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Solubility of Carbon Dioxide in Pentaerythritol Tetrabutyrate (PEC4) and Comparison with Other Linear Chained Pentaerythritol Tetraalkyl Esters

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Abstract Carbon dioxide (CO_2) is one of the most promising natural refrigerants that can be employed as an alternative to hydrofluorocarbons (HFC), due to its low global warming potential (GWP). Nevertheless, CO_2 presents several technical problems when employed as a working fluid in refrigeration systems. In particular, the selection of the most suitable lubricant for each application is far from being resolved. The thermodynamic behavior of a CO_2 + lubricant system must be well-known for a correct oil selection. This work is part of a research project to study the solubility of CO_2 in commercial oils and their precursors. Here, solubility measurements of CO_2 in pure pentaerythritol tetrabutyrate (PEC4) between 243 K and 343 K are presented and compared with miscibility data of CO_2 in pentaerythritol tetrahexanoate (PEC6) and pentaerythritol tetraoctanoate (PEC8). The experimental data were correlated with a thermodynamic model based on a cubic equation of state with Huron–Vidal mixing rules and the UNIQUAC equation for the excess Gibbs energy at infinite pressure.

Keywords Carbon dioxide (CO_2) · Experimental data · Linear chained pentaerythritol tetraalkyl esters · Refrigerants · Solubility

1 Introduction

The polyol ester lubricants (POE) have proved to have adequate characteristics to work together with carbon dioxide (CO_2) in a refrigeration system, in terms of solubility

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and miscibility. After the phase-out of CFCs in the refrigeration industry, considerable interest has been placed on synthetic oils, such as POEs, polyalkylene glycol (PAG), alkyl benzenes (ABs), and poly-alpha olefin (PAO), which are blends of pure components of defined structure and molar mass, in an effort to verify their compatibility with hydrofluorocarbons (HFCs) and natural refrigerants. Since the effective composition and the constituents proportion in commercial POE lubricants are not available, the use of general laws able to describe the phase behavior of lubricant + refrigerant blends, which are the real operative fluids inside a refrigeration plant, is very difficult. Indeed, only through the use of a molecular structure and a molar mass is it possible to produce theoretical models that describe the phase behavior of such systems. Moreover, the regression of these models requires a large number of experimental data to determine the dependence of the solubility on pressure, temperature, and molecular structure. Unfortunately, in the literature there is a lack of such information, except for few systematic works, as [1–7]. For this reason, our group is involved in a research program to provide experimental measurements and the development of a general predictive model focused on the phase behavior of lubricant + refrigerant blends, with particular attention to systems of POE precursors and CO_2 [8–14].

The main components of POE are pentaerythritol esters, which can be linear chained, branched chained, and cyclic chained esters [15]. For a complete comprehension of the solubility dependence on the structure of the constituents and the possible appearance of miscibility limits, it is useful to have experimental data for pentaerythritol esters, considering also, within a homologous series the influence of differences in molar mass of various POEs.

This work completes a series of solubility measurements and data correlation for binary systems composed of carbon dioxide and linear chained precursors of POE lubricants (PECs), after previous studies of CO_2 + PEC6 [13] and CO_2 + PEC8 [14] systems, and preliminary results on CO_2 + PEC4, which have been reported already [12]. Here, complete experimental results for the solubility of CO_2 + PEC4, with modeling with the Peng–Robinson equation of state with Huron–Vidal mixing rules, are presented.

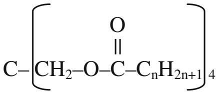
Furthermore, an analysis of the influence of the molar mass on the solubility and the miscibility of carbon dioxide in PECs over a wide range of temperatures and pressures is performed.

2 Experimental

2.1 Materials

Carbon dioxide (CO_2, CASRN 124-38-9), with 99.95 % purity, was supplied by Air Liquide. The three pure esters, i.e., pentaerythritol tetrabutyrate (PEC4, $C_{21}H_{36}O_8$, CASRN 7299-98-1), pentaerythritol tetrahexanoate (PEC6, $C_{29}H_{52}O_8$, CASRN 7445-47-8), and pentaerythritol tetraoctanoate (PEC8, $C_{37}H_{68}O_8$, CASRN 3008-50-2), were synthesized by Chemipan on a laboratory scale with a stated purity better than 98 %. They are pentaerythritol tetraalkyl esters obtained by combining an alcohol (pentaerythritol) with four equal alkyl linear chains, derived from carboxylic acids with different number of carbons.

