1618 *J. Chem. Eng. Data* **2008,** *53,* 1618–1621

Phase Behavior of 2,2-Dimethyl-1,3-propanediol in Carbon Dioxide

Kyung-Kyu Park, Sang-Hun Han, and Sang-Ho Lee*

Department of Chemical Engineering, Dong-A University, Hadan2-dong, Busan, Republic of Korea

High pressure experimental data are presented on the phase behavior of 2,2-dimethyl-1,3-propanediol in carbon dioxide. Pressure-composition ($P-x$) isotherms were measured from 352.3 K to 403.2 K. The single phase of the mixture greatly reduces with decreasing temperature due to the hydrogen bonding of 2,2-dimethyl-1,3-propanediol. The $P-x$ isotherms at 352.3 K and 353.3 K exhibited an open loop whereas the $P-x$ isotherms at the higher temperatures did a closed loop. The 2,2-dimethyl-1,3-propanediol + CO_2 phase behavior was modeled with Peng−Robinson equation of state with two mixture parameters. A reasonable fit of the high temperature isotherms is obtained if k_{ij} is allowed to increase with decreasing temperature. The fit of the data becomes inaccurate with deceasing temperature due to the hydrogen bonding between 2,2-dimethyl-1,3-propanediol molecules.

Introduction

2,2-Dimethyl-1,3-propanediol is commercially used to produce plasticizers, polyester resins for powder coatings, synthetic lubricant, pharmaceutical, and pesticide, etc.[1,2] To develop and optimize separation process, it is essential to know phase behavior data of target materials. The purpose of this study is to present phase behavior data for 2,2-dimethyl-1,3-propanediol in CO_2. 2,2-Dimethyl-1,3-propanediol has two hydroxyl groups at the 1 and 3 carbons and two methyl groups at the middle carbon. The two hydroxyl groups are separated by the end carbons and the α carbon whose two hydrogens are substituted with methyl groups. Because of its unique molecular structure, 2,2-dimethyl-1,3-propanediol is not expected to perform intramolecular hydrogen bonding. Table 1 lists the physicochemical characteristics of 2,2-dimethyl-1,3-propanediol and CO_2. The property difference between 2,2-dimethyl-1,3-propanediol and CO_2 leads to the type IV of phase behavior depicted in Figure 1.[3] Type IV phase behavior is observed when the differences in structure, size, or intermolecular force between the mixture components is very large, such as in Squalane + CO_2, 1-decanol + CO_2, and 1,8-octanediol + CO_2 binary mixtures.[4–6] The single phase region in temperature−pressure space shrinks remarkably as the properties of the mixture components become more dissimilar.

Table 1. Physical Properties of CO_2[9] and 2,2-Dimethyl-1,3-propanediol

	2,2-dimethyl-1,3-propanediol	carbon dioxide
chemical formula	$HOCH_2C(CH_3)_2CH_2OH$	CO_2
molecular weight	104.15	44.01
T_c/K	657.75	304.12
P_c/MPa	4.203	7.374
acentric factor, ω	0.800	0.225
dipole moment, μ/D	2.9[a]	0.0

[a] The dipole moment of 2,2-dimethyl-1,3-propanediol was calculated using Hartree−Fock molecular orbital model.[13]

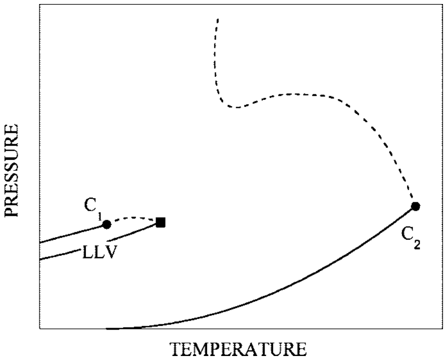

Figure 1. Schematic pressure−temperature diagram for a type-IV binary mixture.[3] C1 and C2 (closed circles, ●) are the critical points of high and low volatile component, respectively. LLV line represents liquid−liquid−vapor coexistence line. The dashed curve is the critical mixture curve for the binary mixture. The closed square (■) represents critical end point.

