(2-((2-ethylhexoxy(methoxy)phosphoryl)oxy)ethoxy)ethoxy)ethyl 2-ethylhexyl methyl phosphate (EG3EH) and 2-(2-(2-((2-ethylhexoxy(methoxy)phosphoryl)oxy)propoxy)propoxy)propyl 2-ethylhexyl methyl phosphate

(PG3EH), as shown in Figure 1. Moreover, in view of the shielding effect of branched alkyl chain to metal ions in metal

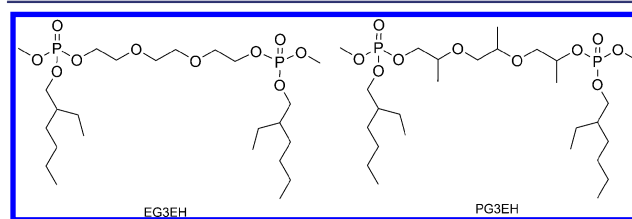


Figure 1. Structures and abbreviations of the new compounds.

chelate systems, 2-ethylhexyl groups were incorporated as the side tail, which may increase CO₂-philicity to metal chelates.⁴ A vacuum method was employed for the preparations, and their solubilities in scCO₂ were determined over the pressure range of (10 to 19) MPa and at temperatures of (313 to 333) K, which were also correlated by the Bartle semiempirical model.¹⁸

EXPERIMENTAL SECTION

Chemicals and Experimental Apparatus. Methanol ($w = 0.99$, mass fraction), 2-ethylhexanol ($w = 0.99$), triethylene glycol ($w = 0.99$), tripropylene glycol ($w = 0.99$), and phosphorus oxychloride (POCl₃) ($w = 0.99$) were purchased from Aladdin-Reagent Co., Ltd. (Shanghai, China). Acetone ($w = 0.98$) and dichloromethane ($w = 0.98$) were bought from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Methanol was treated with magnesium wires. Carbon dioxide ($w = 0.9999$, mass fraction) was commercially purchased from B.O.D. Company (Shanghai, China). Silica gel (300 to 400 mesh) was purchased from Qingdao Haiyang Chemical Group Co. (Qingdao, China). ¹H- and ¹³C NMR experiments were performed on Bruker

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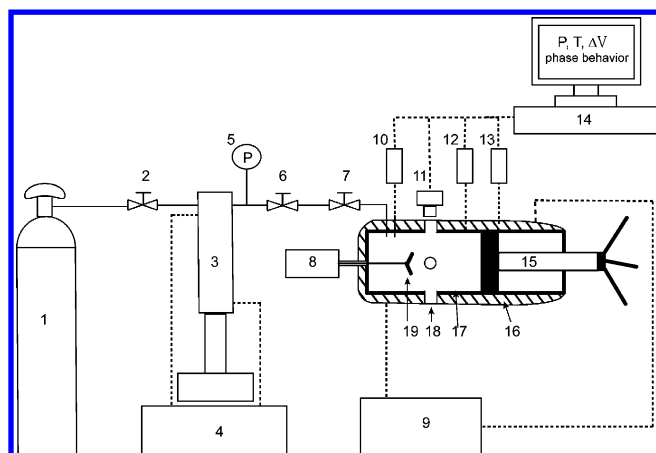


Figure 2. Schematic diagram of the high-pressure equilibria apparatus. 1, CO₂ cylinder; 2, 6, 7, stop valves; 3, manual metering pump; 4, low-temperature thermostat bath controller; 5, pressure gauge; 8, magnetic stirring motor; 9, oil bath pump and controller; 10, temperature sensor; 11, CCD camera; 12, pressure sensor; 13, volume sensor; 14, computer; 15, volume controller; 16, heating jacket; 17, equilibrium cell; 18, three sapphire windows; 19, stirrer.

