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Solubilities of Carbon Dioxide in a Dipentaerythritol Ester and in a Polyether[†]

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The solubility of carbon dioxide, CO_2, in dipentaerythritol hexaheptanoate (DiPEC7) and a polypropylene glycol dimethyl ether (PAG1) was measured at 283.15 K, 298.15 K, 323.15 K, and 348.15 K, and pressures up to 7 MPa in a high-pressure gas solubility apparatus. A total of 42 *pTx* values were measured with an isochoric technique, having a mole fraction relative uncertainty of 4 %. The results for DiPEC7 together with the experimental literature data show that, in the present analyzed range, the CO_2 solubility expressed in mole fraction in the polyolester oils increases with the number of the polar carboxyl groups. In mass fraction, the solubilities of CO_2 in DiPEC7 are lower than in PAG1 and also lower than in several other pentaerythritol esters (PEs).

Introduction

Often vehicles have some limitations like the loss of efficiency during the use of their air-conditioning system. The common vapor compression refrigeration systems derive power from the transmission to run a compressor to pressurize the refrigerant. For the correct operation of the compressor it is necessary to use a refrigeration lubricant. Because part of the oil always migrates from the compressor the working fluid of the system is changed from a pure refrigerant with well-known properties to a mixture with properties that are poorly understood and dependent on the concentration. Thus, the presence of oil in the system induces changes in the flow of the refrigerant circulating through the cycle and the pressure drop increases and changes of the thermodynamic properties of actual refrigerant (viscosity, liquid−vapor equilibrium, etc.).[1] On the other hand, the refrigerant and the oil come into contact in the compressor, and part of the gas is dissolved in the oil changing the lubricant properties. Accordingly, the lubricant of the compressor is changed from a lubricant with suitable antiwear properties to a mixture with lower viscosity, which depends on the refrigerant solubility.

So far, in automotive air-conditioning systems and other refrigeration applications hydrofluorocarbons (HFCs) are being used as refrigerants, but because of the greenhouse effect, they should be replaced by other gases such as carbon dioxide, CO_2, or isobutane. However, the use of CO_2 still presents several unsolved technical problems, such as the selection of the most suitable lubricant for each application. Carbon dioxide does not have a good solubility in the traditional refrigeration lubricants used for chlorofluorocarbons, that is, mineral oils.[2−4] Polyalkylene glycols (PAGs) and polyolester (POE) oils are among the most versatile types of synthetic lubricants for air-conditioning systems operating with carbon dioxide. To formulate appropriate lubricants based in PAGs or POEs, it is necessary to know several properties of their mixtures with CO_2, solubility being one of the most important.

On the other hand, it is interesting to remark that the solubility of CO_2 in PAGs could be of interest because PAGs composed by oligomers of dimethyl ether of polyethylene glycol are used as a physical solvent for the absorption of CO_2 (and other contaminants) from raw natural gas.[5−7]

In previous works[8,9] we studied the CO_2 solubility in four pentaerythritol tetraalkanoates (pentaerythritol tetrapentanoate, PEC5, pentaerythritol tetraheptanoate, PEC7, pentaerythritol tetranonanoate, PEC9, and pentaerythritol tetra-2-ethylhexanoate, PEBE8). Furthermore, Bobbo et al.[10−16] have also performed carbon dioxide solubility measurements of CO_2 in several pentaerythritol esters (PEs) having linear and branched chains. From all of these solubility data[10−18] for the mixtures with a mole fraction of carbon dioxide lower than 0.8, it has been concluded that the solubility expressed as CO_2 mole fraction increases slightly with the length and the branching of the PE acid chains. Besides, Pensado et al.[19,20] have determined the density and the viscosities in broad ranges of temperature and pressure of binary mixtures of carbon dioxide with PEC5, PEC7, PEC9, and PEBE8 at high refrigerant concentrations, concluding that small quantities of lubricant affect the refrigerant viscosity strongly.

