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Solubility Temperature Dependence and Data Correlation of Carbon Dioxide in Pentaerythritol Tetra-2-methylbutyrate

Laura Fedele,*,† Sergio Bobbo,† Francesco Pernechele,† 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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In the past years, the employment of carbon dioxide as an alternative is becoming significant. Its compatibility with synthetic compressor lubricants is still a problem far from a solution. In the literature, only a few data on the mutual solubility of the carbon dioxide−lubricant systems are present, although it is one of the main properties affecting the selection of the proper lubricant. At our laboratories, a systematic study on the solubility of carbon dioxide in lubricants has been started, trying to identify its dependence on pressure, temperature, and oil chemical structure. In this work, experimental solubility data of carbon dioxide in pentaerythritol tetra-2-methylbutyrate, i.e., a precursor of polyol ester oil, are presented in the temperature range of (243 to 343) K and pressure up to 10 MPa. 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 pressure was represented by the UNIQUAC equation assuming a temperature dependence of the fitted parameters.

Introduction

Carbon dioxide (CO_2) is one of the most promising alternatives to refrigerants, characterized by high global warming potential (GWP).

However, the behavior of CO_2 mixtures with lubricants is still little known. The knowledge of the thermodynamic behavior of the refrigerant−lubricant system is very important in the design of the refrigeration plants, since the actual circulating fluid in the circuit is a refrigerant−lubricant mixture. In fact, it is widely known that the lubricant does not remain contained in the compressor tank, but a certain amount of oil is dragged into the circuit.

Commercial synthetic oils are mixtures of several components and additives, generally not well-specified by the producers. Hence, the definition of theoretical models able to represent the thermodynamic properties of these mixtures presents several difficulties and cannot be based only on experimental data, due to the undefined composition of oils. Experimental data on the precursors of commercial lubricants should be more useful to develop such kinds of models.

For this reason, a research program on the experimental measurements and modeling of the phase behavior of commercial polyol ester oils (POE) and their precursors mixed with carbon dioxide has been started in our laboratories. In particular, solubility of CO_2 in lubricants, e.g., Bobbo et al. (2005),[1] Bobbo et al. (2007),[2] Bobbo et al. (2008),[3] and compressed liquid densities of pure POE precursors, e.g., Fedele et al. (2008),[4] have been studied.

Here, the solubility measurements and data correlation for the system CO_2−pentaerythritol tetra-2-methylbutyrate (PEBM5) are presented in the temperature range between (243 and 343) K and pressure up to 10 MPa.

The experimental data were next correlated as a combined set by means of the Peng−Robinson[5] equation of state with the Huron−Vidal[6] mixing rules in which the excess Gibbs energy at infinite pressure was represented by the UNIQUAC[7] equation. A temperature dependence of the fitted parameters was applied due to the wide experimental temperature range.

Experimental Section

Materials. The studied PEBM5 ($C_{25}H_{44}O_8$, CASRN 25811-38-5) was synthesized by Chemipan (Poland) on a laboratory scale with a declared purity higher than 98 %. Figure 1 shows the chemical structure of PEBM5.

To eliminate the noncondensable gases, the sample was put under vacuum and then used with no further purification. Table 1 shows some characteristics of PEBM5.

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

Experimental Apparatus and Procedure. The apparatus employed for these measurements has been already described in previous papers,[1,3] and here only its main characteristics will be specified.

The thermodynamic equilibrium between CO_2 and PEBM5 was reached in a stainless steel cell with a calibrated volume of about 180 cm^3, endowed with glass windows for the visual observation of the mixture. A magnetic engine moved a helical stirrer inside the cell, to facilitate the achievement of equilibrium.

The cell was immersed in an 80 L thermostatic bath, filled with water or ethyl alcohol for temperatures higher or lower than 273 K, respectively. Temperature was regulated with a stability of about 0.01 K by a PID control, governing a heating resistance, which compensated the cooling capacity of an external thermostatic bath. Temperature was measured by means of a 100 Ω platinum resistance thermometer with an accuracy of about 0.02 K, resulting in a total temperature measurement uncertainty of about 0.03 K. A Druck DPI 145 pressure gauge,

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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.

