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Solubility of Carbon Dioxide in Two Pentaerythritol Ester Oils between (283 and 333) K

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In this work, the solubility of carbon dioxide, CO_2, in pentaerythritol tetrapentanoate (PEC5) and in pentaerythritol tetra(2-ethylhexanoate) (PEBE8) has been performed from (283 to 333) K and pressures up to 7 MPa in a new high-pressure gas solubility apparatus. The results show that in the present analyzed range CO_2 is highly soluble in these oils and that the solubility expressed as CO_2 mole fraction is practically not dependent on the branching of the acid chain, whereas it increases slightly with the length of the PE acid chains in the present range of compositions. The gas solubility data were satisfactorily correlated with the Soave−Redlich−Kwong (SRK) equation of state (EOS) using the conventional quadratic mixing rule with two interaction parameters for each temperature.

Introduction

International efforts to reduce the global production and consumption of most ozone-depleting substances, as well as to tackle global climate change, have been carried out with different destinies.[1–4] Thus, whereas absorption chillers are justified by fuel prices or peak-electric demand avoidance, mechanical vapor compression dominates in most locations based on significant advantages in efficiency, size, and equipment cost.[5,6] Both vapor compression and absorption refrigeration systems employ a refrigerant, which is the most essential component of this equipment. In the past decades, a renewed interest in the classic refrigerant, carbon dioxide (CO_2),[1,7,8] as an environmentally friendly working fluid has been generated. Thus, CO_2 is being considered as a potential candidate to replace existing refrigerants, especially in small and medium systems.[8]

Any refrigerant requires proper lubricant oil for the vapor compression cycle. Correct lubrication in the refrigeration equipment contributes to their longer life, better security, and a large savings in energy and materials.[9–11] In the case of refrigeration cycles, the circulating fluid comes into contact with the compressor lubricant, and some of the refrigerant may be dissolved into the oil depending on the solubility.[12,13] Hence, mutual solubility is one of the main problems to solve concerning the identification and development of suitable lubricants.[8,9,12–15] The solubility of the refrigerant in the lubricant affects to the lubrication properties of actual oil in the compressor.[16] Thus, the decrease in the viscosity of the oil due to the dissolved refrigerant can impact negatively the wear performance in the shaft and the bearings of the compressor, sealing efficiency in certain compressor designs, or heat removal from the compressor.[14]

Moreover, part of the lubricant oil migrates from the compressor to other parts of the system such as the evaporator, condenser, expansion device, and piping.[6] Thus, a small amount of compressor lubricant, as a part of the working fluid, circulates with the refrigerant.[15] So, the thermophysical properties of the actual refrigerant are not the same as those of the pure refrigerant. In addition, the vaporization of dissolved refrigerants can disrupt the oil film at bearings, increase oil volume, or in certain cases, lead to excessive foaming leading to flood-back problems. Consequently, to evaluate the suitability of these lubricants, it is necessary to study the diverse thermophysical properties of their mixtures with CO_2, especially the solubility. It is of fundamental importance since it allows determining the lubricant composition of the compressor oil (which contains refrigerant) and therefore its properties, as well as the composition and properties of the real refrigerant (which contains lubricant). The oil tends to accumulate in the evaporator and in some configurations in the suction pipe.[17] Thus, the circulating oil exists as an oil film on the tube walls, and the oil film thickness is affected by the system conditions.[17] When the solubility of CO_2 in oil is lower, the viscosity and surface tension of the oil film in the tubes are higher.[18] Hence, the oil layer in the inner wall is much thicker and moves at a very low speed, leading to a higher pressure drop and a lower heat transfer.[19] Thus, in heat exchangers and the suction line, it is recommended to use oil that has high CO_2 solubility.[18] Carbon dioxide, however, does not have good total mutual miscibility with several common lubricants.[16] Several families of new lubricants[8] have already been identified to be acceptable, such as polyalkyleneglycols, PAG, polyol esters, POE, or alkylbenzenes, AB. Nevertheless, they are still far from having been optimized in relation to the refrigerant, working conditions, and the existence of miscibility limits.

Different studies point out[10,11,20–22] that several POEs could be considered green lubricants because they optimize energy efficiency and minimize wear in the machinery.[10] Furthermore, they were proposed as important components of the lubricants for use with CO_2 for reasons of miscibility and also because of their inherently good lubricity.[22,23] The availability of experimental solubility data is essential to develop both predictive and correlation thermodynamic models. In the refrigeration field,

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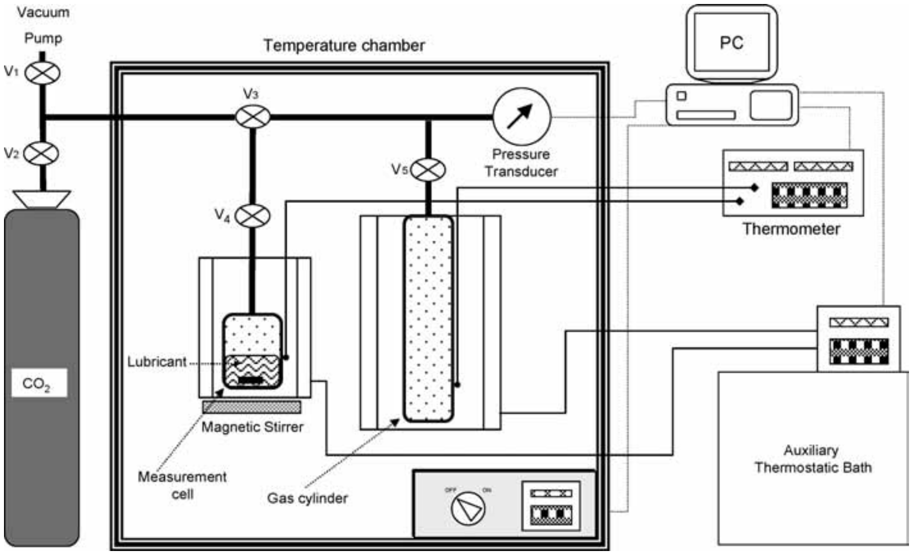

Figure 1. Scheme of the solubility apparatus.

solubility data on oils with a defined structure and composition are specially needed. Thus, in this work, pure pentaerythritol esters (PEs) with defined structure have been selected.