Experimental Section

Apparatus and Procedures. Phase transition pressure was determined using high-pressure, variable-volume cell constructed of stainless steel 316 (7.0 cm o.d., 1.6 cm i.d. fitted with a 1.9 cm thick sapphire window) capable of operating to pressures of 200 MPa. Before loading 2,2-dimethyl-1,3-propanediol, the cell was purged several times with CO_2 at room temperature to remove the entrapped air. 2,2-Dimethyl-1,3-propanediol was loaded into the cell to within ± 0.0001 g. CO_2 was then added to the cell to within ± 0.002 g from a high-pressure cylinder. The mixture in the cell was stirred with a magnetic bar. The transitions of the mixture in the cell were observed through the sapphire window using a video monitor and a camera connected to a borescope (Olympus Corporation, model R080−024−000−50). Schematic diagram of the view cell and experimental apparatus is described in detail elsewhere.[7]

At a fixed temperature, the mixture was compressed to the desired pressure by moving a piston located within the cell. Pressures greater than 68.9 MPa were measured with a Heise gauge (Dresser Ind., model CM-128639, 0 MPa to 206.8 MPa, accurate to ± 0.21 MPa). Pressures less than 68.9 MPa were measured with a different Heise gauge (Dresser Ind., model CM-135721, 0 MPa to 68.9 MPa, accurate to ± 0.07 MPa). The solution temperature, maintained to within ± 0.2 K, was

---

* Corresponding author. E-mail: Sangho@dau.ac.kr.

10.1021/je8001514 CCC: $40.75

measured with a platinum-resistance temperature detector that is accurate to ± 0.2 K (Thermometrics Corp., Class A).

To make the mixture in the cell reach thermal equilibrium, the cell was maintained at the measuring temperature for at least 30 min. The mixture in the cell was compressed up to high pressure enough to make a single phase. The pressure was then slowly decreased until a second phase appeared in the mixture. A bubble point was determined if small bubbles appear in the cell and a dew point was determined if small drops appear in the cell. A cloud point was determined as the point at which the mixture becomes so opaque that it is no longer possible to see the stir bar in the mixture. In the bubble, dew, and cloud point transitions, the composition of the predominant phase is supposed to equal the overall mixture composition because the mass present in the second phase is negligible. Each data point was reproduced at least 4 times in a given pressure and temperature. The data for each isotherm were obtained from several independent loading of the apparatus at each concentration. The lowest temperature of the pressure-composition ($P-x$) isotherm presented in this study was limited by the highest operating pressure of the experimental apparatus.

Materials. The 2,2-dimethyl-1,3-propanediol was obtained from Sigma-Aldrich Co. (98 % minimum purity). Carbon dioxide with purity of 99.99 % was supplied by Korea Standard Gas. These materials were used without further purification.

Results and Discussions

Table 2 lists the high pressure portions of 2,2-dimethyl-1,3-propanediol + CO_2 isotherms from 352.3 K to 403.2 K. Figure 2 shows the $P-x$ isotherms for 2,2-dimethyl-1,3-propanediol + CO_2 mixture at 403.2 K, 383.3 K, and 373.3 K. At 403.2 K, the $P-x$ isotherm is essentially flat at 2,2-dimethyl-1,3-propanediol mole fractions between 0.10 and 0.22. As the temperature decreases, the $P-x$ isotherms shift to higher pressures. The extent of hydrogen bonding between 2,2-dimethyl-1,3-propanediol molecules is expected to increase with decreasing temperature, which make it more difficult to dissolve 2,2-dimethyl-1,3-propanediol in CO_2. We did not measure the exact critical-mixture compositions. However, mixture-critical pressure and temperature can be determined from each $P-x$ isotherm.

Figure 3 shows the $P-x$ isotherms for 2,2-dimethyl-1,3-propanediol + CO_2 mixture at 363.3 K, 358.4 K, and 355.3 K. As the temperature decreases, the $P-x$ isotherms move to higher pressure region. The temperature dependency is fundamentally identical to that of the isotherms measured at 403.2 K, 383.3 K, and 373.3 K. However, the maximum pressure of these isotherms abruptly increases. The increase in the maximum pressure was 43 MPa when the mixture temperature decreased from 363.3 K to 355.3 K. This is in contrast to the pressure increase of 18 MPA when temperature decreased from 403.2 K to 373.3 K. The large pressure increase in the $P-x$ isotherms is mainly the consequence of hydrogen bonding of 2,2-dimethyl-1,3-propanediol. The effect of hydrogen bonding was more apparent as the temperature decreases below 355.3 K. Figure 4 shows the $P-x$ isotherms at 353.3 K and 352.3 K. At 353.3 K, which is only 2 K lower than 355.3 K, the dew- and bubble-point pressures increase so steeply that we were unable to measure the phase transition pressures at 2,2-dimethyl-1,3-propanediol mole fraction between 0.103 and 0.220. The $P-x$ isotherm changed to open loop and a single phase was not obtained even at 200 MPa. Additional decreasing of the temperature from 353.3 K to 352.3 K further shrank the single phase region. Figure 3 and 4 well demonstrate that the shrinkage of the single phase region becomes more apparent as the temperature decreases.

