High-Pressure Viscosity and Density of Carbon Dioxide + Pentaerythritol Ester Mixtures: Measurements and Modeling

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This article reports densities and viscosities up to 60 MPa and from 303.15 to 353.15 K on two binary mixtures of CO_2 and lubricant pentaerythritol tetra-2-ethylhexanoate with 7.8% and 14.4% mass fraction of lubricant. Because CO_2 and the lubricant are not in the same phase at atmospheric pressure and room temperature, a specially-designed vibrating-wire apparatus has been used. The experimental data, together with our previous data for six mixtures of CO_2 and three polyolesters, have been used to test the predictive and correlation ability of several models: simple mixing laws, the self-referencing method, and the hard-sphere and free volume models. In general, it is not possible to predict the viscosity with deviations smaller than 10%. The hard-sphere model and the self-referencing model are the more adequate to represent the viscosity of these mixtures. Most of the models studied underestimate the viscosities over the investigated (T,p) range.
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Introduction

The problem of the choice of appropriate lubricants for the use with new environmentally acceptable refrigerants, including carbon dioxide, is still unsolved. Different families of new oils as polyalkylene glycol (PAG), polyolester (POE), polyalphaolefins (PAO), alkylbenzenes (AB), or polyvinylether (PVE) have been selected to replace the mineral oils, generally used in the past, which are not compatible with the new refrigerants.[1] In refrigeration cycles, a lubricant is usually present with the refrigerant. The lubricant can change the thermophysical properties of the working fluid,[2,3] and this change is highly dependent of the considered refrigerant and lubricant. It is, therefore, desirable to have models that

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can accurately represent the properties of refrigerant + lubricant mixtures. These systems are more difficult to model than refrigerant + refrigerant mixtures because of much larger size differences of the constituent molecules.

Few data are available on the thermophysical properties of the refrigerant + lubricant systems,[1–17] and most of them refer to hydrofluorocarbons (HFC) and commercial oils, the structure and composition of the latter being usually not well-defined, since they are mixtures of different components and additives. This makes difficult the development of reliable models able to predict the behavior of the thermophysical properties of refrigerant + lubricant mixtures.

Some publications concerning the study of viscosity vs. temperature, pressure, and composition have been published in the past few years. Thus, Hauk and Weidner,[18] Seeton et al.,[8] and Li and Rajewski[11] have measured the viscosity of mixtures CO_2 with POEs, PAGs, or PAOs. However, in these works, no experimental values and information about the composition and molecular structure of the lubricants are reported. Hence, new experimental measurements of CO_2 + lubricant systems should be performed in order to verify the existing viscosity models.

At present, our research group is studying the density[19–21] and viscosity[22–24] in broad ranges of temperature and pressure of pentaerythritol esters considered as precursors of POE oils (i.e., as components of refrigerant commercial oils), the solubility[25] of carbon dioxide in pentaerythritol esters, and the density and viscosity[17] of mixtures containing POE lubricants and CO_2.

In a previous article,[17] density and viscosity measurements of carbon dioxide with three pentaerythritol ester lubricants (with mass content of lubricant around 8% and 15%) were reported. In this work, we present the density and viscosity values for mixtures of carbon dioxide with pentaerythritol tetra-2-ethylhexanoate (PEB8) at low lubricant concentrations (7.8% and 14.4% mass fraction of lubricant) from 303 to 353 K and at pressures up to 60 MPa. The two properties were measured simultaneously using a vibrating-wire instrument[17,26–28] specially developed for the study of gas-condensate mixtures. Mixtures with low content of lubricant are of high interest in engineering because, in vapor compression refrigeration and heat pump systems, a small amount of compressor lubricant, as a part of the working fluid, circulates with the refrigerant.[29] The working fluid is changed then from a pure refrigerant, with well-defined properties, to a mixture with properties that are poorly understood and dependent on the lubricant concentration. The migrated oil affects the heat-transfer coefficient, which is an important characteristic of any working fluid, changing the evaporator pressure drop and degrading the performance of both the gas cooler and the evaporator.[30]

The viscosity data for the mixtures analyzed in this work, combined with those previously measured[17] for the systems carbon dioxide + pentaerythritol tetrapentanoate (PEC5), carbon dioxide + pentaerythritol tetraheptanoate (PEC7), and carbon dioxide + pentaerythritol tetranonanoate (PEC9) have been used to test the ability of different mixing rules[31,32] and several models developed in the literature, which have different origins and theoretical backgrounds. The existing models are mainly used to correlate the viscosity as a function of the pressure and temperature of the pure compounds. Subsequently, using appropriate mixing rules, the viscosity of the mixtures can be predicted. The most usual models to perform this task over broad pressure ranges are based on the free-volume concept,[33–35] the hard-sphere (Enskog) theory,[36–39] reaction rate theory,[40] or a friction model.[41,42] Other methods used to calculate viscosity based on molecular theory[43–48] (molecular simulation and QSPR methods) are not yet competitive for the studied systems. In this work, we have verified the prediction ability of the self-referencing method, the hard-sphere model, and the free-volume model.

