Solubility Measurements and Data Correlation of Carbon Dioxide in Pentaerythritol Tetrahexanoate (PEC6)

Sergio Bobbo,[†] Francesco Pernechele,[†] Laura Fedele,*[,†] and Roman Stryjek[‡]

National Research Council, Institute of Construction Technologies, Division of Padova, Corso Stati Uniti 4, 35127 Padova, Italy, and Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01−224 Warsaw, Poland

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The compatibility of carbon dioxide with synthetic oils, employed as lubricants for compressors in the refrigeration and air conditioning plants, is a fundamental and still unsolved problem. Mutual solubility with the refrigerant is one of the properties that influences the choice of a particular lubricant for a specific application. A systematic study of the solubility of carbon dioxide in polyolester oils (POE) has been started at our laboratories with the aim to investigate the dependence of this property on various parameters, such as pressure, temperature, and oil chemical structure. In this paper, experimental measurements of solubility of carbon dioxide in pentaerythritol hexanoate (PEC6), which is a precursor of polyol ester based lubricants, are presented in a temperature range of (243 to 343) K and pressures up to about 10 MPa. The uncertainty in the liquid composition measurements was estimated to be from 0.002 (high CO_2 molar fraction) to 0.02 (low CO_2 molar fraction). The experimental data were correlated by means of the Peng−Robinson equation of state with the Huron Vidal mixing rules in which the excess Gibbs energy at infinite pressures was represented by the UNIQUAC equation.

Introduction

Carbon dioxide (CO_2) is currently being considered as a possible alternative to the high global warming potential (GWP) refrigerants for some particular applications, but many problems still remain regarding the design of the working systems. A refrigerating plant using carbon dioxide is characterized by operative pressures roughly ten times higher than those typical for traditional plants, causing very severe conditions for the compressor. From this observation, the role assumed by the lubricant becomes fundamental, to preserve the mechanical moving elements from wear, while maintaining its thermal and chemical stability. Moreover it is worthwhile to mention that the presence of lubricant is not confined to the compressor tank, but because of its solubility with the refrigerant, a certain amount of lubricant is dragged along all the circuits. The actual circulating fluid is then a refrigerant + lubricant mixture with its own thermophysical and thermodynamical properties.[1]

For these reasons, the knowledge of the phase behavior of refrigerant−oil mixtures becomes of specific importance for the correct design of various refrigeration plant components. However, finding theoretical models able to represent properties such as the solubility and miscibility limits for this system is possible only if extensive and accurate experimental data are available. Since the commercial synthetic lubricants are unspecified mixtures of several pure components and additives, hence ill-defined from chemical and thermodynamic points of view, experimental data regarding the solubility of a refrigerant in a specific commercial lubricant give significant technical information. This information is not sufficient to define proper thermodynamic models able to work both in a correlative and predictive way. Indeed, the development of such models requires a wide production of experimental data on the precursors of commercial lubricants.

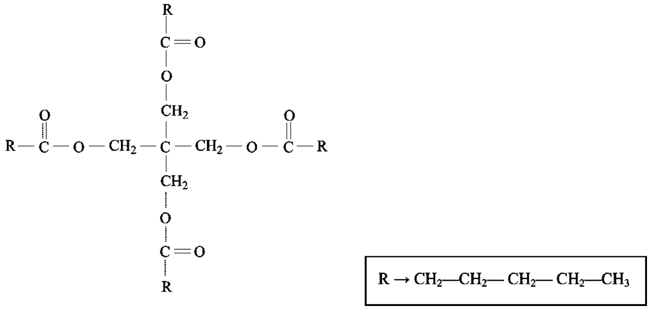

Figure 1. Chemical structure of the pentaerythritol tetrahexanoate.

Among all the classes of lubricants that proved to give acceptable results with carbon dioxide, there are polyol ester oils (POE). A long-term research program has been started by our group, focusing on the analysis of the phase behavior of pure and commercial POE lubricants in mixtures with carbon dioxide. Particular attention has been given to the dependence of solubility in pure pentaerythritol esters on molecular mass, molecular structure of oils, temperature, and pressure.[2−5]

This paper presents the measurements and the data correlation for the system composed by CO_2 and the pentaerythritol tetrahexanoate (PEC6) in the temperature range of (243 to 343) K and for pressures up to 10 MPa, i.e., in typical conditions for a refrigerating plant working with CO_2.