In addition, the studies of Bobbo et al.[11−16] together with those of our group[8,9] show that carbon dioxide is quite soluble in pentaerythritol tetraalkanoates. So, there is a need to study also more viscous POEs because, if the refrigerant is very soluble in the lubricant, it can cause a drastic viscosity reduction which can impact negatively in the wear performance in the shaft and the bearings of the compressor, sealing efficiency in certain compressor designs, or heat removal from the compressor. Hence, it is convenient to extend the previous studies on POEs to pure dipentaerythritol esters (DiPEs) or blended with PEs to get the correct viscosity grade to prevent wear in the compressor.

With this aim, in this article new experimental data of the solubility of CO_2 in dipentaerythritol hexaheptanoate, DiPEC7, are reported. These values permit us to evaluate the influence of the number of ester groups on the carbon dioxide solubility.

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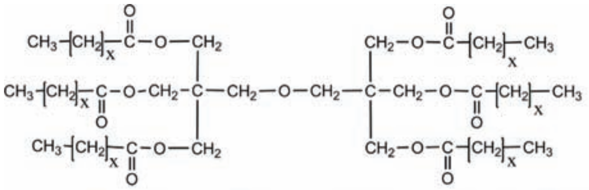
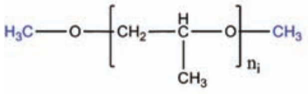


a) Dipentaerythritol hexaheptanoate, DiPEC7 (x=5)



b) Polypropylene glycol dimethyl eter, PAG1 (n$_i$=23)

Figure 1. Chemical structure of the oils studied in this work.

Previously, we have determined experimentally the viscosity and the densities in broad ranges of temperatures and pressures of DiPEC7 and dipentaerythritol hexapentanoate, DiPEC5.[18,21] We have concluded that viscosity and density increases strongly with the number of esters groups but does not change substantially with the length of the acid chain.

On the other hand, PAGs can be also suitable lubricants for air-conditioning systems using carbon dioxide as a refrigerant. For this application to avoid hydrolysis, polypropylene glycol dialkyl ethers are preferred.[4,17,22] This is because polyglycols with propylene units (PO) and double-end-capped (no terminal OH) have a lower tendency to the hydrolysis. In this work we also present solubility measurements of CO_2 in a polypropylene glycol dimethyl ether, PAG1 (with an average molecular mass of 1384.7 $g\cdot mol^{-1}$). Previously, we have also determined the densities[17] and the viscosities[23] in broad ranges of temperature and pressure of PAG1 and other PAG with more PO units and an average molecular mass of 1717 $g\cdot mol^{-1}$. It has been found that viscosities and densities increase with the number of PO units.

For DiPEC7 and PAG1, the CO_2 solubility measurements were performed with an isochoric technique at four temperatures, 283.15 K, 298.15 K, 323.15 K, and 348.15 K, and at pressures up to 7.0 MPa.

Experimental Section

Materials. The carbon dioxide, with 99.998 % mole fraction purity, was supplied by Air Liquide. Dipentaerythritol hexaheptanoate (DiPEC7, CAS 76939-66-7, $C_{52}H_{94}O_{13}$), kindly supplied by Croda Lubricants, was analyzed by ^1H, ^{13}C NMR, and mass spectroscopy. The estimated mole fraction purity for the DiPEC7 was found to be better than 95 %. PAG1 is a dimethoxy double-end-capped poly(propylene glycols), $CH_3O[CH_2CH(CH_3)O]_mCH_3$, also kindly provided by Croda. The average mass of the PAG1 was determined with matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF)[24] mass spectrometry. A weight average molar mass, M_w, of 1384.7 $g\cdot mol^{-1}$ and a polydispersity index, M_w/M_n, of 1.0165 were obtained. So, PAG1 can be considered as monodisperse. The estimated uncertainties of M_w and M_w/M_n are lower than 0.1 $g\cdot mol^{-1}$ and 0.0001. Taking into account its molecular structure, it can be concluded that the average number of PO units, m, is 23. To reduce the water content and volatile compounds of these chemicals to negligible values, vacuum (10 Pa), stirring, and moderate temperature (298 K) for at least 24 h were applied to the samples prior to the measurements. The molecular structures of both molecules are presented in Figure 1. As already mentioned, the density of both oils has been determined previously in our laboratory from 283.15 K to 398.15 K and up to 60 MPa[17,18] with an Anton Paar DMA HPM densimeter. At 298.15 K and atmospheric pressure, the experimental densities are $(989.7 \pm 0.7)\ kg\cdot m^{-3}$ and $(984.6 \pm 0.7)\ kg\cdot m^{-3}$ for DiPEC7[18] and PAG1,[17] respectively. In these conditions the viscosities measured with a Stabinger viscometer are (109 ± 1) mPa·s and (80.3 ± 0.8) mPa·s for DiPEC7[21] and PAG1,[23] respectively.