This paper presents the first results obtained with a new high-pressure gas solubility apparatus, developed to measure solubility in isochoric conditions. The solubility of carbon dioxide in two PEs, pentaerythritol tetrapentanoate (PEC5) and pentaerythritol tetra(2-ethylhexanoate) (PEBE8), has been measured for temperatures ranging from (283 to 333) K and pressures up to 7 MPa. The results have been compared with those available in the literature at 283.15 K.[24–27] In addition, we have analyzed the effect on the solubility of CO_2 of both length and branching of the acid chains of the PEs. The gas solubility data were correlated with the Soave−Redlich−Kwong (SRK) equation of state (EOS) using the conventional quadratic mixing rule with two interaction parameters for each temperature.

Experimental Section

Materials. The carbon dioxide, with 99.998 % purity, was supplied by Air Liquide. Pentaerythritol tetra(2-ethylhexanoate) (PEBE8, CAS 7299-99-2, $C_{37}H_{68}O_8$) was obtained from Nikkol Chemical with a chemical purity of 99 %, and pentaerythritol tetrapentanoate (PEC5, CAS 15834-04-5, $C_{25}H_{44}O_8$) was supplied by Hatco Corporation with 99 % purity. The density of the PEBE8 has been determined previously in our laboratory from (278.15 to 353.15) K and up to 45 MPa[28,29] with an Anton Paar DMA 512P, whereas PEC5 densities were recently measured from (283.15 to 398.15) K and up to 70 MPa[30] with an Anton Paar DMA HPM densimeter. At 283.15 K and atmospheric pressure, the experimental densities are 1.0267 $g \cdot cm^{-3}$ and 0.9687 $g \cdot cm^{-3}$ for PEC5[30] and PEBE8,[26] respectively.

Solubility Measurements. The solubility measurements were carried out by means of an isochoric experimental technique (Figure 1) similar to that used by Maaβen et al.,[31] Melzer et al.,[32] and Wahlström and Vamling.[33–36] The experimental technique consists of determining the amount of gas absorbed in a known quantity of liquid solvent from the pressure change in a gas system of known volume, observed during the absorption of the gas. This procedure is adequate when, as in the present case, the vapor pressure of the solvent can be considered negligible. The vapor pressures of PEC5 and PEBE8 have been reported by Razzouk et al.[37] between (334 and 476) K. The vapor pressure of PEC5[37] at 334.02 K is $2.55 \cdot 10^{-4}$ Pa, and the vapor pressure of PEBE8[37] at 353.96 K is $1.27 \cdot 10^{-4}$ Pa. Accordingly, in the range of the present solubility measurements, (283 to 333) K, the vapor pressures of both PEs are even lower than the above values. Hence, these values are negligible with respect to high equilibria pressure of both CO_2 + PE systems.

Figure 1 shows a scheme of the apparatus. The measurement cell, made in stainless steel and with an internal volume around 23 cm^3, is located in a liquid bath thermostat, which controls the temperature with fluctuations lower than 0.01 K. The temperature of the cell is measured using a calibrated Pt-100 resistance thermometer with an accuracy of 0.02 K. A magnetic stirrer with a remote control is placed below the thermostatted cell. The gas bottle of calibrated volume and the pressure transducer are connected to the equilibrium cell with different valves and tubes. This whole setup is inside a temperature chamber. The temperature is kept constant at ± 0.3 K inside this chamber. A second calibrated Pt-100 resistance thermometer with an accuracy of 0.02 K is placed in contact with the gas bottle. A Heise digital pressure transducer was used to measure the pressure of the system with an estimated accuracy of 0.002 MPa.

After the introduction of the pure PE into the evacuated equilibrium cell, it was degassed under vacuum using a system similar to that developed by Battino et al.[38] The amount of degassed oil has been determined by the difference of weight with a precision digital Sartorius micro MC1 balance with an accuracy of 0.002 g. Subsequently, the equilibrium cell with the degassed oil was placed into the liquid-bath thermostat. The CO_2 was fed into the evacuated gas bottle and into the interconnection tubes and valves (named here "gas system") which are located in the temperature chamber. Before connecting the gas system with the equilibrium cell, the temperature was kept constant in the two system parts, equilibrium cell and gas system, although it should be slightly higher in the gas system to prevent condensation. Then the initial pressure was recorded. After the interconnecting valve (V_4) was opened, the absorption of the gas in the stirred solvent was started. The progress of absorption was indicated by the decrease of the pressure. When the pressure remained constant (after several hours), the magnetic stirrer was stopped, and an additional time was waited (~1 h) to ensure the achievement of the thermodynamic equilibrium in the experimental cell. An intensive stirring of gas-saturated liquids such as refrigerant−oil solutions leads to a decrease of the concentration of the refrigerant in the liquid phase, increasing pressure, and failure to achieve the thermodynamic equilibrium.[39,40] Subsequently, the pressure value in the equilibrium was also measured. The next step was to change the temperature of the system. When the pressure again became constant, a new equilibrium point had been reached. The measurements for one initial pressure value were finished when solubilities at all the desired temperatures were performed. Afterward, the procedure described above was repeated for other initial pressures.