Experimental Section

Materials

Pentaerythritol tetra-2-ethylhexanoate (PEB8, $C_{37}H_{68}O_8$, CAS 7299-99-2) was obtained from Nikko Chemicals with a purity of 99%. It was degassed and dried by keeping it under vacuum (~1 Pa) for 8 h to 15 h at a temperature above 303 K. Carbon dioxide was obtained from AGA/Linde Gaz with a mole fraction purity of 99.995%.

Measurement technique

Viscosity and density were measured simultaneously using the vibrating-wire method. The working principle of measurement, the apparatus, and the experimental procedure for the density and viscosity determination are described in detail in a previous work.[17] The mixtures are prepared in an additional high-pressure variable-volume cell equipped with a piston in order to isolate the lubricant/refrigerant mixture from the pressurizing fluid. This vessel is pressurized up to a pressure higher than the saturation pressure to ensure that the mixture is in a single phase.

It is also necessary to ensure the homogeneity of the mixture inside the measurement apparatus. This has been done using a high-pressure circulation pump connected to the pressure line. Homogeneity of the mixture is verified by performing measurements with the vibrating-wire sensor. The temperature in the high-pressure vessel, which is surrounded by an isothermal shield in the interior of a vacuum chamber, is controlled better than ± 0.005 K. Two platinum resistance thermometers are used to measure the temperature of the pressure vessel at different places (one of them is read in four-wire mode). Three other thermometers monitor the temperature of the isothermal shield. The uncertainty in temperature is estimated to be ± 0.02 K. Pressure was measured with two transducers (Keller mod. PA-25HTC, Switzerland) with ranges up to 40 and 100 MPa. The pressure uncertainty is $\pm 0.1\%$ of the full scale. The estimated uncertainties in the density and viscosity measurements are $\pm 0.2\%$ and $\pm 3\%$, respectively.

Results and Discussion

Measurements of density and viscosity of the mixtures 0.9942 CO_2 + 0.0058 PEB8 and 0.9885 CO_2 + 0.0115 PEB8 (7.8% and 14.4% mass fraction of lubricant) were performed along six isotherms between 303.15 K and 353.15 K and at pressures up to 60 MPa. A total of 216 experimental points were obtained. The results are presented in Table 1. In Figures 1 and 2 we have plotted respectively the experimental densities and viscosities, for the mixtures against pressure, along the several isotherms. In Figure 3, the density for these

Table 1. Experimental Values of Densities, ρ (kg m^{-3}) and Viscosity, η (mPa s) for x CO_2 + (1−x) PEB8 Mixtures at Different Temperatures and Pressures

p (MPa)	ρ (kg m^{-3})	η (mPa s)	ρ (kg m^{-3})	η (mPa s)	ρ (kg m^{-3})	η (mPa s)
			0.9942 CO_2+0.0058 PEB8			
	T = 303.15 K		T = 313.15 K		T = 323.15 K	
10	805.5	0.089				
15	865.5	0.103	815.9	0.090		
20	902.9	0.115	865.0	0.102	817.8	0.091
25	931.0	0.125	898.7	0.113	860.2	0.102
30	953.7	0.134	925.0	0.122	891.3	0.111
35	973.0	0.142	946.8	0.131	916.3	0.120
40	989.8	0.150	965.6	0.138	937.3	0.128
45	1004.9	0.157	982.2	0.145	955.7	0.135
50	1018.5	0.164	997.1	0.152	972.1	0.141
55	1030.9	0.171	1010.6	0.158	986.9	0.148
60	1042.4	0.178	1023.1	0.165	1000.5	0.154
	T = 333.15 K		T = 343.15 K		T = 353.15 K	
20	765.7	0.082				
25	819.1	0.093	774.2	0.087	729.9	0.085
30	855.7	0.103	818.6	0.097	784.0	0.093
35	884.2	0.112	851.5	0.105	821.8	0.101
40	907.8	0.120	878.1	0.113	851.6	0.109
45	928.3	0.127	900.8	0.119	876.6	0.116
50	946.4	0.134	920.6	0.126	898.3	0.122
55	962.7	0.140	938.3	0.132	917.6	0.128
60	977.6	0.147	954.5	0.138	935.1	0.133
			0.9885 CO_2+0.0115 PEB8			
	T = 303.15 K		T = 313.15 K		T = 323.15K	
10	839.0	0.099				
15	887.2	0.112	837.9	0.098		
20	919.4	0.123	880.5	0.109	837.4	0.100
25	944.1	0.134	910.6	0.119	874.2	0.109
30	964.3	0.144	934.3	0.128	901.8	0.118
35	981.6	0.153	954.1	0.137	924.3	0.127
40	996.8	0.161	971.1	0.146	943.3	0.135
45	1010.3	0.169	986.2	0.154	960.0	0.143
50	1022.6	0.177	999.7	0.162	975.0	0.151
55	1033.9	0.184	1012.0	0.169	988.5	0.159
60	1044.3	0.191	1023.4	0.176	1000.9	0.166
	T = 333.15 K		T = 343.15 K		T = 353.15 K	
20	793.8	0.090				
25	838.3	0.100	800.1	0.088	760.8	0.080
30	870.2	0.109	838.8	0.098	806.8	0.090
35	895.5	0.117	867.8	0.107	839.8	0.098
40	916.8	0.125	891.5	0.115	866.0	0.106
45	935.3	0.133	911.7	0.122	888.1	0.114
50	951.7	0.141	929.4	0.129	907.4	0.121
55	966.6	0.148	945.3	0.136	924.5	0.127
60	980.1	0.156	959.6	0.143	940.0	0.134