Experimental Section

Materials. The pentaerythritol tetrahexanoate ($C_{29}H_{52}O_8$, CASRN 7445-47-8) used for the present measurements was synthesized by Chemipan (Poland) on a laboratory scale with a declared purity higher than 98 %. Two synonyms of this chemical are tetra-*o*-hexanoyl pentaerythritol and pentaerythritol

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* Corresponding author. Tel.: +39 049 8295831. Fax: +39 049 8295728. E-mail: laura.fedele@itc.cnr.it.
[†] Institute of Construction Technologies.
[‡] Polish Academy of Sciences.

10.1021/je800429j CCC: $40.75

Table 1. Some Characteristics of Pentaerythritol Tetrahexanoate

chemical name	(acronym)	chemical formula	$\frac{MM_o}{g \cdot mol^{-1}}$	$\frac{\text{density}^a}{kg \cdot m^{-3}}$
pentaerythritol tetrahexanoate	PEC6	$C_{29}H_{52}O_8$	528.73	1004.2

[a] $p = 1$ bar, $T = 283.15$ K.

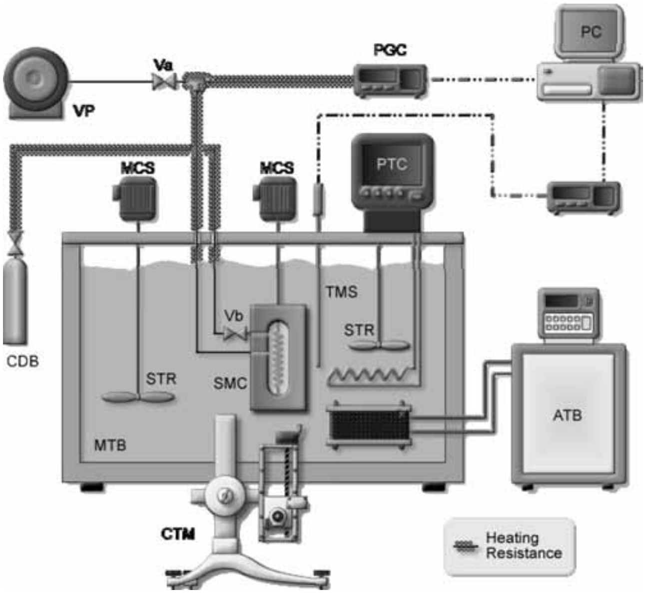

Figure 2. Schematic diagram of the apparatus. ATB, auxiliary thermostatic bath; CDB, carbon dioxide bottle; CTM, cathetometer; PC, data acquisition computer; MCS, measurement cell stirrer; MTB, main thermostatic bath; PGC, pressure gauge for measurement cell; PTC, PID temperature controller; SMC, solubility measurement cell; STR, stirrer; TMS, temperature measurement sensor; $V_{a,b}$, valves; VP, vacuum pump.

ester of hexanoic acid. This compound is obtained by the reaction of pentaerythritol with a carboxylic acid, here, *n*-hexanoic acid. The pentaerythritol ester molecule, with its four equal linear acid chains, is shown in Figure 1. To eliminate the noncondensable gases, PEC6 was put under a vacuum and then used with no further purification. Table 1 shows some characteristics of the oil considered in this work. Carbon dioxide (CO_2 CASRN 124-38-9) was supplied by Air Liquide with a declared purity of 99.95 %.

Experimental Apparatus. A specifically built apparatus based on the static synthetic method, shown in Figure 2, was used to perform the solubility measurements at the laboratories of ITC-CNR. The apparatus has already been described in Bobbo et al.,[4] but for the present measurements, some changes were necessary and here explained. The equilibrium between the two substances was reached in a stainless steel cell with a calibrated volume of about 180 cm^3, endowed with glass windows for observing the mixture. A helical stirrer moved by a magnetic engine was used to force the vapor phase through the liquid one to accelerate the achievement of the equilibrium. The cell was immersed in an 80 L thermostatic bath, in which the temperature was regulated by a PID controller, governing a heating resistance, which compensated the cooling capacity of an external auxiliary thermostatic bath with a stability of about 0.01 K. The two thermostatic baths were filled with water for temperatures higher than 273 K and with ethyl alcohol for lower temperatures. A 100 Ω platinum resistance thermometer was used to measure temperature with an accuracy of about 0.02 K, resulting in a total uncertainty for temperature (ΔT) of 0.03 K. For the pressure measurement, a Druck DPI 145 pressure gauge, with a full scale of 35 MPa and an uncertainty (Δp) of 20 kPa, was employed.