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 PE, 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[35]

$$n_1 = n_1^0 - n_1^1 \tag{1}$$

where n_1^0, the initial number of moles of gas in the system, is given by:

$$n_1^0 = \frac{V_{\text{gas syst}}(T_{\text{beg}})}{v_1^{\text{v}}(T_{\text{beg}}, p_{\text{beg}})} \tag{2}$$

and n_1^1, the number of moles of gas remaining in the system once it reaches equilibrium, is

$$n_1^1 = \frac{V_{\text{gas syst}}(T_{\text{equilib gas syst}})}{v_1^{\text{v}}(T_{\text{equilib gas syst}})} + \left(\frac{V_{\text{cell}} - V_{2,\text{cell}}}{v_1^{\text{v}}(T,p)} - \frac{V_{\text{abs gas}}}{v_1^{\text{v}}(T,p)}\right) \tag{3}$$

where $V_{\text{gas syst}}$ and V_{cell} are the volume of the gas system and the volume of the equilibrium cell, respectively. $V_{2,\text{cell}}$ is the volume of the pure PE in the cell which is calculated from its mass and density values at the pressure p and the temperature T conditions of the cell in equilibrium, from Fandiño et al.[28–30] for PEBE8 and PEC5. $T_{\text{equilib gas syst}}$ is the temperature in the gas system at the equilibrium. The molar volume v_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[41] using the REFPROP 8 database.[42]

Taking into account that $V_{\text{abs gas}}$, the volume of CO_2 absorbed in the solvent, can be expressed as $V_{\text{abs gas}} = n_1 v_{\text{abs gas}}$, the number of moles of gas, n_1, absorbed in the solvent is

$$n_1 = \left[\frac{V_{\text{gas syst}}(T_{\text{beg}})}{v_1^{\text{v}}(T_{\text{beg}}, p_{\text{beg}})} - \frac{V_{\text{gas syst}}(T_{\text{equilib gas syst}})}{v_1^{\text{v}}(T_{\text{equilib gas syst}}, p)} + \frac{V_{2,\text{cell}} - V_{\text{cell}}}{v_1^{\text{v}}(T,p)}\right] \Bigg/ \left[1 - \frac{v_{\text{abs gas}}}{v_1^{\text{v}}(T,p)}\right] \tag{4}$$

T_{beg} and p_{beg} are the conditions of the gas system at the beginning of the measurement. The molar volume $v_{\text{abs gas}}$ of the absorbed gas in the solvent is calculated as the liquid molar volume of the gas at equilibrium conditions T and p, if CO_2 is liquid at these conditions; otherwise, $v_{\text{abs gas}}$ is calculated as the partial molar volume in the liquid phase at infinite dilution.

This procedure has been used by several authors, among them Walhström and Vamling[35,36] to determine solubilities of HFCs in PEs, Bonifácio et al.[43] to estimate solubility of xenon in *n*-hexane, Dhima et al.[44] to calculate solubility of CO_2 and of hydrocarbons in water, Hong et al.[45] to evaluate the solubility of 1,1,1,2-tetrafluoroethane (R134a) and propane in squalane, and Fischer and Wilken[46] to determine the oxygen and nitrogen solubility in some organic solvents. To calculate this volume, we have applied the correlation proposed by Heidemann and Prausnitz,[47] based on the work of Lyckman et al.[48] We must point out that Dhima et al.[44] have found for mixtures containing water that partial molar volumes at infinite dilution of CO_2 and of different hydrocarbons are well estimated at saturated water vapor pressure at 344.15 K by the correlation proposed by Lyckman et al.[48] Thus, in this paper $v_{\text{abs gas}} = v_1^{\infty}$ was calculated by using[47]

$$\frac{p_{\text{c1}} v_1^{\infty}}{RT_{\text{c1}}} = 0.095 + 2.35\frac{Tp_{\text{c1}}}{c_2 T_{\text{c1}}} \tag{5}$$

where p_{c1} and T_{c1} are the critical pressure and the critical temperature of CO_2; T is the absolute temperature of the liquid solution; R is the gas constant; and c_2 is the cohesive energy density of the solvent, which was evaluated at each temperature from the enthalpies of vaporization[37] and the density values reported by Fandiño et al.[28,29] and by Segovia et al.[30] Cohesive energy densities for PEC5 range from (243 to 253) MPa in the studied conditions, whereas for PEBE8 this property changes from (179 to 186) MPa.

To determine the initial amount of CO_2 in the system and the amount of CO_2 dissolved in the solvent, it is necessary to know previously the volumes $V_{\text{gas syst}}$ and V_{cell}. These volumes have been determined, at each temperature, filling the system with a well-known amount of N_2, measuring the pressure and the temperature, and evaluating in the T,p conditions the density of the reference equation of state of Span et al.[49] At 298.15 K, the system total volume is 370.9 cm^3, with the volume of the tubing and connections being lower than 3 % of that value. 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 % in the worst of the cases. The highest contribution to this uncertainty is due to the estimation of the volume of the mixture CO_2 + PE. This contribution becomes more important when the CO_2 mole fraction increases. To verify the procedure, we have compared our solubility results for CO_2 + PEC5 with those of Bobbo et al.[25] The comparisons between both solubility data series are presented in the next section.

Results and Discussion

The solubility measurements of CO_2 in pentaerythritol tetrapentanoate (PEC5) and in pentaerythritol tetra(2-ethylhexanoate) (PEBE8) have been performed for temperatures ranging from (283 to 333) K and pressures up to 7 MPa. The experimental values are presented in Table 1.