Their chemical formula is



$$\mathrm{C}{-}\left[\mathrm{CH_2{-}O{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}C_nH_{2n+1}}\right]_4$$

where $n = 3,\ 5,$ and 7 for PEC4, PEC6, and PEC8, respectively.

To eliminate the non-condensable gases, the sample was put under vacuum and then used with no further purification.

2.2 Experimental Apparatus and Procedure

The solubility measurements were performed with an apparatus that has already been extensively described [8,13], so here only its main features will be noted. The equilibrium between the two substances was reached in a stainless steel cell with a calibrated volume of 180 cm^3, equipped with glass windows to observe the mixture. A helical stirrer moved by a magnetic motor was used to force the vapor phase through the liquid in order to achieve equilibrium. The cell was immersed in an 80 l thermostatic bath, in which the temperature was controlled by a heating resistance regulated by a PID controller, which compensated the cooling capacity of an external auxiliary thermostatic bath, with a stability of about 0.01 K. The two thermostatic baths were filled with water for temperatures higher than 273 K, and with ethyl alcohol for lower temperatures. A 100 Ω platinum resistance thermometer was used to measure temperature with an uncertainty of about 0.02 K, whereas for the pressure measurement, a pressure gauge (Druck DPI 145) with a full scale of 35 MPa and an uncertainty of 20 kPa was employed.

The solubility of CO_2 in lubricants was determined from measurements of the level of the liquid phase in the equilibrium cell, as explained below, measured by means of a cathetometer (Gaertner Scientific M940LE). The resolution of the cathetometer was 0.0001 mm, while the uncertainty in the level measurement was estimated to be 0.05 mm. Considering all the estimated contributions to experimental uncertainties, the overall uncertainty in the liquid composition was estimated to be from 0.002 (high CO_2 mole fraction) to 0.02 (low CO_2 mole fraction).

The desired amount of oil was charged directly into the cell. Its mass was measured by means of an analytical balance (Gibertini E42S 240 g full scale) with an uncertainty of 0.001 g; also, the CO_2 mass transferred inside the cell was gravimetrically measured. Once equilibrium was attained, the level of the meniscus between the liquid and the vapor phase was measured by means of the cathetometer, and then the liquid volume was calculated through a specific calibration equation, correlating the volume and the meniscus level. The vapor phase volume could be calculated subtracting the liquid volume from the total volume of the cell and multiplied by the CO_2 vapor density, calculated using the Refprop 8.0 database [16], allowing the determination of the CO_2 mass in the vapor phase. Considering that only CO_2 was in the vapor phase, due to the low vapor pressure of PECs, as also confirmed by [1], the mass of CO_2 dissolved in the liquid was calculated by simple subtraction from the total mass charged.

For temperatures higher than ambient, the connection pipes outside the bath and the diaphragm of the pressure gauge were heated with a wire resistance regulated by a PID controller, to reduce the CO_2 density deviations due to the temperature differences, which could reduce the measurement accuracy.

3 Results and Discussion

3.1 Experimental Data

The temperature range covered by the solubility measurements of CO_2 in PEC4, as for the other systems, is from 243.15 K to 343.15 K, therefore including isotherms below the critical temperature of CO_2 (about 304 K) and isotherms above it. This temperature range was chosen in order to represent the usual working conditions of a refrigeration plant operating with CO_2. It is worth noting that, even if the actual melting temperature was not measured, a melting point was observed below 263.15 K for PEC4. For the other studied PECs, i.e., PEC6 and PEC8, the melting points were observed below 273.15 K and 283.15 K, respectively. For this reason, the isotherms at lower temperatures present a first point (with low CO_2 concentration) slightly far from the one corresponding to the pure liquid oil, since, in these cases, the pure oil was solid.

Considering the pressure measurement range, for temperatures below the critical temperature of CO_2, it was limited by the saturation pressure of CO_2. On the contrary, for temperatures above the critical temperature of CO_2, the concentration range was limited by the upper reachable pressure, being roughly 10 MPa, due to the high pressure limit of the cell.

On average, 11 points were measured for each isotherm, resulting in 83 data points for CO_2 + PEC4, as summarized in Table 1 and Fig. 1, while for the other systems the available experimental data were 91 and 56 points for PEC6 + CO_2 [13] and for PEC8 + CO_2 [14], respectively.