Solubility Measurements. The solubility was carried out using an isochoric technique which determines the amount of gas dissolved in a known volume of liquid from a fixed volume of gas.[8] This procedure is adequate when, as in the present case, the vapor pressure of the solvent can be considered negligible.[25,26] García et al.[27] measured the vapor pressures of DiPEC7, finding values even lower than those of PEs. [28] Taking into account the molecular structure of PAG1, we also expect very low vapor pressures for this oligomer. [22] The gas solubility setup consists essentially of two stainless steel cells of different sizes named as equilibrium and gas system cells.[8] Both cells are immersed in separate jacketed vessels whose temperature is controlled with a thermostatic bath with fluctuations less than 0.01 K. The temperatures of the cells are measured using two calibrated Pt-100 resistance thermometers placed in contact with each cell, with an accuracy of 0.02 K. The calibration was performed with Pt probes (T-012 and T-033) and regularly checked with triple-point water cells. A magnetic stirrer with a remote control is placed below the thermostatted equilibrium cell. A Paroscientific digital pressure transducer, 42K-HT-101, was used to measure the pressure of the system with an estimated accuracy of 1.4 kPa. The manometer was calibrated as a function of the temperature with two primary pressure standards. The gas bottle of calibrated volume and the pressure transducer are connected to the equilibrium cell with different valves and tubes. The gas system consists of the gas system cell and this tubing.[8,9] All of this setup is inside a temperature chamber. The temperature is kept constant within 0.3 K inside this chamber. Both the complete experimental equipment and the experimental procedure have been previously described in detail.[8] The amount of oil, degassed under vacuum inside the equilibrium cell, and the quantity of CO_2 fed into the evacuated gas bottle are determined by weighing, with a precision digital Mettler Toledo XP5003S balance with an accuracy of 0.001 g. Before connecting the gas system with the equilibrium cell, the temperature was kept constant in both system parts, equilibrium cell and gas system, and then the initial pressure was recorded. After the interconnecting valve was opened, the absorption of the gas in the stirred solvent is started. When the pressure remained constant, the magnetic stirrer was stopped, and an additional amount of time was spent waiting. Subsequently, the pressure value at the equilibrium was also measured.

Gas Solubility Calculation. The amount of absorbed gas was calculated from the pressure change in the system.[8] The mole fraction x_1 of absorbed CO_2 (1) in the solvent (2) is calculated according to, $x_1 = n_1/(n_1 + n_2)$, where n_2, the number of moles of the solvent, in this case the oil, is calculated from the degassed mass introduced in the equilibrium cell. The number of moles of gas n_1 absorbed in the solvent is calculated from:[8]

$$n_1 = \left[\frac{m_1}{M_{w,1}} - \frac{V_{\mathrm{gas\,syst}}(T_{\mathrm{eq\,gas\,syst}})}{v_1^{\mathrm{v}}(T_{\mathrm{eq\,gas\,syst}}, p)} + \frac{V_{2,\mathrm{cell}}(T_{\mathrm{eq\,liq}}) - V_{\mathrm{cell}}(T_{\mathrm{eq\,liq}})}{v_1^{\mathrm{v}}(T_{\mathrm{eq\,liq}}, p)}\right] \Bigg/ \left[1 - \frac{v_{\mathrm{abs\,gas}}(T_{\mathrm{eq\,liq}})}{v_1^{\mathrm{v}}(T_{\mathrm{eq\,liq}}, p)}\right] \quad (1)$$