AVANCE DMX 500 (Bruker, Billerica, MA, USA) using tetramethylsilane (TMS) as an internal standard and CDCl₃ as the solvent. Elemental analysis was conducted on Flash EA-1112 (Thermo Finnigan, Rodano, Italy). All high-resolution mass spectrometry was recorded on APCI-MS device where the detection was performed on an Agilent LC/MSD Trap SL mass spectrometer with an APCI interface (Agilent Technologies,

Stuttgart, Germany). The density was determined using a DMA 5000 oscillating U-tube densimeter (Anton Paar, $\pm 5 \cdot 10^{-5}$ g·mL⁻¹) at $298.150 \pm 5 \cdot 10^{-3}$ K.

The solubility measurement was performed on the SEPREX phase equilibria apparatus made in France, as shown in Figure 2. The internal variable volume of the stainless steel cell was (35.43 to 65.43) mL. The accuracy of internal volume was up to ± 0.01 mL. The temperature was detected by an inside temperature probe and precisely controlled by a circulation oil bath (Huber, Germany). The pressure was accurately adjusted by varying the internal volume through a piston, which was measured with the inside high-pressure transducer. The cell was equipped with three sapphire windows and a charge-coupled device (CCD) camera, by which the phase behaviors inside could be clearly observed either from the windows or from the computer display screen. The temperature, pressure, and internal volume could be displayed on the software interface.

General Procedure for the Synthesis. A modified vacuum method was employed.²⁰ A 250 mL three-neck round-bottom flask was equipped with one thermometer, one dropping funnel, and one condenser connected with a hydrogen chloride gas adsorption apparatus. After the system was cooled to 273 K with an ice bath, excess POCl₃ (16.863 g, 110 mmol) was added into the flask. Triethylene glycol (7.505 g, 50 mmol) or tripropylene glycol (9.610 g, 50 mmol) was then added dropwise to the reaction system over 2 h under vacuum with agitation. The mixture was stirred at 273 K under vacuum for 4 h. 2-Ethylhexanol (13.023 g, 100 mmol) was added dropwise under vacuum at 283 K over 2 h, and the reaction was over after 15 h under vacuum with agitation. Methanol (30 mL) was added to

Table 1. Solubility (Mole Fraction x) of EG3EH and PG3EH in scCO₂^a

T K	EG3EH					PG3EH				
	P MPa	ρ kg·m ⁻³	10^3x		ARD %	P MPa	ρ kg·m ⁻³	10^3x		ARD %
313	11.20 ± 0.01	687.61	2.15	2.21	2.62	10.12 ± 0.01	707.61	2.02	1.99	0.42
	11.45 ± 0.01	702.32	2.45	2.47	0.97	10.43 ± 0.01	687.56	2.35	2.34	0.58
	11.81 ± 0.01	713.80	2.70	2.69	0.11	10.71 ± 0.01	673.02	2.63	2.61	0.33
	12.26 ± 0.01	724.97	2.90	2.91	0.40	11.10 ± 0.01	658.91	2.92	2.90	1.62
	12.86 ± 0.01	741.14	3.21	3.27	2.01	11.61 ± 0.01	638.80	3.38	3.37	0.25
318	12.39 ± 0.01	675.05	2.15	2.14	0.85	11.33 ± 0.01	699.12	2.02	1.94	3.97
	12.86 ± 0.01	691.06	2.45	2.41	1.31	11.79 ± 0.01	678.44	2.35	2.34	0.22
	13.28 ± 0.01	703.31	2.70	2.65	1.69	12.13 ± 0.01	665.12	2.63	2.62	0.19
	13.76 ± 0.01	714.61	2.90	2.87	0.86	12.53 ± 0.01	650.51	2.92	2.89	0.91
	14.28 ± 0.01	728.23	3.21	3.18	0.83	13.15 ± 0.01	626.82	3.38	3.36	0.44
323	13.75 ± 0.01	665.70	2.15	2.13	0.56	12.63 ± 0.01	689.61	2.02	2.01	0.19
	14.26 ± 0.01	681.51	2.45	2.42	1.14	13.08 ± 0.01	669.33	2.35	2.35	0.34
	14.72 ± 0.01	694.02	2.70	2.67	1.28	13.43 ± 0.01	654.71	2.63	2.61	0.58
	15.25 ± 0.01	705.74	2.90	2.90	0.00	13.91 ± 0.01	641.30	2.92	2.91	0.28
	15.85 ± 0.01	718.99	3.21	3.19	0.50	14.55 ± 0.01	621.51	3.38	3.38	0.10
328	15.05 ± 0.01	656.46	2.15	2.16	0.60	13.85 ± 0.01	679.21	2.02	2.07	2.61
	15.50 ± 0.01	669.40	2.45	2.39	2.22	14.28 ± 0.01	659.72	2.35	2.36	0.65
	16.15 ± 0.01	686.04	2.70	2.72	0.86	14.74 ± 0.01	646.71	2.63	2.67	1.63
	16.55 ± 0.01	695.30	2.90	2.88	0.46	15.21 ± 0.01	630.80	2.92	2.93	0.75
	17.27 ± 0.01	710.43	3.21	3.20	0.18	15.87 ± 0.01	614.02	3.38	3.40	0.60
333	16.25 ± 0.01	646.02	2.15	2.18	1.22	14.96 ± 0.01	668.41	2.02	2.10	4.00
	16.80 ± 0.01	660.81	2.45	2.45	0.00	15.43 ± 0.01	649.02	2.35	2.39	1.92
	17.45 ± 0.01	676.41	2.70	2.76	2.34	15.92 ± 0.01	636.42	2.63	2.70	2.65
	17.80 ± 0.01	683.01	2.90	2.89	0.08	16.41 ± 0.01	620.81	2.92	2.96	0.08
	18.51 ± 0.01	697.51	3.21	3.23	0.65	17.11 ± 0.01	604.12	3.38	3.43	0.65