In Figure 2, we have plotted our solubility results at 283.15 K for the system CO_2 + PEC5 together with those from Bobbo et al.[25] To perform numerical comparisons, we have correlated the p, x data of Bobbo et al. of the system $x\text{CO}_2 + (1 - x)\text{PEC5}$ with an empirical $p(x)$ equation with a standard deviation of 0.0013 MPa. The absolute average deviation[50] (AAD) between our experimental pressures and the correlated values of Bobbo et al.[25] for CO_2 + PEC5 is 2.0 %. The Bias[50] is 1.5 %, and the maximum deviation is presented at higher pressures, being 3.6 %. These results are in agreement with the uncertainties of both experimental methods. Moreover, we must point out that the samples of PEC5 have different origin, the purity of that used by Bobbo et al.[25] being 98 % while that of our sample is 99 %.

Figure 3 shows the solubility isotherms for the two CO_2 + PE systems, expressed in terms of mole fraction of CO_2 in the liquid phase. It can be seen that for both systems the solubility

Table 1. Mole Fraction Solubility of Carbon Dioxide (CO_2) in PEC5 and in PEBE8

T/K	x_{CO_2}	p/MPa	T/K	x_{CO_2}	p/MPa	T/K	x_{CO_2}	p/MPa
CO_2 + PEC5								
283.14	0.389	0.887	303.15	0.255	0.771	323.14	0.199	0.841
283.15	0.533	1.498	303.12	0.304	0.983	323.13	0.243	1.071
283.18	0.678	2.339	303.15	0.441	1.661	323.12	0.369	1.812
283.13	0.685	2.357	303.14	0.586	2.647	323.15	0.516	2.928
283.15	0.788	3.210	303.14	0.596	2.671	323.14	0.526	2.958
283.12	0.913	4.329	303.15	0.702	3.724	323.13	0.636	4.180
293.15	0.277	0.738	303.14	0.744	4.300	323.16	0.683	4.859
293.15	0.339	0.938	313.15	0.227	0.806	323.13	0.769	6.016
293.17	0.484	1.581	313.12	0.273	1.028	333.13	0.183	0.872
293.19	0.626	2.501	313.13	0.400	1.738	333.15	0.222	1.113
293.15	0.639	2.519	313.14	0.548	2.790	333.12	0.342	1.885
293.16	0.737	3.486	313.16	0.559	2.818	333.14	0.491	3.060
293.15	0.860	4.822	313.15	0.668	3.956	333.16	0.498	3.095
298.16	0.272	0.753	313.16	0.708	4.590	333.15	0.610	4.396
298.15	0.323	0.960	313.15	0.793	5.637	333.16	0.660	5.129
298.15	0.462	1.621				333.16	0.751	6.387
298.12	0.610	2.571						
298.12	0.615	2.599						
298.15	0.720	3.605						
298.14	0.841	5.034						
CO_2 + PEBE8								
283.23	0.242	0.388	303.15	0.147	0.430	323.15	0.108	0.464
283.15	0.319	0.703	303.15	0.251	0.769	323.16	0.194	0.832
283.2	0.491	1.235	303.21	0.417	1.350	323.01	0.352	1.461
283.16	0.639	1.940	303.17	0.550	2.151	322.92	0.478	2.347
283.17	0.839	3.605	303.23	0.659	3.055	323.10	0.599	3.374
283.15	0.885	4.098	303.21	0.759	4.157	323.08	0.706	4.655
283.15	0.910	4.380	303.15	0.815	4.844	323.15	0.769	5.510
293.15	0.155	0.414	303.13	0.833	5.252	323.14	0.798	6.012
293.17	0.288	0.736	313.16	0.121	0.448	333.15	0.093	0.481
293.16	0.447	1.294	313.13	0.223	0.801	333.11	0.179	0.862
293.21	0.591	2.048	313.15	0.385	1.406	333.14	0.309	1.518
293.22	0.691	2.890	313.09	0.513	2.251	333.04	0.456	2.444
293.15	0.794	3.891	313.20	0.626	3.217	333.14	0.574	3.529
293.15	0.831	4.509	313.12	0.730	4.409	333.13	0.685	4.897
293.15	0.856	4.853	313.15	0.789	5.184	333.15	0.753	5.829
298.12	0.269	0.752	313.16	0.815	5.643	333.16	0.786	6.379
298.19	0.419	1.324						
298.22	0.570	2.100						
298.13	0.781	4.021						
298.15	0.821	4.680						

increases with the pressure and decreases with the temperature, as usual for gases.

In the literature, there are available solubility data only at 283.15 K of CO_2 in lineal pentaerythritol esters[25] (PEC4, PEC5, PEC6, PEC7, PEC8). At the same temperature, Bobbo et al.[27] have also measured the solubilities of CO_2 in the branched pentaerythritol esters: 2-methylbutyric, 2-methylvaleric, and 2-methylhexanoic pentaerythritol tetraester, named as PEBM5, PEBM6, and PEBM7, respectively, where M means methyl, B branched, and 5, 6, 7 are the number of carbon atoms of the acid chains. Furthermore, the solubility of CO_2 in the commercial oils ICI Emkarate RL32S and Mobil EAL Arctic 32, Castrol Icematic SW32,[24] were measured at 333.15 K. For this last lubricant, there are also CO_2 solubility data[26] at 283.15 K. The solubilities at 283.15 K of the isomers PEBE8 and PEC8[25] are almost identical. In their works, Bobbo et al.[24–27] have found at 283.15 K that by expressing the solubility data in terms of mole fraction of the refrigerant in the solution the solubilities practically do not change with the size and the branching of the acid chains. At mole fractions of CO_2 lower than 0.8, these authors found that the solubility slightly increases with the molecular weight. Our results at 283.15 K for PEBE8 and PEC5 confirm this behavior. Besides, we have found that at each one of the other analyzed temperatures in this work the solubility data are also very similar in terms of mole fractions of CO_2 in both PEs.