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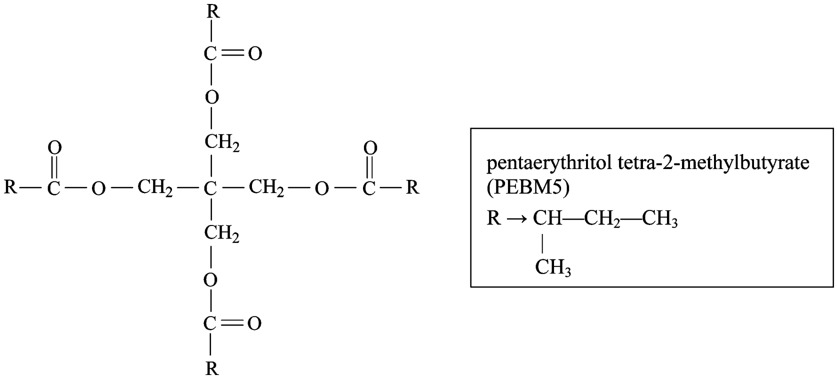

Figure 1. Chemical structure of the pure PEBM5.

Table 1. Some Characteristics of PEBM5

chemical name	(acronym)	chemical formula	MM_o $g \cdot mol^{-1}$	density[a] $kg \cdot m^{-3}$
pentaerythritol tetra-2-methylbutyrate	PEBM5	$C_{25}H_{44}O_8$	472.62	1023.2

[a] $p = 0.1$ MPa, $T = 283.15$ K.

Table 2. Solubility of CO_2 in PEBM5

	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	
nc[a]							0.355	0.609
nc							0.486	0.966
am[b]					0.563	0.962	0.525	1.103
nc							0.630	1.520
am			0.705	1.096	0.670	1.320		
nc			0.747	1.223	0.715	1.499	0.680	1.756
am							0.699	1.852
am	0.813	1.053	0.791	1.366	0.761	1.702	0.728	2.018
am	0.845	1.139	0.826	1.502	0.802	1.888	0.772	2.274
am	0.879	1.219	0.865	1.634	0.846	2.105	0.821	2.589
am	0.900	1.270	0.890	1.717	0.875	2.242	0.855	2.805
am	0.926	1.323	0.921	1.812	0.913	2.402	0.900	3.088
am	0.949	1.360	0.947	1.870	0.943	2.506	0.937	3.274
am	0.968	1.386	0.967	1.910	0.966	2.565	0.965	3.369
	$T = 283.15$ K							
nc	0.114	0.185						
am	0.259	0.496						
am	0.400	0.897						
am	0.531	1.394						
am	0.576	1.605						
am	0.654	2.040						
am	0.749	2.700						
am	0.826	3.350						
am	0.893	3.940						
am	0.966	4.360						
	$T = 303.15$ K		$T = 323.15$ K		$T = 343.15$ K			
nc	0.109	0.273	0.093	0.307	0.081	0.338		
nc	0.239	0.670	0.206	0.757	0.182	0.836		
nc	0.331	1.021	0.289	1.157	0.257	1.281		
nc	0.438	1.533	0.388	1.747	0.349	1.941		
nc	0.520	2.024	0.467	2.321	0.425	2.587		
nc	0.651	3.057	0.595	3.554	0.554	4.000		
nc	0.720	3.793	0.662	4.461	0.623	5.064		
nc	0.819	5.124	0.763	6.222	0.730	7.197		
nc	0.887	6.217	0.837	7.899	0.809	9.376		
am	0.939	6.897	0.888	9.401				

[a] nc = new charge. [b] am = adding method.

with a full scale of 35 MPa and an uncertainty of 0.02 MPa, was used for the pressure measurements.

PEBM5 was directly charged in the cell, after purging with acetone, simply opening the cell, and introducing a weighed amount of oil by means of a glass syringe. The syringe weight was measured before and after the charge by means of an analytical balance (Gibertini E42S 240 g full scale) with an uncertainty of 0.002 g. Then the apparatus was reassembled and the measurement circuit put under vacuum. Carbon dioxide was transferred inside the cell from a sample bottle, simply exploiting the difference in pressure, and 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.