Table 2. Experimental Pressure-Composition Data for 2,2-Dimethyl-1,3-propanediol in Supercritical Carbon Dioxide at Temperature between 352.3 K and 403.2 K

x_2, y_2	P/MPa	transition[a]	x_2, y_2	P/MPa	transition[a]
	T = 352.3 K			T = 353.3 K	
0.0044	20.68	DP	0.0044	20.68	DP
0.0109	30.55	DP	0.0109	30.34	DP
0.0219	49.81	DP	0.0219	48.09	DP
0.0466	90.0	DP	0.0466	83.6	DP
0.0728	106.3	DP	0.0728	100.9	DP
0.0971	173.1	DP	0.0971	127.6	DP
0.2542	155.3	BP	0.1023	157.2	DP
0.2993	101.7	BP	0.2199	166.0	BP
0.3403	66.77	BP	0.2542	134.5	BP
0.3886	52.95	BP	0.2993	93.1	BP
0.5060	24.72	BP	0.3403	65.50	BP
			0.3886	51.71	BP
			0.5060	24.65	BP
	T = 355.3 K			T = 358.4 K	
0.0044	20.37	DP	0.0044	20.24	DP
0.0109	29.59	DP	0.0109	28.44	DP
0.0219	45.68	DP	0.0219	42.99	DP
0.0466	76.0	DP	0.0466	70.0	DP
0.0728	92.0	DP	0.0728	83.8	DP
0.1023	115.1	DP	0.1023	95.0	DP
0.1264	121.8	CP	0.1264	100.2	CP
0.1503	125.5	CP	0.1503	102.5	CP
0.1849	119.7	BP	0.1849	101.4	BP
0.2199	115.0	BP	0.2199	96.9	BP
0.2542	103.6	BP	0.2542	88.8	BP
0.2993	85.0	BP	0.2993	78.4	BP
0.3403	59.98	BP	0.3403	57.92	BP
0.3886	49.54	BP	0.3886	48.02	BP
0.5060	24.65	BP	0.5060	24.54	BP
	T = 363.3 K			T = 373.3 K	
0.0044	19.66	DP	0.0044	19.48	DP
0.0109	27.33	DP	0.0109	25.85	DP
0.0219	40.64	DP	0.0219	36.37	DP
0.0466	60.30	DP	0.0466	49.47	DP
0.0728	72.4	DP	0.0728	58.09	DP
0.1023	79.3	DP	0.1023	62.66	DP
0.1264	81.5	CP	0.1264	64.55	CP
0.1503	82.1	CP	0.1503	64.81	BP
0.1849	81.4	BP	0.1849	64.36	BP
0.2199	79.7	BP	0.2199	63.17	BP
0.2542	74.9	BP	0.2542	60.67	BP
0.2993	68.77	BP	0.2993	57.81	BP
0.3403	53.09	BP	0.3403	48.43	BP
0.3886	45.13	BP	0.3886	41.30	BP
0.5060	24.51	BP	0.5060	24.37	BP
	T = 383.3 K			T = 403.2 K	
0.0044	19.18	DP	0.0044	18.93	DP
0.0109	24.30	DP	0.0109	21.50	DP
0.0219	33.14	DP	0.0219	30.68	DP
0.0466	43.83	DP	0.0466	37.78	DP
0.0728	50.33	DP	0.0728	42.73	DP
0.1023	54.47	DP	0.1023	45.86	DP
0.1264	55.24	CP	0.1264	46.45	CP
0.1503	55.46	BP	0.1503	46.88	BP
0.1849	54.95	BP	0.1849	46.40	BP
0.2199	54.57	BP	0.2199	46.30	BP
0.2542	52.38	BP	0.2542	44.85	BP
0.2993	51.19	BP	0.2993	44.30	BP
0.3403	43.95	BP	0.3403	39.30	BP
0.3886	38.78	BP	0.3886	35.78	BP
0.5060	24.10	BP	0.5060	23.79	BP

[a] BP, CP, and DP represent bubble-, cloud-, and dew-point, respectively.