Table 1. Experimental Values of the CO_2 (1) in DiPEC7 and PAG1 at Different Equilibrium Temperatures and Pressures, Expressed in Mole Fraction x_1 and in Mass Fraction w_1

T/K	p/MPa	x_1	w_1	T/K	p/MPa	x_1	w_1
			CO_2 + DiPEC7				
283.15	0.740	0.405	0.031	323.16	0.867	0.299	0.020
283.15	1.294	0.576	0.061	323.15	1.535	0.441	0.036
283.17	2.605	0.777	0.142	323.15	3.203	0.636	0.076
283.16	3.441	0.843	0.203	323.16	4.363	0.695	0.098
298.15	0.788	0.364	0.026	323.02	6.294	0.810	0.168
298.16	1.387	0.519	0.049	348.15	0.944	0.248	0.015
298.15	2.836	0.723	0.110	348.15	1.678	0.379	0.028
298.15	3.803	0.781	0.145	348.15	3.552	0.570	0.059
298.15	5.265	0.860	0.226	348.15	4.895	0.632	0.075
			CO_2 + PAG1				
283.16	1.882	0.784	0.103	323.17	2.278	0.659	0.058
283.15	2.623	0.850	0.153	323.15	3.222	0.728	0.079
283.16	2.795	0.867	0.172	323.15	3.479	0.760	0.092
283.15	3.795	0.918	0.264	323.15	4.949	0.819	0.126
283.14	4.002	0.926	0.285	323.16	5.293	0.834	0.138
283.16	4.140	0.931	0.299	323.16	5.508	0.833	0.137
298.15	2.035	0.739	0.082	348.15	2.510	0.593	0.044
298.15	2.856	0.805	0.116	348.18	3.572	0.665	0.059
298.15	3.061	0.830	0.134	348.16	3.874	0.706	0.071
298.15	4.254	0.881	0.190	348.15	5.605	0.771	0.096
298.15	4.515	0.892	0.208	348.15	6.025	0.790	0.107
298.15	4.684	0.917	0.260	348.15	6.284	0.786	0.105

where m_1 is the CO_2 mass (determined by weighting in the system cell), $M_{w,1}$ is the molecular mass of CO_2, and $V_{gas\ syst}$ and V_{cell} are the volume of the gas system and the volume of the equilibrium cell, respectively. $V_{2,cell}$ is the volume of the pure oil in the cell which is calculated from its mass and density values at the pressure, p, and temperature, T, conditions of the cell in equilibrium, for both oils.[17,18] $T_{eq\ gas\ sys}$ is the temperature in the gas system at the equilibrium, and $T_{eq\ liq}$ is the temperature in the equilibrium cell at the equilibrium. The molar volume, υ_1^{v}, of the CO_2 in the vapor phase at the different conditions is calculated with the reference equation of state of Span and Wagner[29] using the REFPROP 8 database.[30]

In the case of the DiPEC7, the volume of the absorbed gas in the solvent, $\upsilon_{abs\ gas}$, is calculated as the partial molar volume in the liquid phase at infinite dilution. Thus, as in our previous articles,[8] it was calculated using the correlation reported by Heidemann and Prausnitz[31] based on the work of Lyckman et al.[32] To do so, it is necessary to know the cohesive energy density of the solvent,[8,32] c_2, which was evaluated at each temperature from the enthalpies of vaporization and the density values measured by García et al.[27] and Fandiño et al.,[18] respectively. For PAG1 another method was used to calculate $\upsilon_{abs\ gas}$ because its enthalpies of vaporization are unknown. This method is similar to that applied by Walhström and Vamling[25,26] to determine solubilities of HFCs in POEs. At temperatures below the critical ones, $\upsilon_{abs\ gas}$ was calculated as the liquid molar volume of the CO_2 at the saturation conditions T and p_{sat}; otherwise the estimation method of Zellner et al.[33] was applied. Both methods, Heidemann and Prausnitz[31] based on the work of Lyckman et al.[32] and Walhström and Vamling[25,26] modified using Zellner et al.,[33] have been compared in our previous work.[8] The total uncertainty of the solubility data, expressed as mole fraction of CO_2 in the liquid phase, x_1, was estimated to be less than 4 %. This uncertainty was estimated taking into account the influence of uncertainties of the temperature, pressure, and volume of the equilibrium cell, total volume of the system, estimation of volume of the absorbed gas in the solvent, molecular masses, and the density of the nitrogen and carbon dioxide due to the equation of state. The total uncertainty of the experimental solubility data was evaluated using the EA-4/02.[34] The procedure was verified in the previous articles comparing our experimental pressures for CO_2 + PEC5[8] and CO_2 + PEC7[9] and those of Bobbo et al.[10] finding average relative deviations of 2.0 % and 3.4 %, respectively. More details concerning the gas solubility calculation are provided by Fandiño et al.[8]