3.2 Data Correlation

All the solubility data were correlated by means of a Peng and Robinson (PR) equation of state (EoS) [17] with Huron–Vidal mixing rules (HV) [18] and the UNIQUAC equation for the excess Gibbs energy (g^E) at infinite pressure [19]. The critical parameters for PEC4, reported in Table 2, were estimated, i.e., the critical temperature (T_c) by means of the Fedors method [20] and the critical pressure (p_c) by the Somayajulu method [21]; the group size parameter, R_k, and the group surface parameter, Q_k, are also reported in Table 2 for the sake of completeness.

The complete model was already described in [13], in which the following expression was used for the PR EoS a_{22} temperature dependence,

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

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

Table 1 Experimental solubility data for the CO_2 + PEC4 system

x_{CO_2}	P (MPa)	x_{CO_2}	P (MPa)	x_{CO_2}	P (MPa)	x_{CO_2}	P (MPa)
T = 243.15 K		T = 253.15 K		T = 263.15 K		T = 273.15 K	
0.6649	0.754	0.6311	0.940	0.1077	0.126	0.0952	0.142
0.7422	0.920	0.7131	1.171	0.2785	0.379	0.1340	0.205
0.7806	1.009	0.7554	1.302	0.5936	1.123	0.2525	0.427
0.8078	1.073	0.7854	1.401	0.6793	1.422	0.5561	1.295
0.8342	1.135	0.8153	1.500	0.7241	1.604	0.6427	1.664
0.8784	1.233	0.8663	1.661	0.7566	1.745	0.6894	1.894
0.9306	1.331	0.9263	1.828	0.7899	1.893	0.7234	2.080
				0.8486	2.152	0.7594	2.285
				0.9198	2.440	0.8250	2.670
						0.9097	3.165
T = 283.15 K		T = 303.15 K		T = 323.15 K		T = 343.15 K	
0.0872	0.163	0.0890	0.235	0.0753	0.265	0.0655	0.293
0.2397	0.501	0.1259	0.352	0.1067	0.396	0.0929	0.438
0.3919	0.952	0.2041	0.608	0.1746	0.688	0.1537	0.760
0.5016	1.375	0.2915	0.947	0.2531	1.074	0.2243	1.189
0.5972	1.842	0.403	1.456	0.3544	1.662	0.3188	1.847
0.6783	2.341	0.4628	1.811	0.4112	2.073	0.3743	2.310
0.7247	2.653	0.5348	2.285	0.4803	2.631	0.4398	2.944
0.7921	3.187	0.6419	3.185	0.585	3.714	0.5451	4.187
0.8600	3.748	0.6922	3.692	0.6365	4.343	0.5959	4.921
0.9162	4.150	0.7737	4.694	0.7189	5.639	0.6851	6.454
0.9669	4.372	0.8257	5.432	0.7734	6.763	0.7391	7.872
		0.8291	5.491	0.8298	7.993	0.7972	9.555
		0.8798	6.242	0.8759	9.317		
		0.9304	6.863				

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

and

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

The data were regressed by means of the following objective function:

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

where N_p is the number of experimental data.

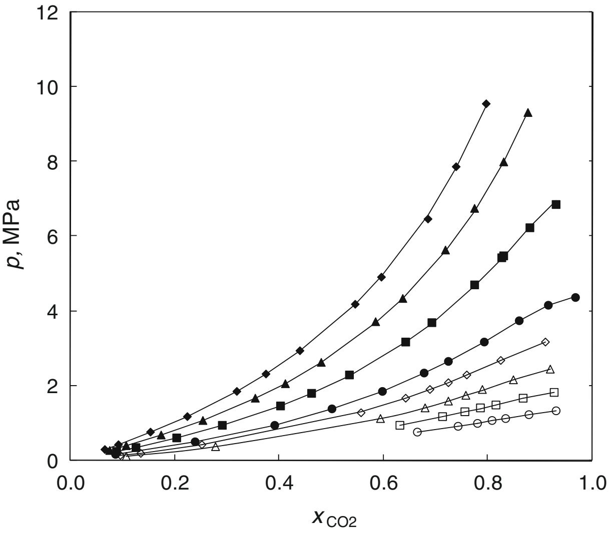


Fig. 1 Solubility in mole fraction of CO_2 in PEC4 at 243.15 K (○), 253.15 K (□), 263.15 K (△), 273.15 K (◇), 283.15 K (●), 303.15 K (■), 323.15 K (▲), and 343.15 K (◆); PR-HV-UNIQUAC EoS model (-)