Figure 5 shows the mixture critical points measured in this experiment in $P-T$ space. The vapor pressure of 2,2-dimethyl-1,3-propanediol was calculated using Riedel corresponding-state method with Vetere rule,[8] suggested by Poling et al.[9] The critical

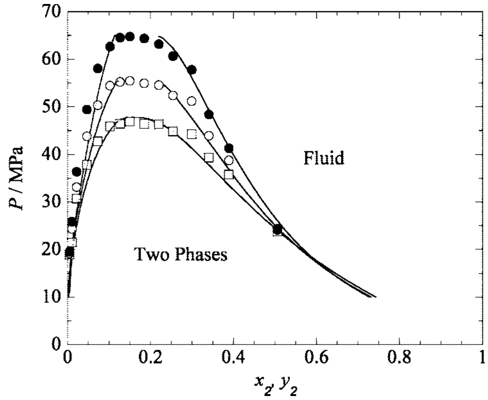

Figure 2. Experimental pressure-composition isotherms for CO_2 (1) + 2,2-dimethyl-1,3-propanediol (2) mixture at different temperatures: ●, 373.3 K; ○, 383.3 K; □, 403.2 K. The lines represent the calculated isotherms with PR equation of state at each temperature.

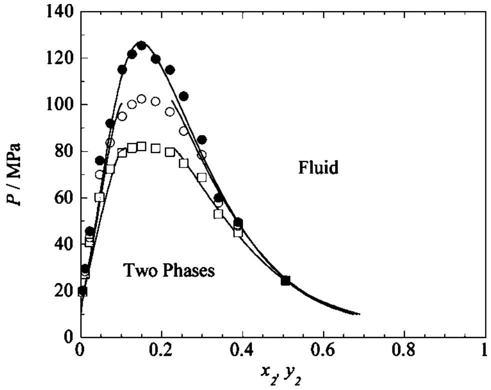

Figure 3. Experimental pressure-composition isotherms for CO_2 (1) + 2,2-dimethyl-1,3-propanediol (2) mixture at different temperature: ●, 355.3 K; ○, 358.4 K; □, 363.3 K. The lines represent the calculated isotherms with PR equation of state at each temperature.

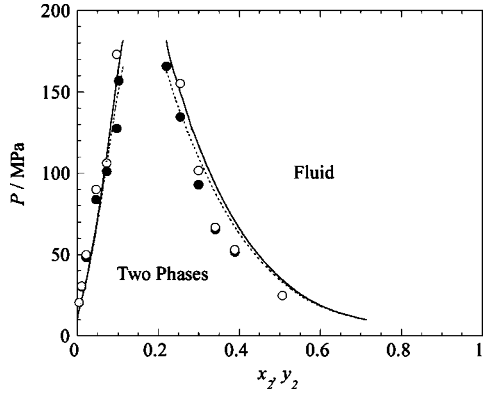

Figure 4. Experimental pressure-composition isotherms for CO_2 (1) + 2,2-dimethyl-1,3-propanediol (2) mixture at temperature: ○, 352.3 K; ●, 353.3 K. The solid line and dashed line represent the calculated isotherms at 352.3 K and 353.3 K, respectively.

properties of 2,2-dimethyl-1,3-propanediol were calculated using group contribution methods suggested by Marrero and Gani.[10] The calculated critical point of 2,2-dimethyl-1,3-propanediol is located at much lower pressure and higher temperature than the experimental mixture critical points. The locus connecting the 2,2-dimethyl-1,3-propanediol critical point with the experimental mixture critical points exhibits that 2,2-dimethyl-1,3-propanediol + CO_2 mixture has type IV phase behavior.