^a ρ is the density of scCO₂; ARD = $|x_{i,cal} - x_{i,exp}|/x_{i,exp} \cdot 100$ %.

the mixture at 313 K with violent agitation, and the reaction was continued for 3 h under vacuum. The residue was purified by silica gel column chromatography (acetone/dichloromethane as the eluent). The prepared EG3EH and PG3EH were characterized by ^1H NMR, ^{13}C NMR, APCI-MS, and elemental analysis. Results are shown as follows.

EG3EH: 2-(2-(2-((2-Ethylhexoxy(methoxy)phosphoryl)oxy)ethoxy)ethoxy)ethyl 2-Ethylhexyl Methyl Phosphate.

The residue was purified by flash chromatography (dichloromethane/acetone = 4:1) to afford EG3EH as a yellow oil (7.029 g, 12.5 mmol; yield: $w = 0.25$, mass fraction). The density is $1.069\text{ g}\cdot\text{mL}^{-1}$. ^1H NMR δ_{H} (500 MHz, CDCl_3 , Me_4Si): 4.17–4.15 (m, 4H, P–O– CH_2 – CH_2), 3.97–3.94 (m, 4H, P–O– CH_2 –CH), 3.78 (s, 3H, P–O– CH_3), 3.76 (s, 3H, P–O– CH_3), 3.70 (t, 4H, $J = 5\text{ Hz}$, P–O– CH_2 – CH_2 –O), 3.66 (brs, 4H, O– CH_2 – CH_2 –O), 1.56 (m, 2H, CH– CH_2), 1.40–1.27 (brm, 16H, CH_2), 0.90 (t, 12H, $J = 7\text{ Hz}$, CH_2 – CH_3). ^{13}C NMR δ_{C} (500 MHz, CDCl_3 , Me_4Si): 70.84, 70.25, 66.77, 54.44, 40.23, 29.95, 29.03, 23.38, 23.16, 14.26, 11.06. APCI-MS: m/z calcd for $[\text{M} + \text{H}]^+$: 563.30; found: 563.29. Anal. Calcd for $\text{C}_{24}\text{H}_{52}\text{O}_{10}\text{P}_2$ (mass fraction): C, 0.5124; H, 0.0932, found: C, 0.5120; H, 0.0939.

PG3EH: 2-(2-(2-((2-Ethylhexoxy(methoxy)phosphoryl)oxy)propoxy)propoxy)propyl 2-Ethylhexyl Methyl Phosphate.