mixtures are compared with the density values of pure PEB8 (previously measured in our laboratory by Fandiño et al.[21]), and of carbon dioxide[17] over the pressure interval of 10–60 MPa and the temperature interval of 303.15–353.15 K. The trends in the density of mixtures with pressure and temperature are similar to those of pure carbon dioxide. The density of the mixtures is, in general, higher than the values for the pure carbon dioxide.

The present results for density were correlated using a modified Tait equation given by the expression:

$$\rho(p,T) = \frac{A_0 + A_1 T + A_2 T^2 + A_3 T^3}{1 - (C_0 + C_1 T)\ln\left(\frac{B_0 + B_1 T + B_2 T^2 + p}{B_0 + B_1 T + B_2 T^2 + p_{\mathrm{ref}}}\right)} \qquad (1)$$

We have chosen 60 MPa as the reference pressure and the values of the coefficients A_i (i = 0, 1, 2, 3) were determined in a preliminary fit to the density at the reference pressure as a function of the temperature. Coefficients B_j (j = 0, 1, 2) and C_k (k = 0, 1) were fitted to the density measurements at pressures different from the reference pressure using the Levenberg-Marquardt[50] algorithm. We have considered a linear temperature dependence for coefficient C, since the quality of the fits was significantly improved in comparison with that obtained with no temperature dependence in this coefficient. Cibulka and coworkers[51–54] have used a similar equation, with C depending on temperature, to correlate density of linear and branched alkanes, alkanols, and aromatic hydrocarbons. In addition, Troncoso et al.[55] also have used this

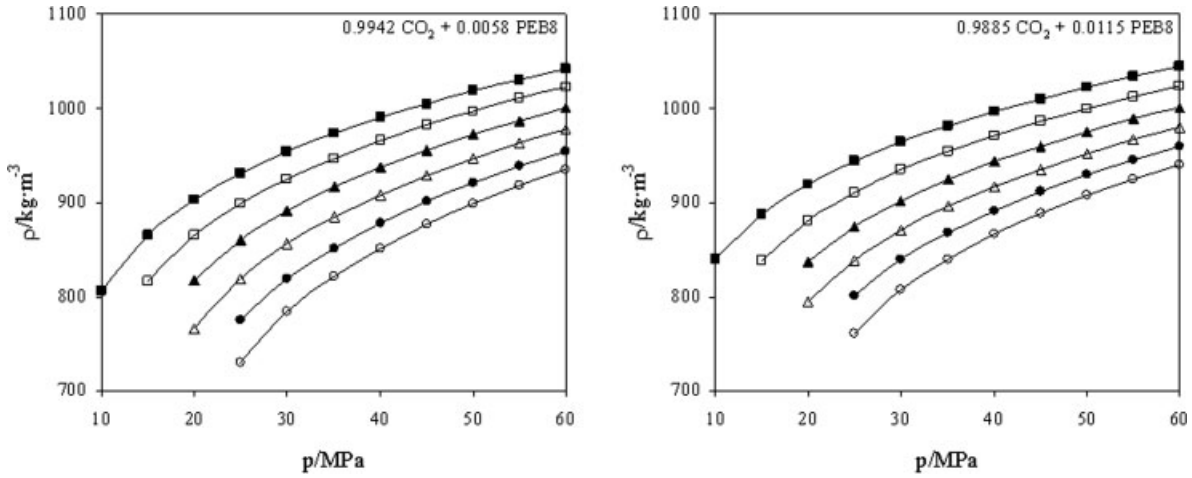

Figure 1. Experimental densities for $xCO_2 + (1 - x)$ PEB8 mixtures: (■) 303.15 K, (□) 313.15 K, (▲) 323.15 K, (△) 333.15 K, (●) 343.15, (○) 353.15 K.

type of modified Tait equation to correlate the density values of mixtures *1*-hexanol + *n*-hexane. The parameters values of Eq. 1 are presented in Table 2. The experimental points fall within a narrow range well-centered with respect to Eq. 1 at each composition, yielding an absolute average deviation (AAD) of 0.05% which is a measure of the dispersion of the data. Unfortunately, to our knowledge no additional points are available in the literature from other researchers so it was not possible perform comparisons against values of independent sources.