At equilibrium, reached at the set temperature, the level of the meniscus 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 in the level's measurement of about 0.05 mm. The liquid volume was calculated correlating volume and meniscus level, by a specific calibration equation. Assuming only CO_2 in the vapor phase, due to the low vapor pressure of PEBM5, the mass of CO_2 dissolved in the liquid was calculated by subtracting the CO_2 in the vapor phase from the total CO_2 mass charged. The CO_2 mass in the vapor phase was determined multiplying the vapor phase volume, calculated by subtracting the liquid volume from the total one of the cell, and the CO_2 vapor density was estimated through the Refprop 8.0 database.[8]

Then, the bath temperature was changed to the next desired value and the entire experimental procedure repeated.

Of course, the temperature change was possible only within the thermostatic fluid's working range. For this reason, experimental data were sorted into two classes, i.e., one for temperatures lower than or equal to 273 K, the other for temperatures above or equal to 283 K.

The experiment was performed employing two different methods in charging CO_2. A part of the solubility data was obtained adding a new amount of CO_2 to the existing in the cell mixture. These data are called as obtained with the "adding method" and denoted in Table 2 with acronym "am". The other part of the solubility data was obtained charging CO_2 to pure PEB5 if a new sample of PEB5 was charged in the cell or if existing CO_2 was removed putting the sample under vacuum. These data are called as obtained with "new charge" and denoted with acronym "nc" in Table 2. All the other details of the solubility measurements are common for both charging options. For the same bulk composition, the system pressures and volumes of liquid and vapor phases were measured for every isotherm. The range of temperatures was adopted relative to the properties (thermal stability, viscosity, and melting temperature) of the thermostatic fluid.

Then, the thermostatic fluid was changed, and all the described procedures were repeated for the new class.

Considering all the estimated contributions to experimental uncertainties, the overall uncertainty in the liquid composition

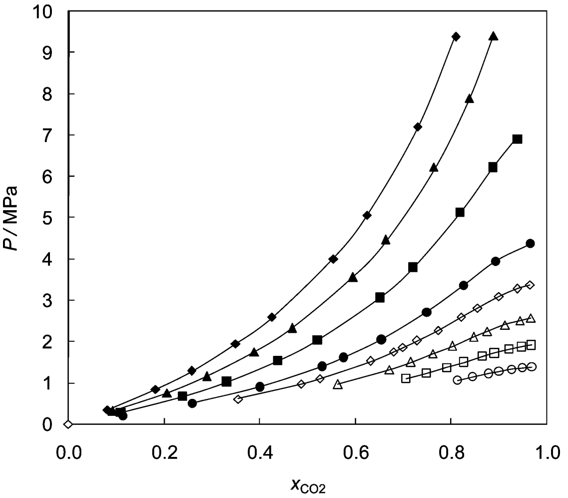

Figure 2. Solubility in molar fraction of CO_2 in PEBM5: ○, 243.15 K; □, 253.15 K; △, 263.15 K; ◇, 273.15 K; ●, 283.15 K; ■, 303.15 K; ▲, 323.15 K; ◆, 343.15 K; and —, PR-HV-UNIQUAC EoS model.

was estimated to be from 0.002 (high CO_2 mole fraction) to 0.02 (low CO_2 mole fraction).

Results and Discussion

Experimental Data. The solubility of CO_2 in PEBM5 was measured at (243.15, 253.15, 263.15, 273.15, 303.15, 323.15, and 343.15) K. The present experimental data are completed by the solubility data at 283.15 K, already measured and published.[2] The experimental data are summarized in Table 2 and shown in Figure 2. In this table, the data obtained for the same bulk composition are evident, being placed in the same row. In addition, points corresponding to a new CO_2 charge after putting the cell under vacuum are indicated with the acronym nc, while those obtained by means of the adding method are indicated as am.

The two isotherms at temperatures higher than the critical temperature of CO_2, specifically (323.15 and 343.15) K, were measured up to 10 MPa, i.e., the pressure limit of our apparatus.

As for the other POE precursors, solubility increases when temperature decreases. The system shows a negative deviation from the Raoult's law, probably due to the great difference in molecular size of the mixture components.

Data Correlation. The solubility data were correlated by means of a Peng−Robinson (PR) equation of state (EoS) with the Huron−Vidal mixing rules (HV) and the UNIQUAC equation for the excess Gibbs energy (g^E) at infinite pressure. The employed method and procedure were already described by us.[3] The PR EoS, the fugacity coefficient for the HV mixing rule, and the UNIQUAC equation for the excess Gibbs energy are not repeated in this paper in their explicit form as being widely known and very popular in use, with the exception of the PR EoS volume parameters, that was obtained as $b = \Omega_b \cdot R \cdot T_c / P_c$ with $\Omega_b = 0.077796$ (for the PR EoS, it is a constant value).