Results

Table 1 shows the solubility values expressed as mole and mass fractions of CO_2 along four isotherms from 283.15 K to 348.15 K for the binary CO_2 + DiPEC7 and CO_2 + PAG1 systems. Figure 2 shows the solubility data for both systems. CO_2 solubility in both mass fraction and mole fraction increases with pressure at constant temperature as it is standard for highly soluble gases and diminishes when temperature increases at constant pressure. A similar behavior of the solubility with the pressure and the temperature has been found by Bobbo et al.[11−16] for the solubility of CO_2 in pure PEs, by Marcelino-Neto[35] for CO_2 + POE ISO56 and by Gainar and Anitescu[5] for CO_2 + a mixture of polyethers.

The solubilities expressed in mass fraction are high in both oils. Interestingly, these values are lower than those in pentaerythritol tetraesters (PEC5, PEC7, PEBE8, PEC9) measured previously by our group.[8,9] The trend found for the solubility of CO_2 expressed in mass fraction for these oils is

$$w(\text{DiPEC7}) < w(\text{PAG1}) < w(\text{PEC9}) < w(\text{PEC7}) \sim w(\text{PEBE8}) < w(\text{PEC5})$$

The solubility expressed as CO_2 mass fraction is strongly dependent on the molar mass of the solvent, since the differences of the molar mass of oils mask the effect of the molecular interactions in the solubility. To analyze the influence of the molecular interactions in the solubility, it is necessary to express the solubility in mole fraction, although lubrication engineers use the mass fraction.

As can be seen in Figure 3, the solubilities of CO_2 in PEs (PEC5, PEC7, PEC9, and PEBE8) are very similar, especially in terms of mole fraction. The sequence of the CO_2 solubility in the fluids above-mentioned in the most of the conditions is:

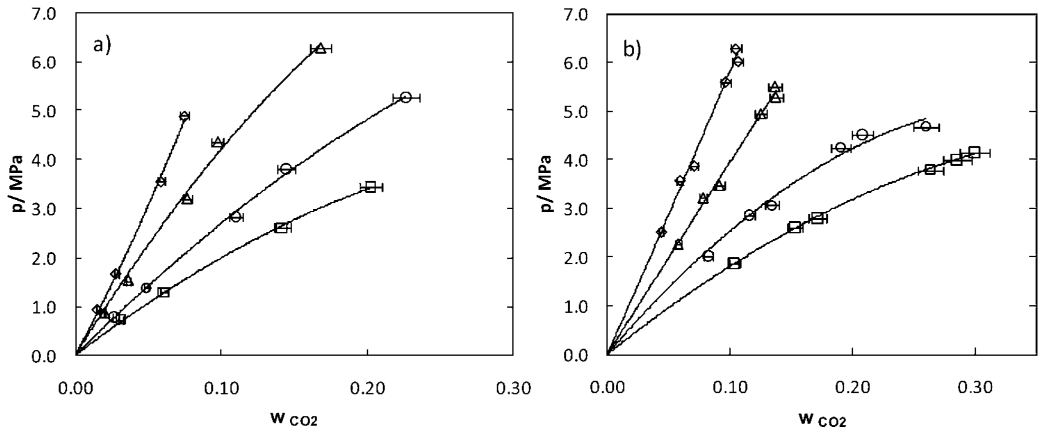


Figure 2. Solubility of CO_2 in (a) DiPEC7 and (b) PAG1 in mass fraction: □, 283.15 K; ○, 298.15 K; △, 323.15 K; and ◇, 348.15 K. Solid lines represent second-order polynomial correlations, *p*(*w*).

