# Solubility Measurements and Data Correlation of Carbon Dioxide in Pentaerythritol Tetra(2-ethylbutanoate) (PEBE6)

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Carbon dioxide is one of the most promising alternative refrigerants, but its compatibility with compressor lubricants is still almost unknown. The solubility of refrigerants in oils is one of the most important properties in the selection of the proper lubricant. For this reason, in our laboratories a systematic research program on the solubility of carbon dioxide in oils has been started, putting particular attention on its dependence on lubricant chemical structure, temperature, and pressure. In this paper, experimental solubility data and their correlation of carbon dioxide in a precursor of polyol ester oil, that is, pentaerythritol tetra(2-ethylbutanoate), are presented in the temperature range of (283 to 343) K and pressures up to 10 MPa.

## Introduction

Because of its low global warming potential (GWP), carbon dioxide ($CO_2$) has returned to popularity as an alternative refrigerant, even if it still presents some problems as a working fluid for its high operating pressure and because its behavior with the common lubricants is little-known.

For this reason, a research study dedicated to the measurements and modeling of solubility data of $CO_2$ in oils is ongoing in our laboratories, for example, Bobbo et al. (2005),[1] Bobbo et al. (2007),[2] and Fedele et al. (2009).[3] Since theoretical models can be difficult to apply to commercial synthetic lubricants that are mixtures of several components and additives, often not well-specified, particular attention has been paid to lubricant precursors.

In this work, the solubility measurements and data correlation for the system $CO_2$ + pentaerythritol tetra(2-ethylbutanoate) (PEBE6) are presented in the temperature range between (283 and 343) K and pressures up to 10 MPa.

These data were correlated by means of the Peng−Robinson[4] equation of state with the Huron−Vidal[5] (HV) mixing rules, in which the excess Gibbs energy at infinite pressures was represented by the universal quasichemical (UNIQUAC)[6] equation.

## Experimental Section

***Materials.*** Pentaerythritol tetra(2-ethylbutanoate) (PEBE6, $C_{29}H_{52}O_8$, CAS RN 139116-32-8) was synthesized by Chemipan (Poland) on a laboratory scale with a declared purity higher than 98 %. To eliminate the noncondensable gases, the sample was put under vacuum and then used with no further purification.

Carbon dioxide ($CO_2$, CAS RN 124-38-9) was supplied by Air Liquide with a declared purity of 99.95 %.

***Experimental Apparatus and Procedure.*** The solubility measurements were performed in a specifically built apparatus, already described in previous papers.[1,2] Here only its main characteristics will be illustrated.

The thermodynamic equilibrium between $CO_2$ and PEBE6 was reached in a stainless steel cell, of about 180 $cm^3$, provided with glass windows for the visualization of the mixture, necessary for the measurements. Moreover, the observation of the mixture enables us to detect possible appearances of second liquid or solid phases.

To get a faster equilibrium, the mixture was stirred by means of a magnetically driven helical stirrer inside the cell.

A 80 L water thermostatic bath, in which the cell was immersed, ensured a temperature stability of about 0.01 K. The temperature was measured by means of a 100 Ω platinum resistance thermometer with an error of about 0.02 K, resulting in a total temperature measurements uncertainty of about 0.03 K. A Druck DPI 145 pressure gauge, with a full scale of 10 MPa and an uncertainty of 0.004 MPa, was used for the pressure measurements.

After cleaning the cell with acetone, a known amount of PEBE6 was directly introduced in it. Considering that pure PEBE6 is a solid at ambient temperature, becoming liquid only at temperature higher than 303.15 K, it was heated at temperatures higher than 333 K and immediately charged in a syringe. By means of this syringe, the oil was then charged in the cell. An analytical balance (Gibertini E42S 240 g full scale), with an uncertainty of 0.002 g, was used to weigh the syringe before and after the charge. Then the measurement circuit was put under vacuum. After that, $CO_2$ was added to the cell from the sample bottle, exploiting the pressure difference, and the $CO_2$ transferred mass was measured by weighing the bottle before and after the transfer. Once the equilibrium was reached at a set temperature, the meniscus level between liquid and vapor phases was measured by means of a cathetometer (Gaertner Scientific M940LE), with a resolution of 0.0001 mm and an uncertainty of about 0.05 mm. Through a specific calibration equation, the liquid volume was calculated relating the volume itself to the meniscus level. Because of the low PEBE6 vapor pressure, the vapor phase was assumed to be occupied only by $CO_2$. Then the $CO_2$ mass solubilized in the liquid was calculated by subtracting the mass of $CO_2$ in vapor phase from the total $CO_2$ mass charged. The $CO_2$ mass in the vapor phase was determined by multiplying the vapor phase volume and sub-