The residue was purified by flash chromatography (dichloromethane/acetone = 5:1) to afford PG3EH as a yellow oil (7.711 g, 12.105 mmol; yield: $w = 0.22$, mass fraction). The density is $1.043\text{ g}\cdot\text{mL}^{-1}$. ^1H NMR δ_{H} (500 MHz, CDCl_3 , Me_4Si): 3.95–3.91 (m, 7H, P–O– CH_2 , P–O–CH), 3.77–3.73 (brm, 6H, P–O– CH_3), 3.71–3.30 (brm, 6H, P–O– CH_2 –CH(CH_3)–O, O– CH_2 –CH, CH–O, P–O–CH(CH_3)– CH_2), 1.56 (m, 2H, CH– CH_2 – CH_3), 1.40–1.28 (brm, 20H, CH_2 , O–CH(CH_3)– CH_2 –O), 1.17–1.13 (m, 6H, P–O–CH(CH_3)– CH_2), 0.89 (t, 12H, $J = 7\text{ Hz}$, CH_2 – CH_3). ^{13}C NMR δ_{C} (500 MHz, CDCl_3 , Me_4Si): 75.42, 74.58, 74.14, 73.20, 72.89, 72.65, 70.13, 54.28, 29.99, 29.02, 23.38, 23.14, 18.59, 17.40, 16.84. APCI-MS: m/z calcd for $[\text{M} + \text{H}]^+$: 605.35; found: 605.20. Anal. Calcd for $\text{C}_{27}\text{H}_{58}\text{O}_{10}\text{P}_2$ (mass fraction): C, 0.5363; H, 0.0967, found: C, 0.5357; H, 0.0972.

The Cloud-Point Pressure Measurement. The solubilities of EG3EH and PG3EH in scCO_2 were determined by the static equilibrium method as Su et al. described previously.²¹ At first, the cell was maintained at the minimum volume ($35.43 \pm 0.01\text{ mL}$), and the air inside was carefully blown out by neat CO_2 . A certain amount of EG3EH or PG3EH ($\pm 0.0001\text{ g}$) was loaded into the cell, and then it was sealed carefully by the head containing the stirrer. When the system was heated to the set temperature, CO_2 was injected slowly into the cell by the manual injection pump until a clearly transparent single phase was observed while being stirred. When the temperature and pressure were kept constant ($\pm 0.1\text{ K}$ and $\pm 0.01\text{ MPa}$) for a period of 2 h, the temperature and pressure were recorded. The stirrer was stopped, and the pressure was decreased carefully until the phase became cloudy. This pressure was defined as the cloud-point pressure at the set temperature. The pressure was then slowly increased to obtain a clear solution which was maintained for 0.5 h. This procedure was repeated at least five times to obtain an average value for the reported cloud point pressures at each temperature. At each condition, the measurements were replicated at least five times. For each time, the mole fractions of EG3EH or PG3EH in scCO_2 were almost the same, which were reproducible within $\pm 3\%$. The uncertainties of equilibrium temperature and cloud point pressure were up to $\pm 0.1\text{ K}$ and

$\pm 0.01\text{ MPa}$. The density of supercritical carbon dioxide was calculated using a CO_2 equation of state.²² The apparatus had been calibrated by determining the solubilities of naphthalene in scCO_2 , and there was a difference of less than 3% from literature values.²³

RESULTS AND DISCUSSION

The solubilities of EG3EH and PG3EH in scCO_2 were measured at temperatures of (313, 323, and 333) K and over a pressure range from (10 to 19) MPa. Each reported cloud-point pressure is the average value of at least five times replicated pressures. The cloud-point pressures and the solubility data are illustrated in Table 1 and also shown in Figure 3. For each compound, at