The solubility of CO_2 in PEC6 was calculated based on the level of the liquid phase in the equilibrium cell, as explained below, measured by means of a cathetometer (Gaertner Scientific M940LE). The resolution of the cathetometer was 0.0001 mm, while the uncertainty in the level's measurement (Δl) was estimated to be 0.05 mm.

Experimental Procedure. The cell volume was determined by calibration with the following procedure. The cell was filled with a weighed amount of nitrogen. After measuring temperature and pressure, the nitrogen density was calculated through the equation of state used by Refprop 8.0 database.[6] Finally, the volume was obtained by simply dividing the charged mass by the calculated density. The procedure was repeated several times at different temperatures and with different amounts of nitrogen, obtaining a repeatability of the results within 0.1 cm^3. The total estimated uncertainty in the calibration of the cell (ΔV_t) was about 0.8 cm^3.

For the measurements, the oil was directly charged in the cell, after purging it with acetone. The upper part of the cell was open, and a weighed amount of oil was introduced inside the cell by means of a glass syringe. The weight of the syringe was measured before and after the charge by means of an analytical balance (Gibertini E42S 240 g full scale) with an uncertainty (Δm_w) of 0.002 g. After this operation, the cell was reassembled, placed inside the bath, connected to the measurement circuit, and kept under vacuum overnight. Then an amount of carbon dioxide was transferred inside the cell from the sample bottle by simply exploiting the difference in pressure. The carbon dioxide mass transferred inside the cell was measured by weighing the bottle before and after the charge with the analytical balance mentioned before. Then the stirrer was turned on, until the inner pressure reached equilibrium, with the continuous acquisition of temperature and pressure. All along this procedure, the bath was set at the desired temperature.

Once the equilibrium was reached, the level of the meniscus between the liquid and vapor phase was measured by means of the cathetometer, and then the liquid volume V_l was calculated through a specific calibration equation, correlating volume and meniscus level. The CO_2 mass in the vapor phase was determined as the product between the vapor phase volume, calculated subtracting the liquid volume V_l (cm^3) from the total one of the cell V_t, and the CO_2 vapor density ρ_v (g·cm^{-3}), calculated through the Refprop 8.0 database.

Assuming only CO_2 in the vapor phase, due to the low vapor pressure of PEC6, the mass of CO_2 solved in the liquid m was calculated by a simple subtraction from the total mass charged m_w (g), as eq 1 shows

$$m = m_w - (V_t - V_l) \cdot \rho_v \tag{1}$$

At this point, the temperature of the bath was moved to the next desired value, and the entire procedure was repeated. It must be underlined that this temperature change was possible only in the thermostatic fluid working ranges. For this reason, the present experiment was performed in two independent runs, which covered the temperature ranges from (243.15 to 273.15) K and from (303.15 to 343.15) K. The isotherm at 283 K was measured in the past, independently from this series of measurements, and has already been the object of a publication.[2] Once all the isotherms of the same class were measured, a new amount of CO_2 was added to the one already present inside the cell, reaching a new mixture composition, and the whole process could start again, until the range of compositions for each isotherm in the actual class of temperature was completed. At this point, the fluid inside the thermostatic bath was changed, and all the operations were repeated for the new class.

For temperatures higher than the ambient temperature, the connection pipes outside the bath and the sensor of the pressure gauge were heated with a wire resistance regulated by a PID controller, to avoid the CO_2 condensation inside the tubes and the density deviations due to the temperature differences between the bath and the ambient temperature.