The sensitivity of the vibrating wire apparatus permits us to estimate the excess molar volumes v^E from the experimental density values.[27] The following relation was used to determine v^E:

$$v^E = \frac{1}{\rho_m}\sum_{i=1}^{2} x_i M_i - \sum_{i=1}^{2}\frac{x_i M_i}{\rho_i} \qquad (2)$$

where ρ_m is the density of the mixture, and x_i, M_i, and ρ_i are the mole fraction, the molar mass, and the density of the component *i*, respectively. The density values of the pure components where taken from Pensado et al.[17] for carbon dioxide, and from the work of Fandiño et al.[21] for the PEB8 lubricant. For the studied mixtures, in the considered (*T*,*p*) range this excess property is negative, being at a fixed composition more negative when the pressure decreases and the temperature increases. Similar behavior have been found in a previous work for mixtures of CO_2 with PEC5, PEC7, and PEC9.[17] The negative values of v^E could indicate a tendency of the molecules of the refrigerant to place themselves in the free space present in the large, branched molecules of the lubricant, as well as a high degree of interaction between the molecules of the CO_2 and the lubricant. Canet,[56] Audonnet and Padua,[27] Marchi et al.,[57] and Comuñas et al.[12,13] also obtained negative values for the excess molar volume of other size-asymmetrical mixtures (methane + decane, HFC-134a + TEGDME, and HFC-134a + TriEGDME).

In Figure 4 we represented the behavior of the dynamic viscosity of the mixtures together with the viscosity values

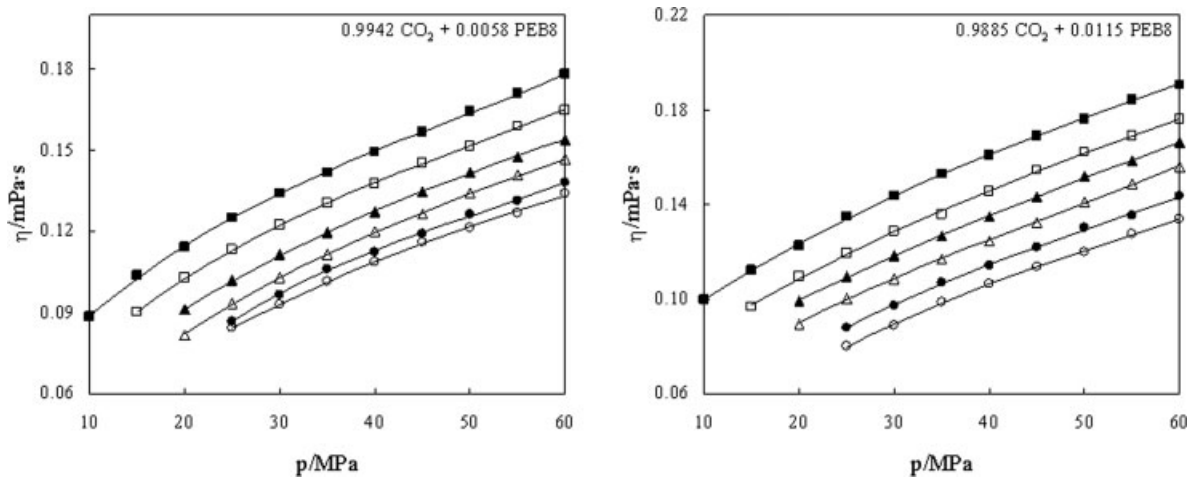

Figure 2. Experimental viscosities for $xCO_2 + (1 - x)$ PEB8 mixtures: (■) 303.15 K, (□) 313.15 K, (▲) 323.15 K, (△) 333.15 K, (●) 343.15, (○) 353.15 K.