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**Table 1. Experimental Solubility Data of $CO_2$ in Pentaerythritol Tetra(2-ethylbutanoate) (PEBE6)**

| $x$ | $p$/MPa | $x$ | $p$/MPa | $x$ | $p$/MPa | $x$ | $p$/MPa |
|---|---|---|---|---|---|---|---|
| $T$ = 283.15 K | | $T$ = 293.15 K | | $T$ = 303.15 K | | $T$ = 313.15 K | |
| | | | | 0.1666 | 0.437 | 0.1504 | 0.465 |
| | | | | 0.1690 | 0.428 | 0.1521 | 0.461 |
| | | 0.3322 | 0.848 | 0.3073 | 0.909 | 0.2853 | 0.970 |
| 0.4610 | 1.115 | 0.4308 | 1.217 | 0.4042 | 1.314 | 0.3779 | 1.409 |
| 0.5699 | 1.585 | 0.5361 | 1.744 | 0.5061 | 1.892 | 0.4784 | 2.034 |
| | | | | | | 0.5785 | 2.857 |
| 0.6747 | 2.193 | 0.6412 | 2.435 | 0.6094 | 2.661 | 0.5815 | 2.876 |
| 0.7480 | 2.726 | 0.7149 | 3.062 | 0.6847 | 3.372 | 0.6552 | 3.662 |
| 0.8602 | 3.720 | 0.8314 | 4.345 | 0.8029 | 4.905 | 0.7758 | 5.417 |
| 0.9442 | 4.298 | 0.9283 | 5.390 | 0.9004 | 6.425 | 0.8737 | 7.325 |
| 0.9633 | 4.386 | 0.9579 | 5.590 | 0.9381 | 7.008 | 0.9088 | 8.297 |
| $T$ = 323.15 K | | $T$ = 333.15 K | | $T$ = 343.15 K | | | |
| | | 0.1328 | 0.514 | 0.1248 | 0.538 | | |
| 0.1439 | 0.483 | 0.1348 | 0.508 | 0.1276 | 0.533 | | |
| 0.2693 | 1.024 | 0.2525 | 1.078 | 0.2359 | 1.128 | | |
| | | | | 0.3202 | 1.641 | | |
| 0.3571 | 1.493 | 0.3398 | 1.576 | 0.3222 | 1.656 | | |
| 0.3619 | 1.533 | 0.3439 | 1.615 | | | | |
| 0.3722 | 1.584 | | | | | | |
| 0.4522 | 2.165 | 0.4314 | 2.290 | 0.4165 | 2.408 | | |
| 0.5577 | 3.073 | 0.5337 | 3.262 | 0.5172 | 3.443 | | |
| 0.6301 | 3.931 | 0.6099 | 4.188 | 0.5913 | 4.429 | | |
| 0.7519 | 5.895 | 0.7332 | 6.341 | 0.7207 | 6.763 | | |
| 0.8573 | 8.123 | 0.8474 | 8.873 | 0.8388 | 9.632 | | |
| 0.8898 | 9.540 | | | | | | |

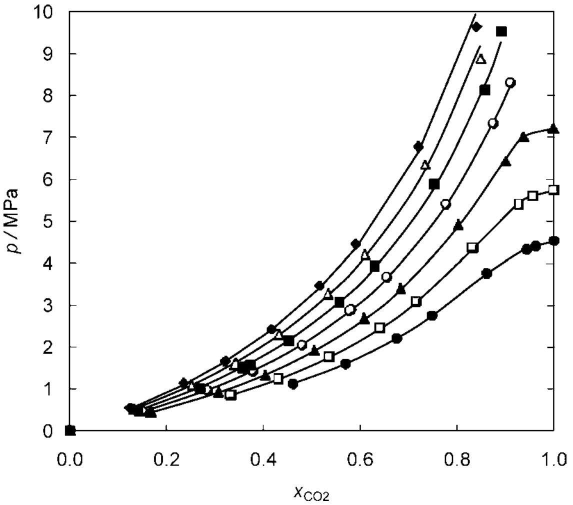

**Figure 1.** Solubility in mole fraction of $CO_2$ in PEBE6 at ●, 283.15 K; □, 293.15 K; ▲, 303.15 K; ○, 313.15; ■, 323.15 K; △, 333.15 K and ♦, 343.15 K. —, PR-HV-UNIQUAC EoS model.