However, the applied model (PR-HV-UNIUAC) was not used in the usual way. The specificity of the method is the derivation of the pure compound parameters for the PEBM5. The a_{22} parameter, characterizing the attractive forces in the cubic EoS, can not be derived from the pure compound saturated pressures because the vapor pressure of PEBM5 is not yet available in the literature. Some vapor pressures for other pentaerythritol esters, such as pentaerythritol tetrapentanoate, pentaerythritol tetraheptanoate, pentaerythritol tetranonanoate, and pentaerythritol tetra-2-ethylhexanoate, were recently measured between (334 and 476) K.[9] For these compounds, experimental vapor pressures were found to be between $5.6 \cdot 10^{-5}$ Pa and 0.94 Pa. For this reason, within the experimental temperature range, the volatility of PEBM5 (and thus its presence in the vapor phase) can be considered practically negligible. The a_{22} parameter is found together with the binary interaction parameters, tuning the experimental solubility data only. The b_{22} parameter is calculated from the estimated critical parameters of PEBM5 with the PR EoS, and in this approach, it is not dependent on the experimental solubility data and the mixing rules used for the data regression.

Table 3. Pure Compound Parameters

compound	T_c/K	p_c/MPa	acentric factor	R_k	Q_k
CO_2	304.13[8]	7.3773[8]	0.225[11]	1.3000	0.982
PEBM5	899.0[12]	0.9481[13]		18.3435	15.904

Table 4. Parameters of Equations 1 to 3 and Resulting Deviations[a,b,c]

i	$a_{22,i}$	$\tau_{12,i}$	$\tau_{21,i}$	AAD(Δp)/MPa	AAD(Δp %)
0	100.9	0.5416	0.3939	0.009	0.34
1	− 0.519	−0.0003	−0.0008		

[a] N_p = number of points. [b] AAD(Δp) = $\sum_{i=1}^{N_p} |p_{i,\mathrm{calc}} - p_{i,\mathrm{exp}}| / N_p$. [c] AAD($\Delta p$ %) = $100 \cdot \sum_{i=1}^{N_p} |p_{i,\mathrm{calc}} - p_{i,\mathrm{exp}}| / p_{i,\mathrm{exp}} / N_p$.

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

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

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

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

and

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

All six parameters appearing in eqs 1 to 3 were found in the process of tuning the data as a combined set.

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] are shown in Table 3.

The parameters were found minimizing the following objective function

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

and the results of the correlations are reported in Table 4.

The deviations between the experimental data and the model are shown in Figure 3. The model is able to represent the data well within 0.02 MPa, i.e., the declared uncertainty of the Druck DPI 145 pressure gauge used. Only five data points showed greater deviations, being either positive or negative, hence rather not systematic.

Conclusions

In this paper, solubility measurements of carbon dioxide in pentaerythritol tetra-2-methylbutyrate are presented 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 pressure. In general, the model is able to represent the data

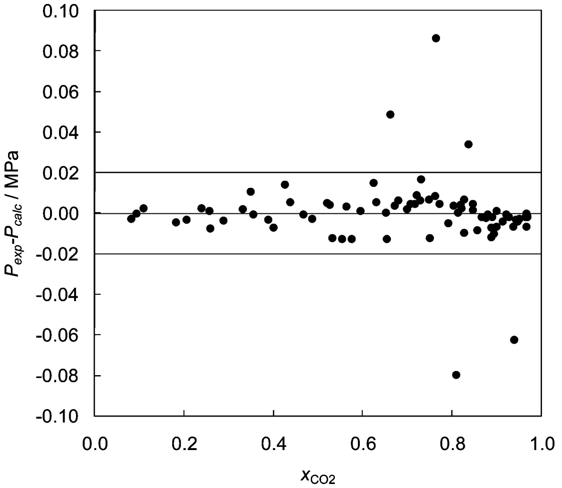

Figure 3. Deviations in terms of pressure between the experimental solubility data and the PR-HV-UNIQUAC EoS model.

within 0.02 MPa, i.e., within the limit of uncertainty of the employed pressure gauge.

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