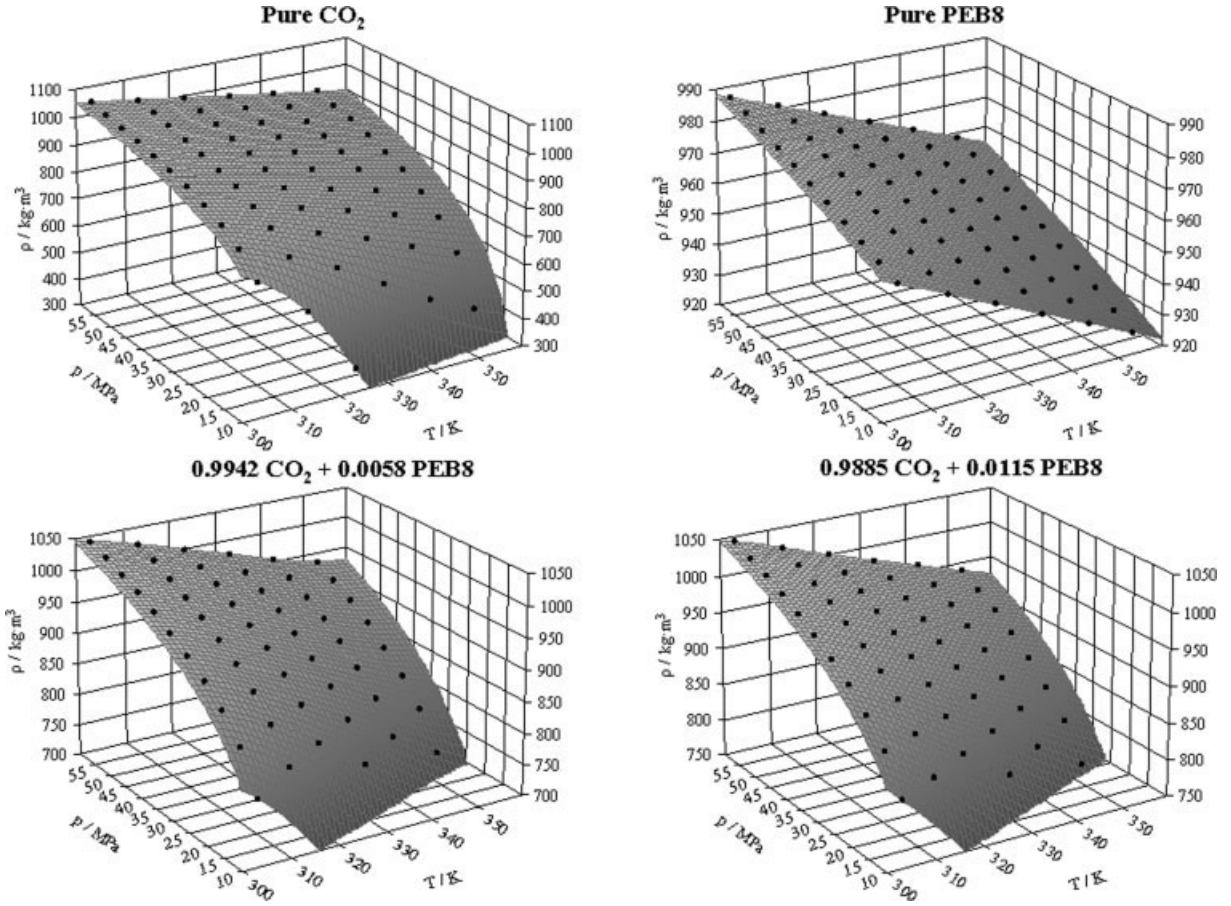

Figure 3. ρTp diagrams for $x\mathrm{CO_2}$ + (1 − x) PEB8 mixtures (this work) and for pure carbon dioxide[17] and pure PEB8.[21]

of the pure compounds,[22,58] as function of pressure at 303.15 K. The addition of a small quantity of lubricant to the pure refrigerant gives rise to a drastic increase of the viscosity of the mixtures; thus, the viscosity of the mixtures with a concentration of 15% in mass of lubricant is around twice the viscosity of the pure carbon dioxide. This could affect, in an important manner, the heat transfer coefficients and the global performance of refrigeration system.[30,59–61] In the (T,p) range analyzed in this work, the viscosity values of the pure lubricants are around two or three orders of magnitude higher than those of the studied mixtures. In the interval of composition considered in this work, the pressure dependence of the viscosity of the mixtures is close to that of the pure carbon dioxide, as can be observed in Figure 4. Mixtures of CO_2 with PEC5, PEC7, and PEC9 show a similar behavior.[17]

The experimental viscosity data for each mixture were correlated as function of temperature and pressure with the

Table 2. Parameter Values of Eq. 1 and Obtained Deviations for the Correlations of the Density of x $\mathrm{CO_2}$ + (1−x) PEB8 Mixtures

	Parameters								
	A_0 (kg m^{-3})	A_1 (kg m^{-3} K^{-1})	10^2 A_2 (kg m^{-3} K^{-2})	10^3 A_3 (kg m^{-3} K^{-3})	B_0 (MPa)	B_1 (MPa K^{-1})	10^3 B_2 (MPa K^{-2})	10^2 C_0	10^3 C_1 (K^{-1})
x = 0.9942	−9610.7	101.36	−31.525	0.3194	162.48	−0.8025	0.8163	−6.7866	0.6039
x = 0.9885	1957.3	−3.7882	0.2565	0	226.74	−1.1847	1.3933	−4.3567	0.4976

	Deviations		
	AAD (%)	MD (%)	Bias (%)
x = 0.9885	0.05	0.2	−0.001
x = 0.9942	0.05	0.2	−0.006