Considering all the estimated experimental uncertainties, the uncertainty in the liquid composition measurements (Δx), according to the following equation

$$\Delta x = \sqrt{\left(\frac{\partial x}{\partial m}\right)^2 \cdot \Delta m^2 + \left(\frac{\partial x}{\partial m_o}\right)^2 \cdot \Delta {m_o}^2 + \left(\frac{\partial x}{\partial \mathrm{MM}}\right)^2 \cdot \Delta \mathrm{MM}^2 + \left(\frac{\partial x}{\partial \mathrm{MM_o}}\right) \cdot \Delta {\mathrm{MM_o}}^2} \tag{2}$$

was estimated to be from 0.002 (high CO_2 molar fraction) to 0.02 (low CO_2 molar fraction). x is the molar fraction; m_o is the mass of the oil; Δm and Δm_o are the total uncertainties in the mass of carbon dioxide and the mass of the oil; and MM and $\mathrm{MM_o}$ ($\mathrm{g \cdot mol^{-1}}$) represent the carbon dioxide and oil molar masses, respectively.

x is calculated as

$$x = \frac{1}{1 + \frac{m_o}{m} \cdot \frac{\mathrm{MM}}{\mathrm{MM_o}}} \tag{3}$$

The two quantities depending on MM and $\mathrm{MM_o}$ ($\mathrm{g \cdot mol^{-1}}$) give negligible contributions to the total uncertainty and can be neglected.

Deriving eq 3, as indicated by eq 2, the Δm_o term being the uncertainty declared for the mass of the samples Δm_g, the only unknown quantity is Δm, which could be calculated through the following expression

$$\Delta m = \sqrt{\left(\frac{\partial m}{\partial m_w}\right)^2 \cdot \Delta {m_w}^2 + \left(\frac{\partial m}{\partial V_t}\right)^2 \cdot \Delta {V_t}^2 + \left(\frac{\partial m}{\partial V_l}\right)^2 \cdot \Delta {V_l}^2 + \left(\frac{\partial m}{\partial p}\right)^2 \cdot \Delta p^2 + \left(\frac{\partial m}{\partial T}\right)^2 \cdot \Delta T^2 + \left(\frac{\partial m}{\partial \rho_v}\right)^2 \cdot \Delta {\rho_v}^2} \tag{4}$$

deriving eq 1.

The term $(\partial m/\partial V_l)^2 \cdot \Delta {V_l}^2$ depends on the level measurements uncertainty (Δl) through the linear relationship $V_l = f(l)$ between the volume of the liquid phase and the level of the meniscus. For this reason, it becomes

$$\left(\frac{\partial m}{\partial V_l}\right)^2 \cdot \Delta {V_l}^2 = [f'(l) \cdot \rho_v] \cdot \Delta l^2 \tag{5}$$

Moreover, in the last term of eq 4, the uncertainty in the vapor phase density calculation ($\Delta \rho_v$) was assumed to be the one declared by the Refprop 8.0 database for the implemented equation of state, i.e., 0.05 %.

Results and Discussion

Experimental Data. The solubility along eight isotherms from (243.15 to 343.15) K was measured for the CO_2 + PEC6 system. All the experimental data are shown in Figure 3 and in Table 2. In this table, it is possible to distinguish the data obtained for the same bulk composition, being in the same row. Moreover, in every column, an asterisk indicates a new CO_2 charge after putting the cell under a vacuum, i.e., the composition for which CO_2 was charged to pure PEC6. It is worth noting that the isotherms at (323.15 and 343.15) K, i.e., over the critical temperature of CO_2, were measured up to 10 MPa, which is the maximum acceptable pressure inside the measurement cell. The figure shows that solubility increases when temperature decreases. Moreover, the system shows a negative deviation from Raoult's law, presumably due to the great difference in molecular size of the mixture components.

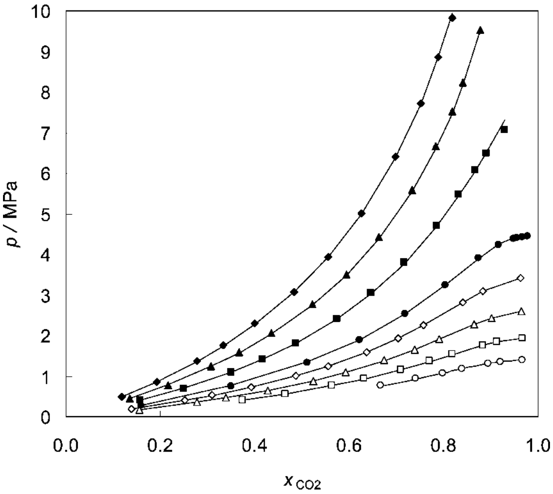

Figure 3. Solubility in molar fraction of CO_2 in PEC6 at: ○, 243.15 K; □, 253.15 K; △, 263.15 K; ◇, 273.15 K; ●, 283.15 K; ■, 303.15 K; ▲, 323.15 K; and ◆, 343.15 K; —, PR-HV-UNIQUAC EoS model.