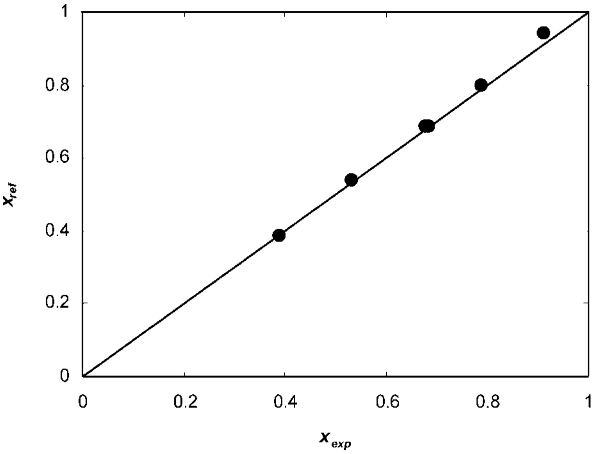

Figure 2. Gas solubility of CO_2 in PEC5 at 283.15 K from Bobbo et al.,[25] x_{ref}, versus the experimental values, x_{exp}, of Table 1: ●, (x_{exp}, x_{ref}). The solid line represents $x_{ref} = x_{exp}$.

Furthermore, Bobbo et al.[25] at 283.15 K also found that by expressing the solubilities in mass fractions of the refrigerant the solubility values decreases with the length of the ester acid chains, that is, with the PE molecular weight. This fact is due simply to the effect of the molecular weight in the calculation of the solubility. In Figure 4, the solubilities of CO_2 in several pure PEs[25,27] with linear and branched chains and in a commercial POE[26] (Castrol Icematic SW32) are plotted together with our data in PEC5 and PEBE8. Our values agree with the expected trend. Thus, the solubility of CO_2 in PEs expressed as percentage in weight of refrigerant decreases with the size of the acid chains and weakly increases with the branching of the acid chains. In the case of the commercial POE, the CO_2 solubility values are similar to those in PEC5. According to Bobbo et al.,[26] the estimated mean molecular weight of this commercial POE is 568 $g \cdot mol^{-1}$ with an uncertainty of 10 %. This value is between that of PEC6, 529 $g \cdot mol^{-1}$, and that of PEC7, 585 $g \cdot mol^{-1}$.

In Figure 5, we compare our solubility results for the CO_2 + PE systems with those for CO_2 in three commercial POE lubricants[24] at 333.15 K. The solubilities expressed as CO_2 mass fractions, w_{CO_2} are very similar for the three commercial POEs to those obtained in PEC5 and are slightly higher than those obtained in PEBE8. Hence, the trends are the same as those obtained for 283.15 K. Unfortunately, the molecular weights of two of the three commercial samples have not been published. As lubricants used for compressors are not pure compounds and mean molecular masses are not always available, the trends of the solubilities expressed in terms of weight fractions have a more practical interest.

The analyzed PEs show good miscibility characteristics with CO_2, but the high solubilities of CO_2 could limit their applications due to the drastic viscosity reduction.[51] Since the viscosity of liquid CO_2 is very low, the more CO_2 that dissolves in the lubricant the more the viscosity of the real oil is diminished (mixture of lubricant + CO_2) in the compressor. Thus, this fact could provoke a lack of lubrication in the compressors, where a higher viscosity of the refrigerant/oil mixture is preferred. Ester lubricants with higher viscosities could be used in a refrigeration compressor with CO_2, to avoid possible wear, but this solution implies more energy consumption. Nevertheless, in heat exchangers and the suction line, a low viscosity of the refrigerant/oil mixture is preferred to minimize the effects of oil on the heat transfer degradation and the pressure drop increase and to enhance the oil transport.[52] Thus, to ensure good oil return to

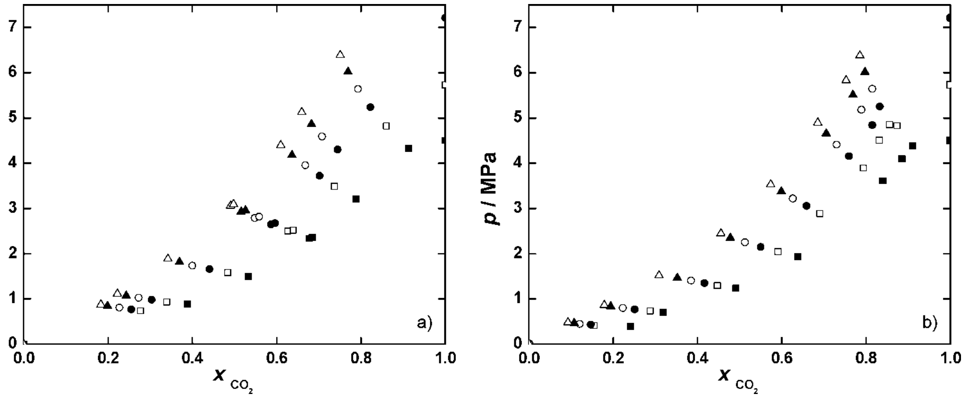

Figure 3. Solubility of CO_2 in (a) PEC5 and (b) PEBE8 at temperatures: ■, 283.15 K; □, 293.15 K; ●, 303.15 K; ○, 313.15 K; ▲, 323.15; △, 333.15 K.