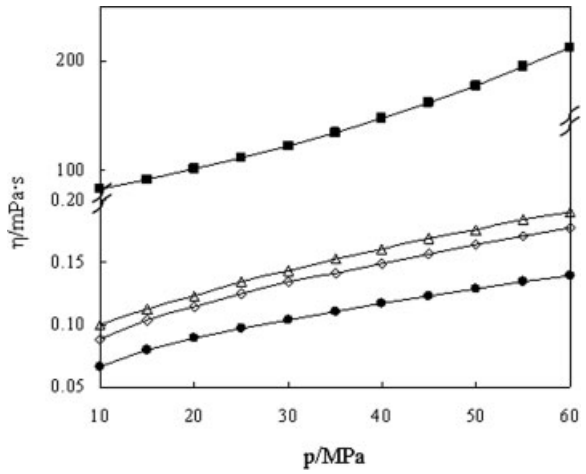

Figure 4. Dependence of the viscosity with the mole fraction and pressure at 303.15 K for the mixtures $xCO_2 + (1 - x)$ PEB8: (■) $x = 0$, (△) $x = 0.9885$, (◇) $x = 0.9942$, (●) $x = 1$.

follow equation, similar to those proposed by Comuñas et al.[62]:

$$\eta(p,T) = \eta(p_{\text{ref}},T)\exp\left[G(T)\ln\left(\frac{p+E(T)}{p_{\text{ref}}+E(T)}\right)\right] \quad (3)$$

where $\eta(p_{\text{ref}},T)$ is the dynamic viscosity as function of temperature at a reference pressure, p_{ref} given by:

$$\eta(p_{\text{ref}},T) = D_0 + D_1T + D_2T^2. \quad (4)$$

The functions $E(T)$ and $G(T)$ have the follow expressions:

$$G(T) = G_0 + G_1T \quad (5)$$

$$E(T) = E_0 + E_1T + E_2T^2 \quad (6)$$

We have selected as reference pressure $p_{\text{ref}} = 60$ MPa. The D_i ($i = 0, 1, 2$) parameters of Eq. 4, presented in Table 3, have been determined in a preliminary fit of the viscosity as a function of temperature at the reference pressure, and coefficients E_j ($j = 0, 1, 2$) and G_k ($k = 0, 1$) have been fitted to the viscosity measurements at pressures different from the reference pressure using the Levenberg-Marquardt[50] algorithm. In Table 3, the deviations obtained for the studied mixtures are reported.

Viscosity modeling

We have used the viscosity values reported in the present work for the mixtures CO_2 + PEB8, together with those presented in a previous work[17] for the mixtures CO_2 + PEC5, CO_2 + PEC7, and CO_2 + PEC9 to test the prediction ability of some models. For pure carbon dioxide, the experimental viscosity values between 303.15 and 353.15 K and from 10 to 60 MPa were taken from a previous work of Pensado et al.[17] For PEC5, PEC7, PEC9, and PEB8 the η values already measured between 303.15 and 353.15 K and from 0.1 to 60 MPa were used.[22,23] The models considered range from the simple classical mixing laws by Grunberg and Nissan[31] and Katti and Chaudhri[32] through empirical general correlations, such as the self-referencing model,[63] to recent approaches with a physical and theoretical background, such as the hard-sphere scheme[36,37,39] and the free-volume model.[33–35]

Mixing laws The objective of these mixing laws is to predict the viscosity of mixtures using only the viscosity and density of the pure substances and their mole fraction (or other composition scale). We have considered two mixing laws without any adjustable parameters, so they can be considered as predictive, and one mixing law that involves one adjustable parameter, i.e., a correlation mixing law. The first mixing law used for viscosity predictions is that proposed by Katti and Chaudhri,[32] given by the follow expression:

$$\ln \nu_{\text{mix}} = x_1 \ln \nu_1 + x_2 \ln \nu_2 \quad (7)$$

where ν is the kinematic viscosity and x the mole fraction. Subscript "mix" refers to the mixture, whereas subscripts 1 and 2 refer to the pure compounds. The AAD between the experimental and the predicted values using this mixing law are high (ranging from 15 to 41%), as can be seen in Table 4. The maximum deviation (MD) was obtained for the mixture 0.9879 CO_2 + 0.0121 PEC9 (47%). The mixing rule predicts always kinematic viscosity values lower than the experimental values (Bias = AAD). Geller et al.[64,65] utilized this mixing law to predict the viscosities of HFC refrigerant + POE lubricant mixtures. These authors have found that this mixing law is more appropriate for high temperatures.

Table 3. Parameter Values of Eq. 3 and Obtained Deviations for the Correlations of the Viscosity of x CO_2 + (1–x) PEB8 Mixtures

	Parameters							
	D_0 (mPa s)	10^3 D_1 (mPa s K^{-1})	10^6 D_2 (mPa s K^{-2})	E_0 (MPa)	E_1 (MPa K^{-1})	10^3 E_2 (MPa K^{-2})	G_0	10^3 G_1 (K^{-1})
$x = 0.9942$	1.477	−7.206	9.634	429.5	−2.441	3.42	0.438	0.037
$x = 0.9885$	0.797	−2.762	2.5	291.57	−1.739	2.652	−0.717	3.98

	Deviations		
	AAD (%)	MD (%)	Bias (%)
$x = 0.9885$	0.4	1.3	0.05
$x = 0.9942$	0.7	2.1	0.001

Table 4. Obtained Results with the Katti and Chaudhri (Eq. 7), Original Grunberg and Nissan (Eq. 8), and Modified Grunberg and Nissan (Eq. 9) Mixing Laws