Data Correlation. Data were correlated using the Peng–Robinson (PR) Equation of State (EoS)[7] in the form

$$p = \frac{RT}{v - b} - \frac{a}{v^2 + 2vb - b^2} \tag{6}$$

where p is the pressure (kPa); R is the universal ideal gas constant ($R = 8.31445\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$); v is the molar volume ($\mathrm{L \cdot mol^{-1}}$); T is the temperature (K); a and b are the EoS parameters; and the PR EoS was used with the Huron–Vidal mixing rules[8] and the UNIQUAC equation[9] for the g^E at infinite pressures.

Applying the HV mixing rules

$$a = b \cdot \left(x_1 \frac{a_{11}}{b_1} + x_2 \frac{a_{22}}{b_2}\right) - g_\infty^E \cdot c \tag{7a}$$

and

$$b = x_1 \cdot b_1 + x_2 \cdot b_2 \tag{7b}$$

with, specifically for the PR EoS,

$$c = \frac{2\sqrt{2}}{\ln\left[\frac{(2 + 2\sqrt{2})}{2 - 2\sqrt{2}}\right]} \tag{8}$$

and subscripts 1 and 2 are related to CO_2 and PEC4 throughout the paper, respectively.

In eq 7a, g_∞^E is represented by the UNIQUAC equation.

Table 2. Solubility of CO_2 in Pentaerythritol Tetrahexanoate (PEC6)

x	P/MPa	x	P/MPa	x	P/MPa	x	P/MPa	x	P/MPa	x	P/MPa	x	P/MPa	x	P/MPa
T = 243.15 K		T = 253.15 K		T = 263.15 K		T = 273.15 K		T = 283.15 K		T = 303.15 K		T = 323.15 K		T = 343.15 K	
				0.1561*	0.182	0.1391*	0.202	0.1592*	0.284	0.1581*	0.403	0.1358*	0.451	0.1188*	0.497
				0.2780*	0.363	0.2520*	0.404	0.3509	0.762	0.2501*	0.695	0.2164*	0.782	0.1929*	0.861
		0.3733*	0.412	0.3397*	0.472	0.3095*	0.527	0.5118	1.341	0.3497*	1.101	0.3079*	1.243	0.2770*	1.371
		0.4649*	0.564	0.4279*	0.649	0.3924*	0.729	0.6215	1.898	0.4162*	1.413	0.3670*	1.600	0.3332*	1.769
		0.5627	0.765	0.5242	0.889	0.4873	1.004	0.7190	2.536	0.4877*	1.816	0.4359*	2.065	0.3997*	2.291
0.6675*	0.767	0.6312	0.938	0.5932	1.099	0.5557	1.250	0.8038	3.258	0.5746*	2.416	0.5217*	2.766	0.4832*	3.083
0.7415	0.936	0.7098	1.166	0.6741	1.388	0.6369	1.597	0.8734	3.906	0.6470*	3.046	0.5937*	3.515	0.5552*	3.939
0.7973	1.074	0.7704	1.369	0.7385	1.661	0.7032	1.938	0.9159	4.239	0.7163*	3.797	0.6634*	4.433	0.6253*	5.008
0.8398	1.183	0.8184	1.541	0.7907	1.912	0.7579	2.268	0.9474	4.385	0.7849	4.710	0.7335	5.601	0.6986	6.399
0.8953	1.309	0.8834	1.764	0.8655	2.281	0.8402	2.822	0.9552	4.406	0.8323*	5.491	0.7833*	6.660	0.7510*	7.714
0.9199	1.352	0.9125	1.843	0.9010	2.436	0.8830	3.097	0.9660	4.427	0.8660*	6.080	0.8178*	7.536	0.7898*	8.851
0.9669	1.401	0.9659	1.930	0.9644	2.592	0.9621	3.410	0.9771	4.441	0.8903	6.501	0.8414	8.244	0.8185	9.821
										0.9290	7.067	0.8787	9.520		

Table 3. Pure Compound Parameters Used in the Data Correlation

compound	T_c/K	p_c/kPa	R_k	Q_k
CO_2	304.13	7377.3	1.3000	0.982
PEC6	931.2[10]	848.7[11]	22.8319	18.992