Table 2 Pure compound parameters used in the data correlation

Compound	T_c (K)	p_c (kPa)	R_k	Q_k	Ref
CO_2	304.13	7377.3	1.3000	0.982	
PEC4	880.8 [20]	1124.9 [21]	17.4367	14.672	
PEC6	931.2 [20]	848.7 [21]	22.8319	18.992	[13]
PEC8	972.5 [20]	681.1 [21]	28.2271	23.3120	[14]

It is worth noting all the parameters reported in Table 2 for all the systems should be used together to reproduce the experimental data.

The critical PEC4 parameters were used only for the calculation of b_2 of the PR EoS from the well-known equation

$$b_2 = 0.0077796\frac{RT_{c,2}}{P_{c,2}} \tag{5}$$

It is assumed that b_2 is temperature independent.

Due to the extremely low saturation pressures of PECs [1], the second parameter of the cubic EoS, $a_{22}(T)$, was considered as a dependent variable and was found simultaneously regressing the solubility data, unlike the standard procedure, where $a_{22}(T)$ values are obtained independently. For this reason, the estimation of the PECs critical parameters is a less crucial factor, as the uncertainty in their adopted values, impacting only the b_2 value, are attenuated by fitting the adjustable parameters.

All the deviations of the experimental data for all the systems from the model are summarized in Table 3. In particular, in Fig. 2 the deviations of the solubility data

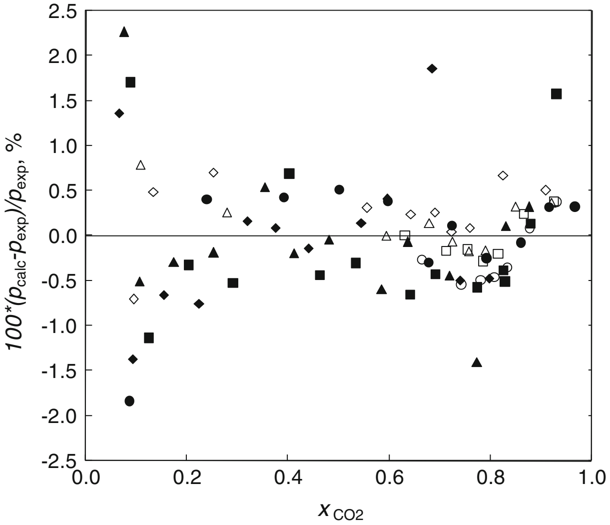


Fig. 2 Deviations in pressures from the PR-HV-UNIQUAC EoS model for the CO_2 + PEC4 system at 243.15 K (○), 253.15 K (□), 263.15 K (△), 273.15 K (◇), 283.15 K (●), 303.15 K (■), 323.15 K (▲), and 343.15 K (◆)

for CO_2 + PEC4 from the model in terms of pressure are shown. It is possible to observe that the deviations are rather randomly distributed with composition, being within ± 0.5 %, except for a few points at x_{CO_2} around 0.2, or less, where clearly greater deviations are evident, probably due to a too small amount of CO_2 mass charged. The percentage absolute average deviation (AAD %) is 0.44 % , with a bias of about −0.01 %. However, the observed deviations are smaller than these expected from the estimated uncertainty in composition measurements, presumably because the error in composition, resulting from the method of mass charging, is random and thus mutually compensated. Moreover, the distribution of the deviations is random, rather than systematic.

3.3 Comparison of Solubility of CO_2 in Homologous Series of PECs

The experimental solubility data for the three CO_2 + PEC4, CO_2 + PEC6, and CO_2 + PEC8 systems were compared. These data are shown in Figs. 3 and 4, for temperatures lower or higher than 273.15 K, respectively.

Unfortunately, for temperatures lower than 273.15 K, it was not possible to measure the solubility of CO_2 in PEC8, since it was solid up to a high concentration of CO_2. Moreover, for the same reason, for all PECs, only a few compositions could be measured at low CO_2 concentrations. On the contrary, as already noted, at 323.15 K and 343.15 K the isotherms could not be completed at higher CO_2 compositions, due to the pressure limits of the apparatus.