	Eq. 7			Eq. 8			Eq. 9		
	AAD (%)	MD (%)	Bias (%)	AAD (%)	MD (%)	Bias (%)	AAD (%)	MD (%)	Bias (%)
0.9942 CO_2 + 0.0058 PEB8	21	27	21	22	32	22	2.3	8.1	0.7
0.9885 CO_2 + 0.0115 PEB8	21	24	21	23	28	23	1.7	6.1	−0.3
0.9919 CO_2 + 0.0081 PEC5	16	19	16	18	23	18	1.4	5.4	−0.2
0.9831 CO_2 + 0.0169 PEC5	28	34	28	31	40	31	3.0	14	1.2
0.9934 CO_2 + 0.0066 PEC7	15	17	15	16	19	16	1.5	9.4	−0.7
0.9872 CO_2 + 0.0128 PEC7	29	34	29	31	39	31	1.7	5.0	0.4
0.9947 CO_2 + 0.0053 PEC9	19	23	19	21	26	21	2.4	6.1	0.5
0.9879 CO_2 + 0.0121 PEC9	41	47	41	43	50	43	4.1	12	−0.3

We have found that the predictions of Eq. 7 become worse when the temperature decreases. From a molecular standpoint this is to be expected since the effect of attractive molecular interactions becomes more important at low temperatures, whereas at high temperatures repulsive collisions dominate and the fluid may be represented correctly by a simpler kinetic model.

The mixing law of Grunberg and Nissan[31] is also often used to predict viscosity of mixtures,

$$\ln \eta_{mix} = x_1 \ln \eta_1 + x_2 \ln \eta_2 \tag{8}$$

This equation predicts the viscosity of the $x$$CO_2$ + (1 − x) POE lubricant mixtures with AADs ranging from 16 to 43%. This mixing law predicts also viscosity values that are always lower than the experimental values (Bias = AAD). The MD (50%) was found at T = 303.15 K, p = 25 MPa for the mixture 0.9879 CO_2 + 0.0121 PEC9. The deviations obtained in this work between the experimental and predicted values with the Katti and Chaudhri and Grunberg and Nissan mixing laws are similar to those obtained by Comuñas et al.[14] and Monsalvo et al.[9,10] for mixtures of HFC134a and polyether, and to those obtained by Baylaucq et al.[66] for mixtures of methane and decane as well as of methane and toluene. These results contrast with those obtained for mixtures of POE lubricants,[24] for which the Katti and Chaudhri and Grunberg and Nissan mixing laws predict the viscosity values with an AAD lower than 5.4%. Hence, it can be concluded that these simple mixing laws are not valid for viscosity predictions of size-asymmetrical mixtures. The Grunberg and Nissan mixing law can be modified by introducing an adjustable parameter believed to be representative, in some way, of the interactions within the system studied. This mixing law has the following form:

$$\ln \eta_{mix} = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 d_{12} \tag{9}$$

By minimizing the average absolute deviation between the calculated and experimental data for each CO_2 + POE lubricant mixtures, we obtained low deviations, with AADs ranging from 1.4 to 4.1%. The MD (14%) was found at T = 353.15 K, p = 25 MPa for the mixture 0.9831 CO_2 + 0.0169 PEC5. The results improve by using Eq. 9, but the model is not anymore predictive.

Self-referencing method. This method was developed by Kanti et al.[63] in order to model the viscous behavior of petroleum cuts that have a complex composition which is difficult to characterize. For this kind of fluid, it is difficult to use equations based on physical properties such as the molar mass, critical parameters or acentric factors, as well as on the exact composition of the mixture.[67] The formulation of the self-referencing method has the advantage of only requiring one experimental value, $\eta(p_{ref},T_0)$, at a pressure p_{ref} and a temperature T_0. This is the reason why this method can be referred to as a self-referencing model. The method does not involve the molar mass or any other physical properties (including critical parameters); more details can be found in the original article.[63] It can be applied without restriction indifferently to pure substances, to well-defined mixtures or to chemically very rich systems, such as petroleum cuts for which the method was originally developed. The method involves nine parameters (a, b,..., i) originally determined by Kanti et al.[63] using numerical analysis on a database containing linear alkanes and AB. Once the values of these coefficients are known, the method can be used directly without additional adjustment, and for this reason it can be considered as general and predictive. The functional form of this method is:

$$\ln\left(\frac{\eta(p,T)}{\eta(p_{ref},T_0)}\right) = (ay^2 + by + c)\ln\left(1 + \frac{(p - p_{ref})}{dy^2 + ey + f}\right) + (gy_0^2 + hy_0 + i)\left(\frac{1}{T} - \frac{1}{T_0}\right) \tag{10}$$

where $y = y_0 + (gy_0^2 + hy_0 + i)(1/T - 1/T_0)$ and $y_0 = \ln[\eta(p_{ref}, T_0)]$. This equation is used with p and p_{ref} in MPa, T_0 and T in K. The viscosity value at the reference pressure and temperature, $\eta(p_{ref},T_0)$, is expressed in mPa s.