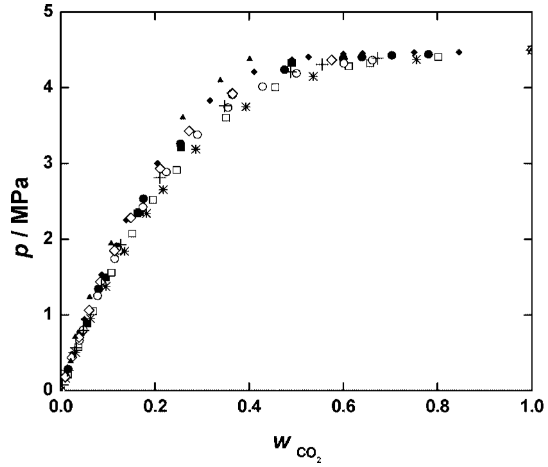

Figure 4. Solubility of carbon dioxide at 283.15 K, expressed in mass fraction, from Bobbo et al.:[25–27] *, PEC4; □, PEBM5; ●, PEC6; ○, PEBM6, ◆, PEC7; ◇, PEBM7; and +, Castrol Icematic SW32. From this work: ▲, PEBE8; and ■, PEC5.

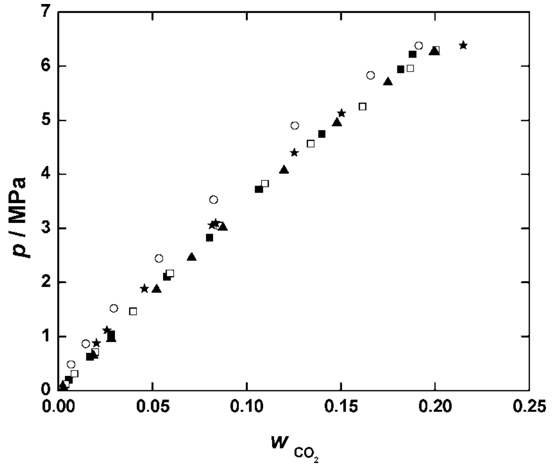

Figure 5. Solubility of carbon dioxide at 333.15 K, expressed as mass fraction, in three commercial POE lubricants: ■, ICI Emkarate RL32s;[24] □, Mobil EAL Arctic 32;[24] ▲, Castrol Icematic SW32;[24] and ○, PEBE8; and ★, PEC5.

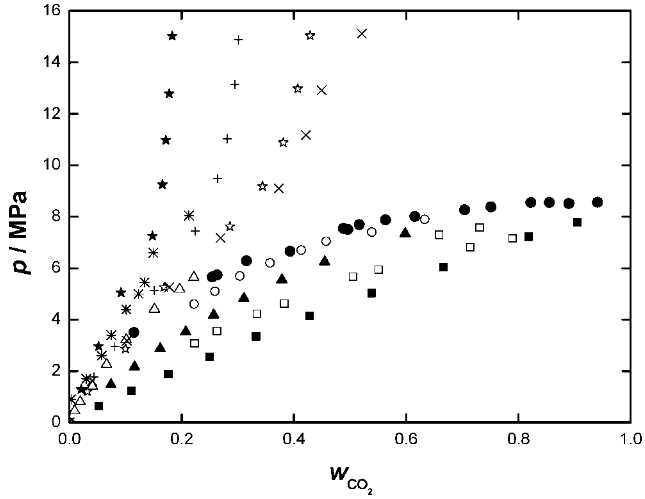

Figure 6. Solubility of carbon dioxide at 313.15 K in mass fraction for: Δ, PEBE8 (640.93 g·mol^{-1}); *, squalane[53] (422.82 g·mol^{-1}); ▲, diethyl methylmalonate[59] (174.18 g·mol^{-1}); ●, hexyl methacrylate[58] (170.25 g·mol^{-1}); ○, ethyl butyrate[57] (116.16 g·mol^{-1}); □, isopropyl acetate[57] (102.1 g·mol^{-1}); ■, ethyl acetate[60] (88.12 g·mol^{-1}); ★, PAO;[54] ☆, PAG-A;[54] +, PAG-B;[54] ×, ester 1.[54]

the compressor, the oil needs to have good solubility and miscibility with the refrigerant. As a result, appropriate oil for a particular application must be carefully selected in regard to its viscosity reduction due to refrigerant solubility.

To clarify the dependence of the CO_2 solubility with the structure of the oil, in Figure 6 its values are plotted for several lubricants (squalane, PAOs, PAGs, and esters). The experimental data were taken from Stratmann and Schweiger[53] in the case of squalane and from Hauk[54] for the other lubricants. In this figure, it can be seen that carbon dioxide has the lowest solubilities in polyalphaolefine (PAO) and in squalane. This is due to the fact that the molecules of these last compounds are nonpolar, thus they have unimportant unlike molecular interactions with CO_2, which is a molecule with an important quadrupole. Thus, PAO and squalane are not suitable lubricants for CO_2 because they do not present a good mutual miscibility with carbon dioxide.[16,55] In Figure 6, it can also be seen that CO_2 is less soluble in PAGs than in esters, but unfortunately PAGs and CO_2 are not mutually miscible in all the conditions of the refrigeration cycle.[14,16,56] In Figure 6, we have included some of the available solubility literature data of CO_2 in alkyl alkanoates and other esters which are not really lubricants, because their viscosity is low, to analyze the dependence of the solubility on the number of ester groups and on the size of the acid and alcohol chains.[57–60] From this figure, it can be deduced that, for all the types of compounds, when the solubility is expressed in terms of mass fraction, it is strongly dependent on the molecular weight. For the esters of known structure (all except the lubricant ester 1), the lowest solubility is for pentaerythritol tetra(2-ethylhexanoate) PEBE8, which has four ester groups and the highest molecular weight, and the highest