It is evident that, as already noted in [8], the solubility of CO_2 in PECs is quite similar within the studied homologous series of PECs. However, small but systematic

Table 3 Values of the binary interaction parameters of the PR-HV-UNIQUAC model for the CO_2 + PEC4 system

i	$a_{22,i}$	$\tau_{12,i}$	$\tau_{21,i}$	AAD(Δp) (kPa)	AAD(Δp%)
CO_2 + PEC4					
0	75943.8	0.6253821	0.3691010	11.37	0.48
1	−386.297	−0.0005911	−0.0005862		
CO_2 + PEC6					
0	148401.8	0.5827213	0.3164054	16.01	0.53
1	−655.020	0.0010159	−0.0003598		
CO_2 + PEC8					
0	254722.1	0.547042	0.287183	35.31	1.06
1	−1314.01	0.000634	−0.0002		

$$\text{AAD}\,(\Delta p) = \frac{\sum_{i=1}^{N_p} \left| p_{i,\text{calc}} - p_{i,\text{exp}} \right|}{N_p}$$

$$\text{AAD}\,(\Delta p\%) = \frac{\sum_{i=1}^{N_p} 100 \cdot \left| \frac{p_{i,\text{calc}} - p_{i,\text{exp}}}{p_{i,\text{exp}}} \right|}{N_p}$$

N_p = number of points

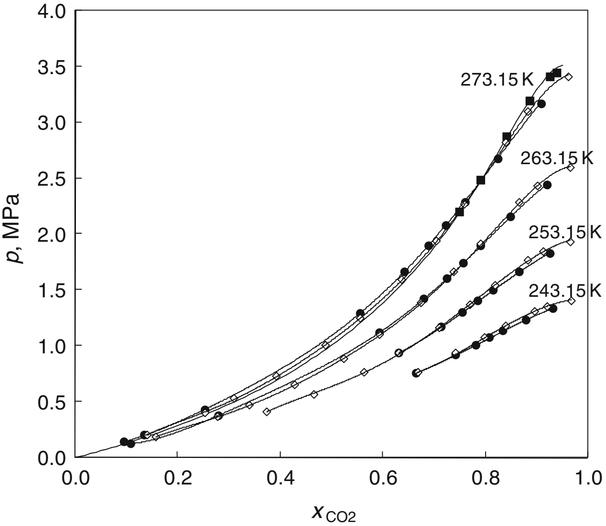


Fig. 3 Solubility in mole fraction of CO_2 in PEC4 (●), and in PEC6 (◇), at 243.15 K, 253.15 K, 263.15 K, and 273.15 K, and in PEC8 (■) at 273.15 K; PR-HV-UNIQUAC EoS model (-)

deviations in solubility should be noted, at mole fractions higher than roughly 0.8, the solubility decreases from PEC4 to PEC8 and, on the contrary, at lower mole fractions, the solubility increases from PEC4 to PEC8. It should be noted Fandiño et al. [5] found similar behavior for the CO_2-pentaerythritol tetravalerate (PEC5) system, in the temperature range between 283 K and 333 K.

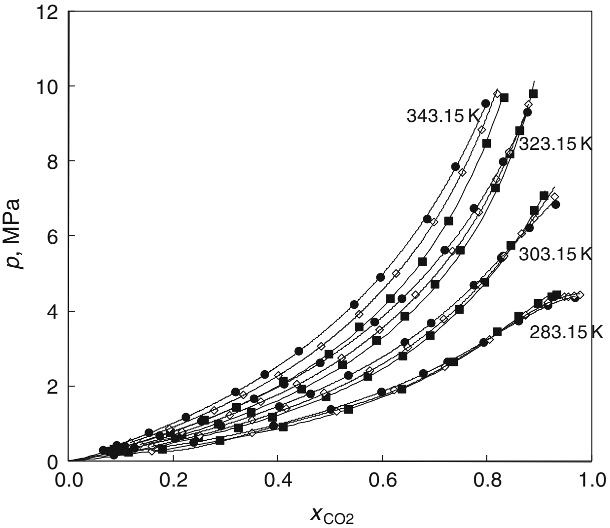


Fig. 4 Solubility in mole fraction of CO_2 in PEC4 (●), PEC6 (◇), and PEC8 (■), at 283.15 K, 303.15 K, 323.15 K, and 343.15 K; PR-HV-UNIQUAC EoS model (-)

Using the determined parameters, the excess Gibbs energy, g^{E}, was calculated from the equation,

$$g^{\mathrm{E}} = RT\left(\ln\varphi - \sum x_i \ln\varphi_i\right) \tag{6}$$

where ψ and ψ_i for the fugacity coefficients for the mixture and pure component, respectively, in the liquid state at the same temperature and pressure. For comparison, the excess Gibbs energy for each system at 273.15 K is presented in Fig. 5.