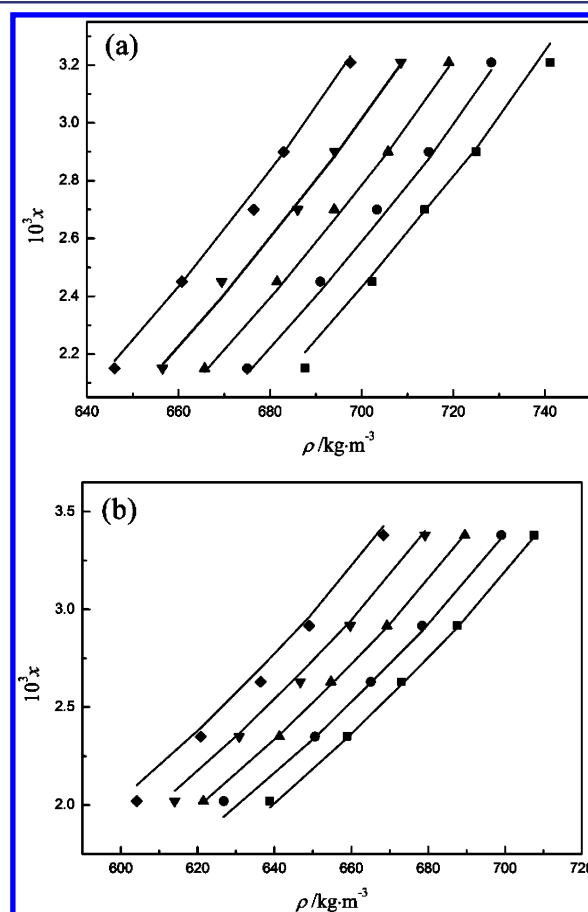


Figure 3. Comparison of experimental and calculated solubilities for the compounds in supercritical CO_2 . (a) EG3EH; (b) PG3EH. Experimental data: \blacksquare , 313 K; \bullet , 318 K; \blacktriangle , 323 K; \blacktriangledown , 328 K; and \blacklozenge , 333 K. Solid curves were calculated using Bartle's model (eq 3).

constant temperature, the solubility increases along with the density of scCO_2 , due to the fact that the increasing density results in the stronger solvation power of scCO_2 .

Both EG3EH and PG3EH with the same branched side tails show a high solubility in scCO_2 . For example, the solubility of EG3EH (molecule weight, $\text{MW} = 562.6$) in scCO_2 is 0.041 (mass fraction) (mole fraction: $3.21 \cdot 10^{-3}$, 313 K, and 12.86 MPa); in comparison, those of PEG ($\text{MW} = 600$) and PEG-DME ($\text{MW} = 400$, dimethyl ether) are 0.00924 (mass fraction) (mole fraction: $6.78 \cdot 10^{-4}$, 313 K, and about 33.8 MPa) and 0.022 (mass fraction) (mole fraction: $2.42 \cdot 10^{-3}$, 313 K, and about 15.9 MPa), respectively.²⁴ Moreover, the solubility of PG3EH ($\text{MW} = 604.6$) in