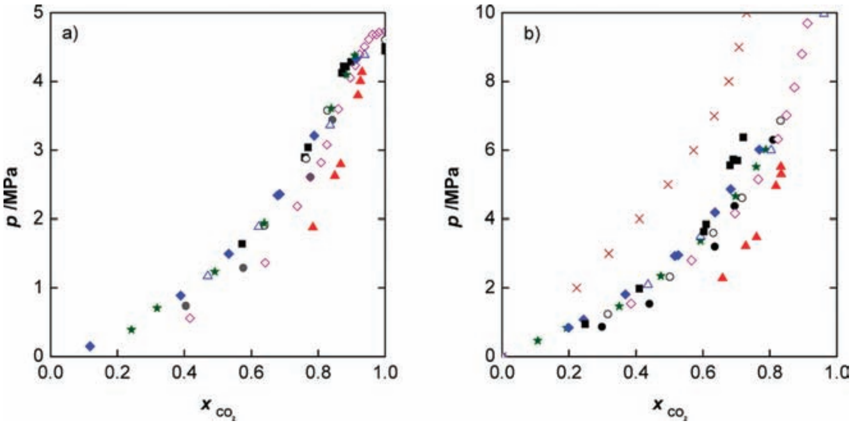


Figure 3. Solubility of CO_2 in several lubricants at (a) 283.15 K and (b) 323.15 K: ×, squalane; ◆, PEC5;[8] ■, PEC7;[9] ★, PEBE8;[8] ○, PEC9;[9] ●, DiPEC7; ◇, POE ISO56;[35] △, PAG;[38] ▲, PAG1.

$$x(\text{PEC5}) \leq x(\text{PEC7}) \leq x(\text{PEBE8}) \leq x(\text{PEC9}) < x(\text{DiPEC7}) < x(\text{PAG1})$$

We shall point out that, as can be seen in Figure 3, these trends can change slightly with the pressure and temperature. The trend found for PEs completely agrees with those found for Bobbo et al. for PEs with linear alkanoic acids and methylalkanoic acids.[16] We have performed all of these comparisons for mixtures with PEs with mole fractions of x_{CO_2} lower than 0.85. At higher mole fractions, Bobbo et al.[10,15,16] had found for several CO_2 + PE mixtures that the trend is inversed. Figure 3 shows the solubility expressed as mole fraction of CO_2 in several oils, at two temperatures (283 K and 323 K). This figure indicates that the sequence found for the solubilities slightly depends on the temperature and the pressure. Thus, the sequence obtained for the solubility in terms to mole fraction at 283.15 K is:

$$x(\text{PEC7}) \approx x(\text{PAG}) < x(\text{DiPEC7}) < x(\text{POE ISO56}) < x(\text{PAG1})$$

and at 323.15 K:

$$x(\text{squalane}) < x(\text{PAG}) \approx x(\text{PEBE8}) < x(\text{POE ISO56}) < x(\text{DiPEC7}) < x(\text{PAG1})$$

A similar trend has been found by Tsuji et al.[36] It is necessary to bear in mind that the values of solubility of Marcelino-Neto[35] represented in these figures were measured at 285 K and 328 K, instead of 283 K and 323 K. Moreover, it can be concluded, when solubility is expressed in mole fraction, that CO_2 is less soluble in the mineral oil (squalane)[37] than in the analyzed POEs and PAGs. This is not always verified when the solubility is expressed in mass fraction. In addition, the solubility of CO_2 in the PAG measured by García et al.,[38] for which the structure is not known, displays a behavior similar to that found for all PEs.