For a wide composition range, g^{E} is negative, increasing with the size of the PECs. For example, at $T = 273.15$ K and $x_{\mathrm{CO}_2} = 0.25$ and $x_{\mathrm{CO}_2} = 0.5$, a linear dependence of the g^{E} values were observed if plotted against the number of carbon atoms in the alkyl chain of PECs. It means that the solubility increases as the difference in molecule size increase, rather than being correlated to the increase of the attractive interactions between unlike molecules, even if strong negative deviations from Raoult's law are evident. Vice versa, at high x_{CO_2} concentrations, the solubility of PEC decreases with an increase of the length of the alkyl chain and it can result from the increasing contribution of repulsive forces between CO_2 and the –CH_2– group. This effect begins to be predominant and appears as positive deviations from Raoult's law with positive g^{E} values that reach their maximum value at about $x_{\mathrm{CO}_2} = 0.98$.

In addition, for the CO_2 + PEC8 system, we detected limited liquid phase miscibility. It is the only system within the series showing this behavior. A more detailed analysis [14] showed that this system presents the lower critical solution temperature (LCST) at about $T = (268 \pm 0.1)$ K and the range of the limited liquid phase immiscibility attains its upper critical end point (UCEP) as the temperature reaches the critical temperature of CO_2.

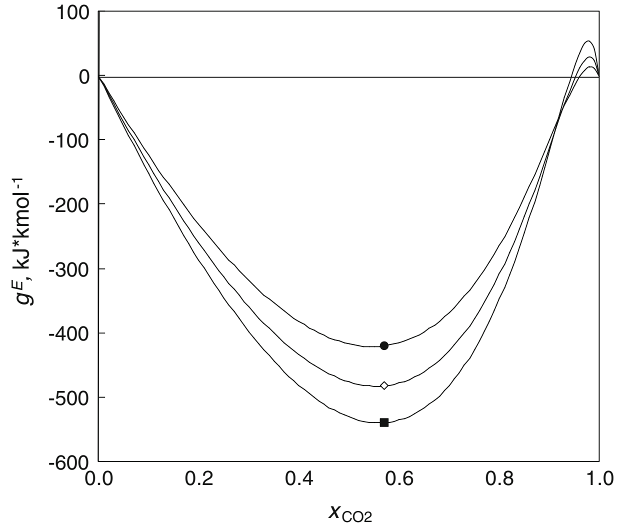


Fig. 5 Calculated excess Gibbs energy (g^E) for PEC4 (●), PEC6 (◇), and PEC8 (■), at 273.15 K

4 Conclusions

Solubility measurements within the temperature from 243.15 K to 343.15 K for the CO_2 + PEC4 system are presented. Experimental data were correlated by means of the PR EoS with HV mixing rules and by employing the UNIQUAC equation for g^E at infinite pressure. The applied model was developed to enable the correlation of the mixtures formed with ill-defined components, for which equation-of-state parameters could not be found from true critical parameters and saturated pressures. Data are well represented by the proposed model with the linear temperature dependence of the regressed parameters. It is worth noting that the regressed parameters represent the solubility data for temperatures both below and above the critical temperature of CO_2.

Moreover, the experimental solubility data for the three CO_2 + PEC4, CO_2 + PEC6, and CO_2 + PEC8 systems were compared over the same temperature range, showing a similar solubility trend. At mole fractions higher than roughly 0.8, the solubility decreases from PEC4 to PEC8. On the contrary, at lower mole fractions values, the solubility increases from PEC4 to PEC8. The systems show a negative trend of the excess Gibbs energy, almost over the whole composition range, passing to positive values for x_{CO_2} greater than about 0.95. It is worth noting that the excess Gibbs energy is more negative with an increase of the chain length of PECs within the series.

This observation suggests that negative deviations from the excess Gibbs energy, phenomenologically visible as negative deviations from Raoult's law, result mostly from great differences in the molecular size of the system components rather than from attractive forces between unlike molecules.

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