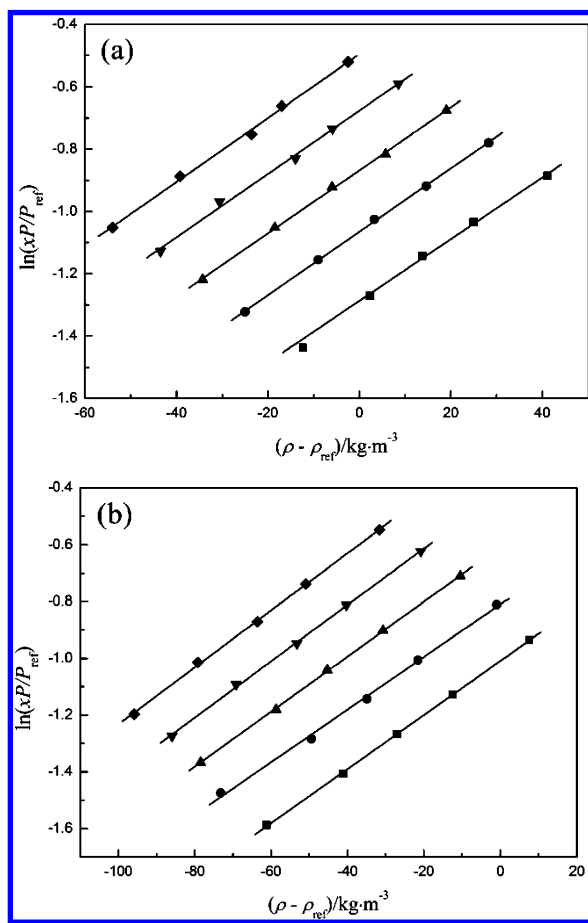


Figure 4. Plots of $\ln(xP/P_{\text{ref}})$ vs $(\rho - \rho_{\text{ref}})/\text{kg}\cdot\text{m}^{-3}$ for the compounds at different temperatures. x , mole fraction; P , CO_2 pressure; P_{ref} 0.1 MPa; ρ , density of pure CO_2 ; ρ_{ref} $700 \text{ kg}\cdot\text{m}^{-3}$. (a) EG3EH, (b) PG3EH. ■, 313 K; ●, 318 K; ▲, 323 K; ▼, 328 K; and ◆, 333 K. Solid curves were calculated using Bartle's model (eq 3).

scCO_2 is 0.036 (mass fraction) (mole fraction: $2.63 \cdot 10^{-3}$, 313 K, and 10.71 MPa), and that of PPG (MW = 400) is 0.031 (mass fraction) (mole fraction: $3.41 \cdot 10^{-3}$, 313 K, and about 11.03 MPa).²⁴

Besides, the additional three methyl groups in the middle oxygenated chain renders PG3EH more CO_2 soluble than EG3EH, reasonably due to the restrained self-interactions of PG3EH and the enhanced interactions with CO_2 .²⁵ In addition, the larger free volume introduced by the three methyl groups of PG3EH are also favorable to the enhancement of CO_2 affinity.²⁶

Data Correlation. The experimental solubility data of EG3EH and PG3EH were correlated using the semiempirical model proposed by Bartle et al.,¹⁸ which is illustrated as follows:

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

where

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

and then

$$\ln(xP/P_{\text{ref}}) = a + b/T + C(\rho - \rho_{\text{ref}}) \quad (3)$$

where x is the mole fraction of the solutes; P is the cloud-point pressure, MPa; P_{ref} is 0.1 MPa; ρ is the density of neat CO_2 at the experimental condition; ρ_{ref} is $700 \text{ kg}\cdot\text{m}^{-3}$; T is the experiment temperature, K; A , C , a , and b are constants.

For each compound, at first, $\ln(xP/P_{\text{ref}})$ values were plotted against $(\rho - \rho_{\text{ref}})$ (Figure 4), and then the C and A parameters at different temperatures could be obtained from the straight line by least-squares regression. The averaged value of different C values was used by eq 1 to estimate constant A at different temperatures. The plots of A versus $1/T$ were fitted to a straight line (Figure 5);

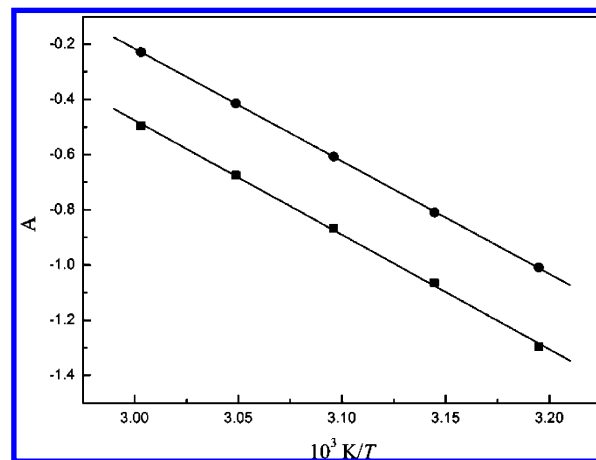


Figure 5. Plots of A vs $1000/T$ for the compounds. ■, EG3EH; ●, PG3EH.

hence the intercept a and the slope b were obtained. The resulting values of a , b , and C , as shown in Table 2, were finally used to

Table 2. Results of the Solubility Data Correlation Using the Bartle Model^a

compound	n	a	b	C	AARD
			K	$\text{m}^3\cdot\text{kg}^{-1}$	%
EG3EH	25	11.972	-4149.37	0.0102	1.03
PG3EH	25	12.022	-4079.53	0.00968	1.20

^aNumber of data points used in the correlation (n), parameters of the Bartle model (a , b , and C), and average absolute relative deviations (AARD).

predict x_{cal} by eq 3, and then the average absolute relative deviation (AARD) was used to assess the correlation results, which was calculated with the following equation:

$$\text{AARD} = 1/n \sum |(x_{i,\text{cal}} - x_{i,\text{exp}})/x_{i,\text{exp}}| \cdot 100 \% \quad (4)$$

where n is the number of experimental points, $x_{i,\text{cal}}$ and $x_{i,\text{exp}}$ are the calculated and experimental data, respectively. The values of AARD are within 2 %, which are fairly good.