Table 4. Values of the Binary Interaction Parameters of the PR-HV-UNIQUAC Model for the CO_2 + PEC6 System

$a_{22,0}$	$a_{22,1}$	$\tau_{12,0}$	$\tau_{12,1}$	$\tau_{21,0}$	$\tau_{21,1}$
148401.8	−655.020	0.5827213	0.0010159	0.3164054	−0.0003598

The temperature dependence a_{22} took the following expression

$$a_{22} = a_{22,0} + a_{22,1} \cdot (T - 273.15) \tag{9}$$

Moreover, two parameters for the UNIQUAC equation had to be found, with similar temperature dependence

$$\tau_{12} = \tau_{12,0} + \tau_{12,1} \cdot (T - 273.15) \tag{10}$$

and

$$\tau_{21} = \tau_{21,0} + \tau_{21,1} \cdot (T - 273.15) \tag{11}$$

The correlation of data about components with unknown general thermodynamic properties, as PEC6, needs a special procedure because it is impossible to define the temperature dependence of the a_{22} parameter in the EoS applied. So, the actual value of the a_{22} parameter and its temperature dependence were found from the correlation of the solubility data together with the regression of UNIQUAC parameters, with their temperature dependence. The second EoS parameter characterizing PEC6, i.e., b_2, was found from the estimated values of the critical parameters of POE, and it was assumed independent of temperature. Six parameters were regressed: two are characteristic for the ill-defined component, i.e., PEC6, and four refer to the interaction between CO_2 and PEC6. The estimated critical parameters[10,11] along with the UNIQUAC (R_k) and (Q_k) parameters obtained from the van der Waals group volume and surface areas given by Bondi[12] are shown in Table 3. The parameters were found minimizing the following objective function

$$\text{obj} = \sum_{i=1}^{Np} \frac{|p_{\text{calc}} - p_{\text{exp}}|}{p_{\text{exp}}} \tag{12}$$

and they are summarized in Table 4.

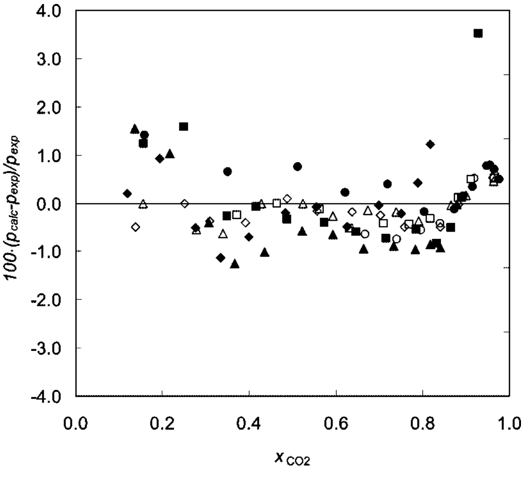

Figure 4. Deviations of the experimental solubility data in pressures from the PR-HV-UNIQUAC EoS model at ○, 243.15 K; □, 253.15 K; △, 263.15 K; ◇, 273.15 K; ●, 283.15 K; ■, 303.15 K; ▲, 323.15 K; and ◆, 343.15 K.

The deviations in pressure are presented in Figure 4. It is evident that data are quite randomly distributed as a function of composition, being mostly within ± 1 %. Greater deviations are observed only for low CO_2 concentration, due to a greater uncertainty in the composition measurements in this domain, as evident from the error analysis. It is worth mentioning that the found parameters with their linear temperature dependence are able to represent experimental data both below and above critical temperature of CO_2. Slightly greater deviations were noted only at pressures above CO_2 critical pressure (p_c). Probably, they could be observed also in proximity of pure CO_2 critical point because of the simplicity of the model applied. In general, however, the overall representation of the experimental data is satisfying.

Conclusions

This paper presents a series of solubility measurements of carbon dioxide in pentaerythritol tetrahexanoate at temperatures between (243.15 and 343.15) K. The solubility data were successfully correlated with a model based on the Peng−Robinson equation of state and Huron−Vidal mixing rules with the UNIQUAC equation for the g^E at infinite pressures.

Acknowledgment

Mauro Scattolini is gratefully acknowledged for his kind help.

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Received for review June 16, 2008. Accepted September 25, 2008.

JE800429J