Modeling. The pressure-composition data obtained in this study were modeled with the Peng–Robinson (PR)[11] equation of state with the following mixing rules:

$$a_{\text{mix}} = \sum_i \sum_j x_i x_j a_{ij} \tag{1}$$

$$a_{ij} = (a_{ii}a_{jj})^{0.5}(1 - k_{ij}) \tag{2}$$

$$b_{\text{mix}} = \sum_i \sum_j x_i x_j b_{ij} \tag{3}$$

$$b_{ij} = 0.5[(b_{ii} + b_{jj})(1 - \eta_{ij})] \tag{4}$$

where, k_{ij} and η_{ij} are mixture parameters that are determined by fitting pressure-composition data and a_{ii} and b_{ii} are pure component parameters. The expression for the fugacity coefficient using these mixing rules is given by Peng and Robinson.[11] Table 1 lists the critical temperature, critical pressure, and the acentric factors for CO_2 and 2,2-dimethyl-1,3-propanediol. To the best of our knowledge, there are no critical properties and acentric factor of 2,2-dimethyl-1,3-propanediol available in the literature. The critical temperature and pressure of 2,2-dimethyl-1,3-propanediol were calculated using the Marrero and Gani[10] group contribution method. The acentric factor was calculated using the method suggested by Poling et al.[9] and Ambrose and Walton.[12]

The binary interaction parameters, k_{ij} and η_{ij}, were obtained by fitting the experimental data in Table 2 to minimize the objective function defined as

$$\text{OF} = \sum_{i=1}^{N} \left| \frac{P_{\text{corr}} - P_{\text{exp}}}{P_{\text{exp}}} \right|_i \tag{5}$$

where Pcorr and Pexp are the correlated and experimental transition pressure, respectively, and N is the number of data points.

Table 3 lists the interaction parameters and average absolute relative deviation (AARD) values for the transition pressure and mole fraction, which were obtained from fitting the 2,2-dimethyl-1,3-propanediol + CO_2 isotherms. One binary mixture parameter, k_{ij}, was used to fit the 2,2-dimethyl-1,3-propanediol-CO_2 isotherms at 403.2K, 383.3K, and 373.3 K. When η_{ij} held constant at zero, a best fit for the 403.2 K isotherm was obtained with $k_{ij} = 0.082$. When the η_{ij} and k_{ij} values were used to fit 383.3 K and 373.3 K isotherms, poor fitting result was obtained. However, it was possible to obtain reasonable fit for the 383.3

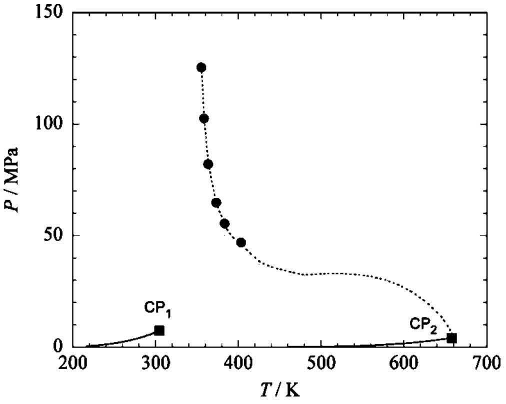

Figure 5. Pressure-temperature diagram for CO_2 (1) + 2,2-dimethyl-1,3-propanediol (2) mixture. The closed circles (●) are the mixture-critical points determined in this study. CP_1 and CP_2 are the critical points for CO_2 and 2,2-dimethyl-1,3-propanediol, respectively. The solid lines represent the vapor pressure curves for CO_2 and 2,2-dimethyl-1,3-propanediol, respectively. The vapor pressure of 2,2-dimethyl-1,3-propanediol was calculated using Riedel corresponding-state method with Vetere rule.[8] The dashed line represents the mixture critical curve of CO_2 (1) + 2,2-dimethyl-1,3-propanediol (2) mixture. Between CP_2 and the binary mixture critical point at 403.2 K, the binary mixture critical curve was not measured but arbitrarily depicted.

Table 3. Interaction Parameters and AARD Values for 2,2-Dimethyl-1,3-propanediol + CO_2 Isotherms

T K	k_{ij}	η_{ij}	AARD(P)[a] %	AARD(x_2)[b] %
352.3	0.117	0.006	22.92	29.40
353.3	0.117	0.008	18.83	22.92
355.3	0.117	0.028	8.22	13.65
358.4	0.116	0.025	7.02	12.41
363.3	0.109	0.020	6.41	19.32
373.3	0.098	0.000	6.98	19.83
383.3	0.091	0.000	6.75	19.61
403.2	0.082	0.000	5.52	15.52

[a] AARD(P) = $1/N\sum_{i=1}^{N} |P_{corr} - P_{exp}/p_{exp}|_i \cdot 100$, where P_{corr} and P_{exp} are the correlated and experimental transition pressure, respectively, and N is the number of data points. [b] AARD(x) = $1/N\sum_{i=1}^{N} |x_{corr} - x_{exp}/x_{exp}|_i \cdot 100$, where x_{corr} and x_{exp} are the correlated and experimental mole fraction, respectively, and N is the number of data points.