**Table 2. Pure Compound Parameters**

| compound | $T_c$/K | $p_c$/MPa | acentric factor | $R_k$ | $Q_k$ |
|---|---|---|---|---|---|
| $CO_2$ | 304.13[7] | 7.3773[7] | 0.225[11] | 1.300 | 0.982 |
| PEBE6 | 899.0[12] | 0.9481[13] | | 21.0411 | 18.064 |

tracting the liquid volume from the total one of the cell and the $CO_2$ vapor density estimated through the Refprop 8.0 database.[7]

The bath temperature was then changed to the next desired value and the entire experimental procedure repeated. Once the same bulk composition was measured at each isotherm, the cell was put under vacuum and then charged at the next required composition.

The uncertainty analysis has been deeply investigated in a previous paper.[8] Considering the total estimated uncertainties in the calibration of the cell, in the syringe weight, at the meniscus level, for temperature and pressure measurements, and in the estimation of the vapor phase density through Refprop 8.0, the overall uncertainty in the liquid composition was estimated to be 0.003.

## Results and Discussion

***Experimental Data.*** Isothermal solubility measurements of $CO_2$ in PEBE6 were performed at (283.15, 293.15, 303.15, 313.15, 323.15, 333.15, and 343.15) K. These data are shown in Table 1 and presented in Figure 1. Pure PEBE6 is a solid at ambient temperature, becoming liquid only at temperature higher than 303.15 K. For this reason, only the compositions and temperatures shown in Table 1 were considered. In this table, the data with the same bulk composition are evident, being in the same row.

The liquid phase compositions at temperatures higher than the critical temperature of $CO_2$, that is, 304.13 K, were measured up to the pressure limit of the apparatus (10 MPa).

***Data Correlation.*** The correlation method and procedure employed on the experimental data have been already described in Fedele et al.,[3] and only its main outlines are described here. The Peng−Robinson (PR) equation of state (EoS), with the HV mixing rules and the UNIQUAC equation for the excess Gibbs energy ($G^E$) at infinite pressure, were applied to the experimental data, but not in the usual way. In fact, the pure compound parameters for the PEBE6 had to be derived, since this fluid is almost unknown in the literature. Saturated pressures cannot be used for the derivation of the $a_{22}$ parameter, characterizing the attractive forces in the cubic EoS. However, some vapor pressures for other pentaerythritol esters were measured to be between ($5.6 \cdot 10^{-5}$ and 0.94) Pa and between (334 and 476) K.[9] For this reason, the volatility of PEBE6 was considered practically negligible in the experimental temperature range. The $a_{22}$ parameter was found together with the binary interaction parameters, tuning the experimental solubility data only. The $b_{22}$ parameter was calculated from the estimated critical parameters of PEBE6 with the PR EoS, and in this approach, it was not dependent by the experimental solubility data and the mixing rules used for the data regression.

The temperature dependence of $a_{22}$ (the PR EoS parameter) took the following expression:

$$a_{22} = a_{22,0} + a_{22,1}(T/\text{K} - 273.15) \tag{1}$$

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

$$\tau_{12} = \tau_{12,0} + \tau_{12,1}(T/\text{K} - 273.15) \tag{2}$$

and

$$\tau_{21} = \tau_{21,0} + \tau_{21,1}(T/\text{K} - 273.15) \tag{3}$$

The estimated critical parameters, along with the UNIQUAC ($R_k$) and ($Q_k$) parameters obtained from the van der Waals group volume and surface areas, according to Bondi,[10] for both compounds are shown in Table 2.