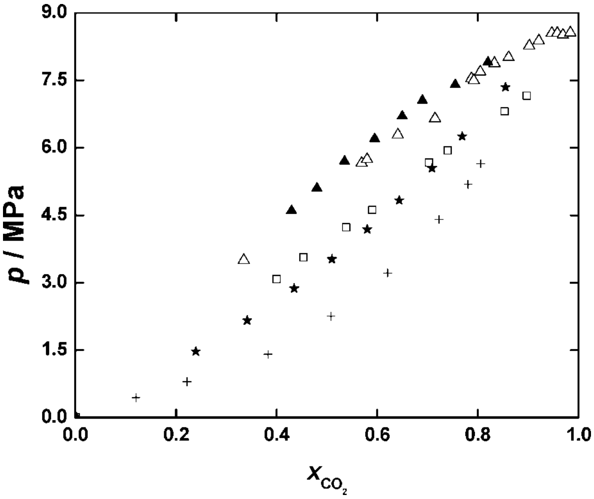

Figure 7. Solubility of carbon dioxide at 313.15 K in molar fraction for +, PEBE8; □, isopropyl acetate;[57] △, hexyl methacrylate;[58] ▲, ethyl butyrate;[57] and ★, diethyl methylmalonate.[59]

Table 2. Critical Parameters and Acentric Factor of PEBE8 and PEC5 Calculated by Razzouk et al.[37] for the SRK EoS

PE	M_W/g·mol^{-1}	T_c/K	p_c/MPa	ω
PEC5	472.62	866.46	1.353	1.0590
PEBE8	640.94	948.75	1.011	0.9910

solubility is for ethyl acetate[60] which has a unique ester group and the lowest molecular weight.

In Figure 7, we have plotted the solubility expressed in terms of mole fraction of carbon dioxide in five esters. In this case, PEBE8 presents the highest solubilities, whereas ethyl butyrate[57] presents the lowest. It seems that the number of ester groups increases the solubilities in terms of mole fractions, as can be expected because of the important unlike quadrupole−dipole interactions.

In the range of concentrations analyzed in this work, at temperatures lower than the critical of CO$_2$, both systems exhibit negative deviations from Raoult's law. This fact shows the presence of stronger interactions between unlike molecules in the mixture. Pensado et al.[51,61] have found from their density measurements at high concentrations of carbon dioxide that excess volumes are negative. This behavior was previously pointed out by Bobbo et al.,[24–27] and it was also found for other systems containing pentaerythritol esters, as is the case of mixtures with HFCs.[35]

Table 3. Binary Interaction Coefficients k_{ij}, l_{ij}, and MADx_1 for CO$_2$ + PEBE8 and CO$_2$ + PEC5 Systems

T/K	k_{ij}	l_{ij}	MADx_1 (%)
	CO$_2$ + PEC5		
283.15	0.0074	0.0383	1.0
293.15	−0.0028	0.0275	1.0
298.15	−0.0105	0.0254	0.7
303.15	−0.0178	0.0229	0.6
313.15	−0.0296	0.0197	0.5
323.15	−0.0407	0.0170	0.5
333.15	−0.0569	0.0128	0.4
	CO$_2$ + PEBE8		
283.15	0.0309	0.0371	2.0
293.15	0.0094	0.0324	2.2
298.15	−0.0019	0.0267	1.3
303.15	−0.0012	0.0318	1.6
313.15	−0.0142	0.0283	1.4
323.15	−0.0316	0.0224	1.1
333.15	−0.0524	0.0130	0.9

Solubility Data Correlation

The Soave−Redlich−Kwong (SRK) equation of state (EoS)[62] is one of the most popular models for the correlation of phase equilibria at high pressures. Furthermore, it is used in industry simulation processes, to predict the thermodynamic properties of multicomponent mixtures. The relevant equations for the standard model are well-known and are not reproduced here. This EoS can be applied if the critical parameters (critical temperature, T_c, and critical pressure, p_c) and the acentric factor, ω, of the pure components are available. Thus, the critical parameters and acentric factor of PEBE8 and PEC5 (Table 2) were taken from recent literature,[37] where these parameters have been estimated from the experimental vapor pressures and density values. For the pure CO$_2$, the critical parameters from REFPROP[42] have been selected.

For the binary mixtures, the quadratic mixing rule offers a maximum of two binary interaction parameters per binary system. Often, the quadratic mixing rule is sufficient for correlation of phase equilibria in systems that do not contain specific interactions. Therefore, the following expressions for the attractive (a_{ij}) and repulsive (b_{ij}) terms of the fluid mixture were selected

$$a_{ij} = \sqrt{a_i a_j}(1 - k_{ij}) \text{ with } k_{ij} = k_{ji} \tag{6}$$

$$b_{ij} = \frac{b_i + b_j}{2}(1 - l_{ij}) \text{ with } l_{ij} = l_{ji} \tag{7}$$

Using these expressions and by correlation of the experimental gas solubility data, the k_{ij} and l_{ij} parameter values were determined for each isotherm. For this purpose, the computations were performed using the phase equilibria (PE2000) software.[63] The k_{ij} and l_{ij} were obtained for each temperature and binary system using as an objective function the mean absolute deviation, MADx_1 (%) = $(1/n)\sum_{i=1}^{n} |x_{1,i}^{\text{exp}} - x_{1,i}^{\text{calcd}}|$, where x_1 is