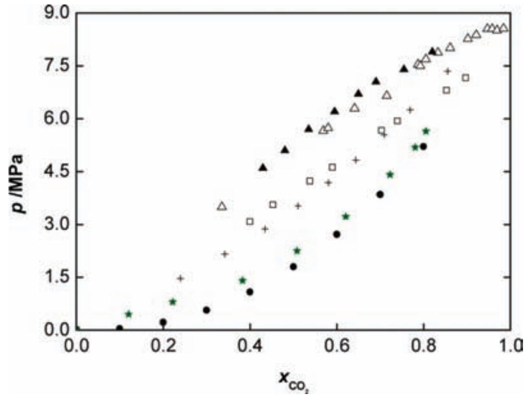


Figure 4. Solubility of CO_2 in mole fraction at 313.15 K in ●, DiPEC7; ★, PEBE8;[8] □, isopropyl acetate;[39] △, hexyl methacrylate;[40] ▲, ethyl butyrate;[39] and +, diethyl methylmalonate.[41]

In Figure 4 we have compared the solubility of CO_2 in six esters with different numbers of ester groups. The solubility is higher in DiPEC7, while the lowest solubility of CO_2 is in ethyl butyrate.[39] Thus, the results suggest that the solubility increases with the number of ester groups, as expected due to the significant quadrupole−dipole interactions.

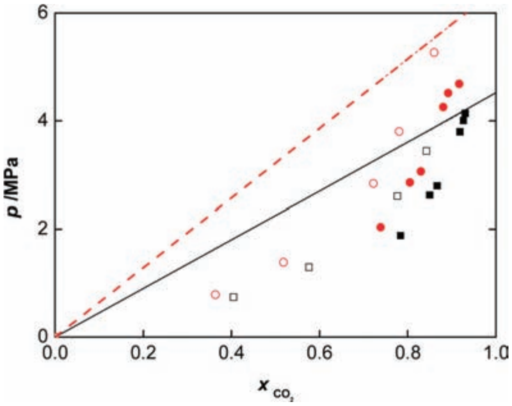


Figure 5. Solubility of the CO_2 in DiPEC7 (unfilled symbols) and PAG1 (filled symbols) at ■, —, 283.15 K and ●, - - -, 298.15 K (symbols are experimental data, and the lines represent the Raoult's law).

It was also observed that the CO_2 + DiPEC7 system shows negative deviations from Raoult's law for all of the studied compositions, which implies strong interactions between unlike molecules and may be attributed to the formation of specific interactions and also to a great difference between the molecular size of the two components. At lower concentrations of CO_2 ($x_{CO_2} < 0.85$), negative deviations were also found by our group and by Bobbo et al.[10−13,15,16] for several CO_2 + PE systems and for the CO_2 + PAG1 system (Figure 5). At mole fractions of CO_2 ($x_{CO_2} > 0.85$) positive values were found by Bobbo et al.[10,15] for several CO_2 + PE systems. Moreover, for CO_2 + PE systems negative excess volumes were reported,[16,19,20] which can be explained also by the formation of specific unlike interactions and also by the large difference between the molecular size of the two components.

Conclusions

In this work, the solubilities of carbon dioxide, CO_2, in dipentaerythritol hexaheptanoate (DiPEC7) and in a polypropylene glycol dimethyl ether (PAG1) have been measured from 283 K to 348 K and pressures up to 7 MPa in a high-pressure gas solubility apparatus. CO_2 solubility increases with pressure and diminishes when temperature increases, as it is standard for highly soluble gases. Expressing the solubility in mass fraction, CO_2 is more soluble in the PAG oil than in DiPEC7. It has been also found that, in mass fraction, carbon dioxide has a lower solubility in DiPEC7 than in several pentaerytritol esters. This feature together with the higher viscosity of the DiPEC7 shows that this compound could be a suitable lubricant to use alone or mixed with other POEs in air-conditioning systems which use carbon dioxide as a refrigerant.

It also found that the solubility of CO_2 in terms of mole fraction in several kinds of esters increases strongly with the number of carboxylate groups of the solvent, presumably due to the dipole−quadrupole interactions. This is in agreement with the negative deviation of the Raoult law displayed for CO_2 + (PE or DiPE) mixtures and the negative excess volumes of CO_2 + PE mixtures. The different molecular size of the components of these systems can also contribute to this behavior.

Acknowledgment

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