CONCLUSION

In summary, the solubilities of EG3EH and PG3EH in supercritical carbon dioxide were determined at temperatures from (313 to 333) K and over a pressure range of (10 to 19) MPa. The solubilities were in the range of $(2.02 \text{ to } 3.38) \cdot 10^{-3}$ (mole fraction). It was demonstrated that the phosphoryl groups were favorable to the CO_2 -philicity. PG3EH was more CO_2 -philic than EG3EH, which was indicated that the branched topology of the bridging oxygenated chains played an important role in the enhancement of CO_2 -philicity.

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Notes

The authors declare no competing financial interest.

REFERENCES

- (1) Subramaniam, B.; Rajewski, R. A.; Snively, K. Pharmaceutical Processing with Supercritical Carbon Dioxide. *J. Pharm. Sci.* **1997**, *86*, 885–890.
- (2) Cooper, A. I. Polymer Synthesis and Processing Using Supercritical Carbon Dioxide. *J. Mater. Chem.* **2000**, *10*, 207–234.
- (3) Ashraf Khorassani, M.; Combs, M. T.; Taylor, L. T. Supercritical Fluid Extraction of Metal Ions and Metal Chelates from Different Environments. *J. Chromatogr., A* **1997**, *774*, 37–49.
- (4) Wai, C. M.; Wang, S. F. Supercritical Fluid Extraction: Metals as Complexes. *J. Chromatogr., A* **1997**, *785*, 369–383.
- (5) Herrero, M.; Mendiola, J. A.; Cifuentes, A.; Ibanez, E. Supercritical Fluid Extraction: Recent Advances and Applications. *J. Chromatogr., A* **2010**, *1217*, 2495–2511.
- (6) Beckman, E. J. Green Chemical Processing Using CO₂. *Ind. Eng. Chem. Res.* **2003**, *42*, 1598–1602.
- (7) Desimone, J. M.; Guan, Z.; Elsbernd, C. S. Synthesis of Fluoropolymers in Supercritical Carbon-Dioxide. *Science* **1992**, *257*, 945–947.
- (8) Desimone, J. M.; Maury, E. E.; Menciloglu, Y. Z.; McClain, J. B.; Romack, T. J.; Combes, J. R. Dispersion Polymerizations in Supercritical Carbon-Dioxide. *Science* **1994**, *265*, 356–359.
- (9) Yazdi, A. V.; Lepilleur, C.; Singley, E. J.; Liu, W.; Adamsky, F. A.; Enick, R. M.; Beckman, E. J. Highly Carbon Dioxide Soluble Surfactants, Dispersants and Chelating Agents. *Fluid Phase Equilib.* **1996**, *117*, 297–303.
- (10) Beckman, E. J. A Challenge for Green Chemistry: Designing Molecules that Readily Dissolve in Carbon Dioxide. *Chem. Commun.* **2004**, 1885–1888.
- (11) Raveendran, P.; Wallen, S. L. Sugar Acetates as Novel, Renewable CO₂-Philes. *J. Am. Chem. Soc.* **2002**, *124*, 7274–7275.
- (12) Kilic, S.; Michalik, S.; Wang, Y.; Johnson, J. K.; Enick, R. M.; Beckman, E. J. Effect of Grafted Lewis Base Groups on the Phase Behavior of Model Poly(Dimethyl Siloxanes) in CO₂. *Ind. Eng. Chem. Res.* **2003**, *42*, 6415–6424.