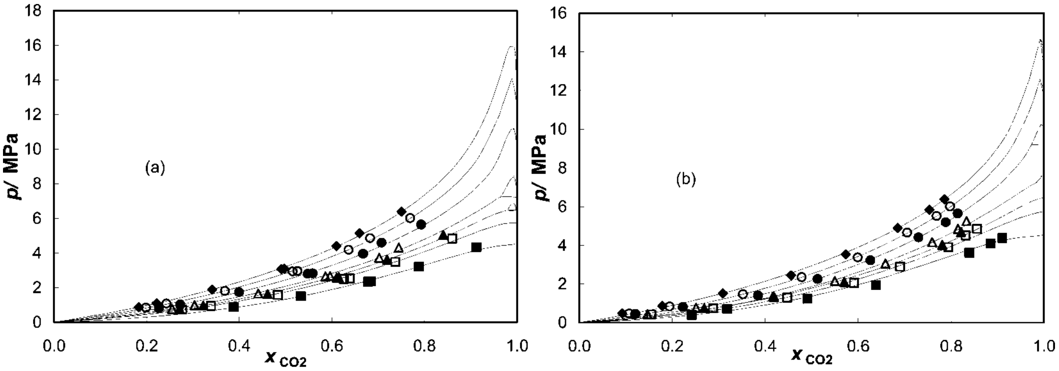

Figure 8. Experimental solubility data (points) together with SRK correlations —, for different temperatures: ■, 283.15 K; □, 293.15 K; ▲, 298.15 K; △, 303.15 K; ●, 313.15 K; ○, 323.15 K; and ◆, 333.15 K. (a) CO$_2$ + PEC5 and (b) CO$_2$ + PEBE8.

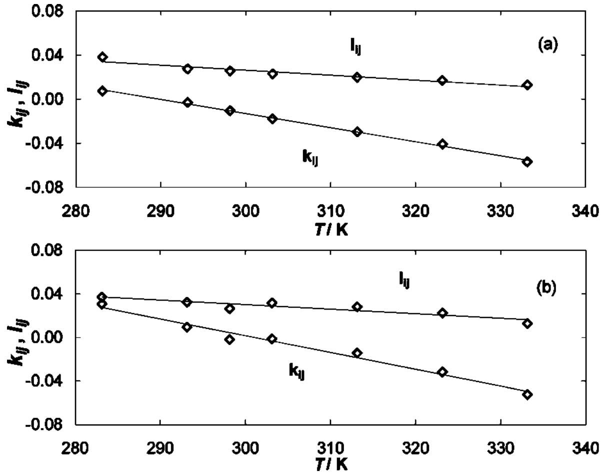

Figure 9. Temperature dependence of k_{ij} and l_{ij} for (a) CO_2 + PEC5 and (b) CO_2 + PEBE8. ◇, k_{ij} and l_{ij} obtained from the isothermal correlations (Table 3). Solid lines represent eqs 8 and 9.

the liquid phase mole fraction of CO_2; n is the number of experimental points; and superscripts exp and calcd denote the experimental and calculated values. Table 3 shows the obtained values for k_{ij}, l_{ij}, and MADx_1(%). The overall MADx_1 (%) obtained is 0.7 % for CO_2 + PEC5 and 1.5 % for CO_2 + PEBE8 mixtures. In Figure 8, it can be seen that these correlations reproduce well the experimental solubilities. This figure shows that for the region richer in refrigerant the following phase equilibria are predicted: for the system CO_2 + PEC5, VLLE and LLE are obtained at (298.15 and 303.15) K, and LLE at 313.15 K, whereas the system containing PEBE8 has a predicted VLLE and LLE at 303.15 K and LLE at 313.15 K. Bobbo et al. have also not found liquid−liquid equilibria for PEC5 at 283.15 K. Nevertheless, these authors have found experimentally liquid−liquid equilibria at this temperature for pentaerythritol tetraoctanoate, which is an isomer of PEBE8.

We must point out that linear temperature dependences of k_{ij} and l_{ij} have been found, as shown in Figure 9. The temperature functions obtained for the parameters k_{ij} and l_{ij} were for CO_2 + PEC5

$$k_{ij} = 0.3702 - 0.001277 \cdot T \quad l_{ij} = 0.1623 - 0.000453 \cdot T \tag{8}$$

and for CO_2 + PEBE8

$$k_{ij} = 0.4638 - 0.001541 \cdot T \quad l_{ij} = 0.1548 - 0.000415 \cdot \mathrm{T} \tag{9}$$

Conclusions

In this work, the solubilities of carbon dioxide, CO_2, in two pentaerythritol esters, PEs, were measured from (283 to 333) K and pressures up to 7 MPa in a new high-pressure gas solubility apparatus. The results show that in the analyzed range CO_2 is highly soluble in these oils. The experimental results at 283.15 K for the system CO_2 + PEC5 were compared with those of Bobbo et al. The comparison reveals a good agreement, the absolute average deviation being 2 %.

In terms of the CO_2 mole fraction in the refrigerant/lubricant solution, the solubility is practically not dependent on the branching of the acid chains, whereas it increases slightly with their length, in the present range of compositions. At higher temperatures, this behavior seems to be very similar.

In the range of concentrations analyzed in this work, at temperatures lower than the critical of CO_2, both systems exhibit negative deviations from Raoult's law, evidencing the presence of stronger interactions between unlike molecules in the mixture.

The SRK model with the classical quadratic mixing rule is appropriate for the correlation of the solubility values studied in this work. The deviations expressed in liquid mole fraction of CO_2 are on average 0.7 % for CO_2 + PEC_5 and 1.5 % for CO_2 + PEBE8 mixtures.

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