K and 373.3 K isotherms if k_{ij} was adjusted to temperature. The k_{ij} has a negative slope of −0.00052 with respect to temperature. To fit the $P-x$ isotherms for 363.3K, 358.4K, and 355.3 K, two binary mixture parameter, k_{ij} and η_{ij}, were used. Both parameters were needed to be adjusted with temperature to obtain reasonable fit. The strength of hydrogen bonding between 2,2-dimethyl-1,3-propanediol molecules is expected to increase with decreasing temperature. Because PR equation of state does not explicitly account for hydrogen bonding and polar interactions, fitting result of the low temperature isotherms becomes more inaccurate as temperature decreases. The AARD values of the $P-x$ isotherms increase with decreasing temperature. At 353.3 K and 352.3 K, the experimental $P-x$ isotherms were opened even at 207 MPa, whereas closed isotherms were measured at temperature higher than 355.3 K. The 353.3 K and 352.3 K isotherms were fitted with $k_{ij} = 0.117$, which is equal to the k_{ij} for 355.3 K isotherm. The fit of the two isotherms is not as good as the fit of 355.3 K isotherm, although the temperature difference is only 2 K and 3 K. The AARD values for 353.3 K and 352.3 K isotherms are approximately more than two times of the values for 355.3 K isotherm.

Literature Cited

(1) Harris, S. T. Brisk demand of neopentyl glycol. *Focus on Powder Coatings* **2007**, *7*, 8.

(2) Harris, S. T. Chemical profile: neopentyl glycol. *Focus on Powder Coatings* **2006**, *10*, 7.

(3) McHugh, M. A.; Krukonis, V. J. *Supercritical Fluid Extraction: Principles and Practice*, 2nd ed.; Butterworth: Stoneham, MA, 1994.

(4) Scheidgen, A. L.; Schneider, G. M. Fluid phase equilibria of (carbon dioxide + a 1-alkanol + an alkane) up to 100 MPa and $T = 393$ K: cosolvency effect, miscibility window, and holes in the critical surface. *J. Chem. Thermodyn.* **2000**, *32*, 1183–1201.

(5) Schneider, G. M. High-pressure investigations of fluid mixtures - review and recent results. *J. Supercrit. Fluids* **1998**, *13*, 5–14.

(6) Spee, M.; Schneider, G. M. Fluid Phase equilibrium studies on binary and ternary mixtures of carbon dioxide with hexadecane, 1-dodecanol, 1,8-octanediol and dotriacontane at 393.2 K and at pressures up to 100 MPa. *Fluid Phase Equib.* **1991**, *65*, 263–274.

(7) Lee, S.-H.; McHugh, M. A. Phase behavior of 4-Methoxyphenyl Acetic Acid in Carbon Dioxide. *J. Chem. Eng. Data* **2002**, *47*, 792–795.

(8) Vetere, A. The Riedel Equation. *Ind. Eng. Chem. Res.* **1991**, *30*, 2487–2492.

(9) Poling, B. E.; Prausnitz, J. M.; O'Connell, J. P. *The Properties of Gases and Liquids*, 5th ed.; McGraw-Hill: New York, 2001.

(10) Marrero; J.; Gani, R. Group-contribution based estimation of component properties. *Fluid Phase Equilib.* **2001**, *183−184*, 183–208.

(11) Peng, D. Y.; Robinson, D. B. A New Two-Constant Equation of State. *Ind. Eng. Chem. Fundam.* **1976**, *15*, 59–64.

(12) Ambrose, D.; Walton, J. Vapor pressure up to their critical temperatures of normal alkanes and 1-alkanols. *Pure Appl. Chem.* **1989**, *61*, 1395–1403.

(13) Hehre, W. J. *A Guide to Molecular Mechanics and Quantum Chemical Calculations*; Wavefunction, Inc: Irvine, CA, 2003.

Received for review March 2, 2008. Accepted April 9, 2008. This study was supported by a research fund from Dong-A University.

JE8001514