- (13) Fan, X.; Potluri, V. K.; McLeod, M. C.; Wang, Y.; Liu, J. C.; Enick, R. M.; Hamilton, A. D.; Roberts, C. B.; Johnson, J. K.; Beckman, E. J. Oxygenated Hydrocarbon Ionic Surfactants Exhibit CO₂ Solubility. *J. Am. Chem. Soc.* **2005**, *127*, 11754–11762.
- (14) Kim, K. H.; Kim, Y. Theoretical Studies for Lewis Acid-Base Interactions and C-H...O Weak Hydrogen Bonding in Various CO₂ Complexes. *J. Phys. Chem. A* **2008**, *112*, 1596–1603.
- (15) Wang, Y.; Hong, L.; Tapriyal, D.; Kim, I. C.; Paik, I. H.; Crosthwaite, J. M.; Hamilton, A. D.; Thies, M. C.; Beckman, E. J.; Enick, R. M.; Johnson, J. K. Design and Evaluation of Nonfluorous CO₂-Soluble Oligomers and Polymers. *J. Phys. Chem. B* **2009**, *113*, 14971–14980.
- (16) Ma, S. L.; Wu, Y. T.; Hurrey, M. L.; Wallen, S. L.; Grant, C. S. Sugar Acetates as CO₂-philes: Molecular Interactions and Structure Aspects from Absorption Measurement Using Quartz Crystal Microbalance. *J. Phys. Chem. B* **2010**, *114*, 3809–3817.
- (17) Yang, Z.; Yang, H. J.; Tian, J.; Guo, C. Y.; Kim, H. High Solubility and Partial Molar Volume of 2,2'-Oxybis(N,N-bis(2-methoxyethyl)-acetamide) in Supercritical Carbon Dioxide. *J. Chem. Eng. Data* **2011**, *56*, 1191–1196.
- (18) 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.
- (19) Kim, K. H.; Kim, Y. Theoretical Studies for the Supercritical CO₂ Solubility of Organophosphorous Molecules: Lewis Acid-Base Interactions and C-H...O Weak Hydrogen Bonding. *Bull. Korean Chem. Soc.* **2007**, *28*, 2454–2458.
- (20) Fan, H.; Chen, Y.; Feng, Q.; Lu, W. Synthesis and Characterization of Bi-Dodecyl Bi-Phosphate. *Chin. J. Appl. Chem.* **2007**, *24*, 1095–1097.
- (21) Su, B.; Lv, X.; Yang, Y.; Ren, Q. Solubilities of Dodecylpolyoxyethylene Polyoxypropylene Ether in Supercritical Carbon Dioxide. *J. Chem. Eng. Data* **2006**, *51*, 542–544.
- (22) Huang, F. H.; Li, M. H.; Lee, L. L. An Accurate Equation of State for Carbon Dioxide. *J. Chem. Eng. Jpn.* **1985**, *18*, 490–496.
- (23) Gonenc, Z. S.; Akman, U.; Sunol, A. K. Solubility and Partial Molar Volumes of Naphthalene, Phenanthrene, Benzoic-Acid, and 2-Methoxy-Naphthalene in Supercritical Carbon-Dioxide. *J. Chem. Eng. Data* **1995**, *40*, 799–804.
- (24) O'Neill, M. L.; Cao, Q.; Fang, R.; Johnston, K. P.; Wilkinson, S. P.; Smith, C. D.; Kerschner, J. L.; Jureller, S. H. Solubility of Homopolymers and Copolymers in Carbon Dioxide. *Ind. Eng. Chem. Res.* **1998**, *37*, 3067–3079.
- (25) Drohmann, C.; Beckman, E. J. Phase Behavior of Polymers Containing Ether Groups in Carbon Dioxide. *J. Supercrit. Fluids* **2002**, *22*, 103–110.
- (26) Johnston, K. P.; Cho, D. M.; DaRocha, S. R. P.; Psathas, P. A.; Ryoo, W.; Webber, S. E.; Eastoe, J.; Dupont, A.; Steytler, D. C. Water in Carbon Dioxide Macroemulsions and Miniemulsions with a Hydrocarbon Surfactant. *Langmuir* **2001**, *17*, 7191–7193.