All six parameters appearing in eqs 1 to 3 were found in the process of tuning the data as a combined set minimizing the following objective function:

$$\text{obj} = \sum_{i=1}^{N_p} \left( \frac{p_{\text{calc}} - p_{\text{exp}}}{p_{\text{exp}}} \right)^2 \tag{4}$$

The results of the correlations are reported in Table 3.

**Table 3. Parameters of Equations 1 to 3 and Resulting Deviations**[a]

| $i$ | $a_{22,i}$ | $\tau_{12,i}$ | $\tau_{21,i}$ | AAD/MPa | 100·ARD |
|---|---|---|---|---|---|
| 0 | 133.280 | 0.486381 | 0.353031 | 0.0368 | 1.02 |
| 1 | −0.756282 | 0.0000545 | −0.0009506 | | |

[a]

$$\mathrm{AAD} = \frac{\sum_{i=1}^{N_p} |p_{i,\mathrm{calc}} - p_{i,\mathrm{exp}}|}{N_p}$$

$$\mathrm{ARD} = \frac{\sum_{i=1}^{N_p} \left|\frac{p_{i,\mathrm{calc}} - p_{i,\mathrm{exp}}}{p_{i,\mathrm{exp}}}\right|}{N_p}$$

$N_p$ = number of points.

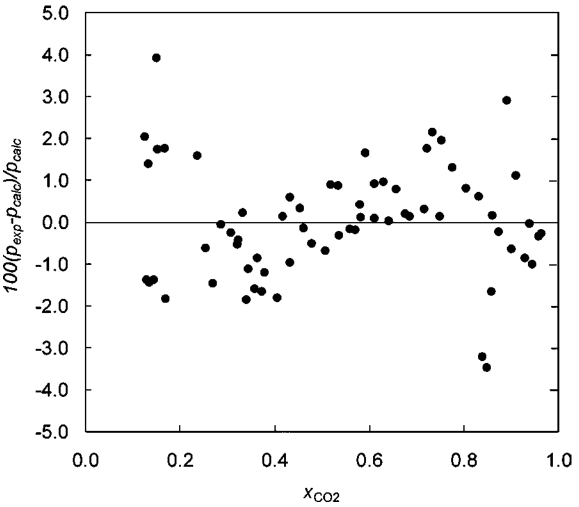

**Figure 2.** Percentage deviations in terms of $CO_2$ composition between the experimental solubility data and the PR-HV-UNIQUAC EoS model.

The deviations between the experimental data and the model are shown in Figure 2. The model represents the system pressures well within 1 %. However, plotting absolute pressure deviations, as shown in Figure 3, greater errors are clearly evident at high pressures, that is, higher than $CO_2$ critical pressure. They are evidently greater than those resulting from random experimental errors, hence rather due to the model (i.e., a two-parameter cubic EoS). For this reason, particular attention must be paid to the VLE prediction at high pressures, especially higher than the critical point.

## Conclusions

In this paper, solubility measurements of carbon dioxide in pentaerythritol tetra(2-ethylbutanoate) are presented between (283.15 and 343.15) K.

As for the other polyolester (POE) precursors, solubility increases when temperature decreases. The system shows a negative deviation from Raoult's law, probably because of the great difference in molecular size of the mixture components. The solubility data were successfully correlated by means of the PR EoS implementing the HV mixing rules with the UNIQUAC equation for the $G^E$ at infinite pressures. In general, the model represents the data within 0.05 MPa.

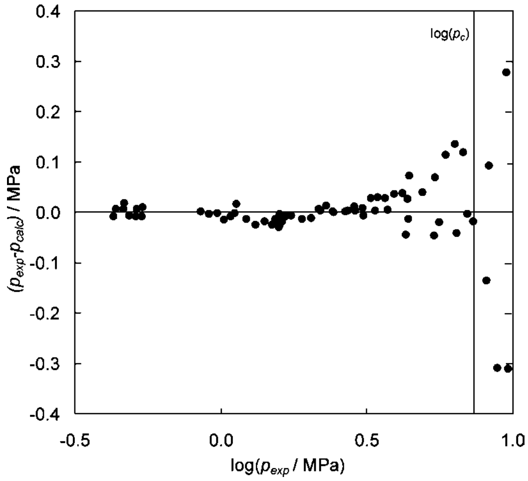

**Figure 3.** Deviations in terms of pressure between the experimental solubility data and the PR-HV-UNIQUAC EoS model.

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