In this work, we have used this formulation to determine viscosity values for CO_2 + POE mixtures. For this objective, in the first step, the parameters a, b,...i determined in the original work by Kanti et al.[63] were used in Eq. 10. We have selected the reference point at T_0 = 303.15 K and p_{ref} = 60 MPa. Under these conditions, the AAD obtained with the 407 experimental points for the eight considered mixtures (415, from which we subtract one reference point for each mixture) was 6.9%. The MD (28%) was found at T = 353.15 K, p = 60 MPa for the mixture 0.9879 CO_2 + 0.0121 PEC9. The results obtained can be considered quite satisfactory, and are similar to those obtained by Et-Tahir et al.[68] and Boned et al.[69] for binary mixtures such as toluene + pristane and toluene + 1- methylnaphthalene, or by

Table 5. Self-Referencing Method

Parameters	CO_2
a	−0.1965
b	−0.4850
c	0.3084
d	−5.8156
e	33.0838
f	154.2309
g	107.8146
h	470.7389
i	1321.0264
Deviations	
AAD (%)	0.5
MD (%)	5.0
Bias (%)	−0.04

Parameters and obtained deviations for pure carbon dioxide.

Baylaucq et al.[70,71] for the ternary mixture heptane + 1-methylnaphthalene + methylcyclohexane. Baylaucq et al.[66] have proposed a modification of the self-referencing method by fitting the nine parameters $a, b, \ldots, i$ against each pure compound. Then, for each composition, the following generalized mixing rule is adopted[66,72]:

$$\alpha_{\text{mix}} = x_1\alpha_1 + (1 - x_1)\alpha_2 \tag{11}$$

where α represent each one of the parameters and x_1 is the mole fraction of carbon dioxide. We have selected 303.15 K and 60 MPa, respectively, as the reference temperature and pressure. For pure POEs, the parameters values were published in previous work.[24] The values of the parameters for pure carbon dioxide were fitted using our experimental viscosity values[17] and minimizing the AAD between the experimental and calculated data. We report in Table 5 the values of the parameters and the deviation results obtained for this compound. With these parameters, the self referencing method correlates the viscosity values of pure CO_2 with an AAD of 0.5%. Using this approach proposed by Baylaucq et al.,[66] the predicted viscosities for the CO_2 + POE mixtures agree with the experimental data with AADs ranging from 2.3 to 9.2%. The MD (26%) was obtained for the mixture 0.9872 CO_2 + 0.0128 PEC7 at T = 303.15 K and p = 10 MPa. The deviations obtained using this alternative approach are similar to those obtained with the original formulation of the method and the original parameters of Kanti et al.[63]

In the third step, we have determined a new set of characteristic parameters of the method by simultaneously fitting the experimental viscosity data for seven of the eight CO_2 + POE lubricant mixtures (we have not considered the viscosity values of the mixture 0.9885 CO_2 + 0.0115 PEB8), taking 303.15 K and 60 MPa, respectively, as the reference temperature and pressure and minimizing the AAD between the experimental and calculated data. The obtained parameters and deviations are presented in Table 6. Using the Eq. 10 together with the parameter set of Table 6, the viscosities for the mixture 0.9885 CO_2 + 0.0115 PEB8 have been predicted without the application of any mixing law, obtaining an AAD of 3.5%, a MD of 9.7%, and a Bias of 3% from the experimental values. The self-referencing method together with the optimized set of parameters of Table 6 could allow the prediction of the viscosity of mixtures of carbon dioxide with real lubricants (at low lubricant concentrations), if one viscosity value at one given temperature and pressure is known.

Free-volume viscosity model. Recently, an approach to model the viscosity of Newtonian fluids (in the condensed phase, with density $\rho > 0.2$ g cm^{-3}) was proposed by Allal et al.[33] This approach connects the viscosity, η, to the molecular structure via a representation of the free-volume fraction. In its first version,[33] the model could be applied only to dense fluids, but a version valid for low-density states has also been developed.[34,35] In this latter version, the viscosity has the following representation:

$$\eta = \eta_0 + \frac{\rho\ell\left(\alpha\rho + \frac{pM}{\rho}\right)}{\sqrt{3RTM}}\exp\left[B\left(\frac{\alpha\rho + \frac{pM}{\rho}}{RT}\right)^{3/2}\right] \tag{12}$$

where M is the molar mass, ρ is the density, η_0 is the diluted-gas viscosity term (for which we have used the expression proposed by Chung et al.[73]), and ℓ, α, and B are adjustable parameters for each fluid. This model can also be applied to mixtures using the following mixing rules

$$\alpha_{\text{mix}} = \sum_{i,j=1}^{N} x_i x_j \alpha_{ij} \quad \text{with } \alpha_{ij} = \sqrt{\alpha_i \alpha_j} \tag{13}$$

$$B_{\text{mix}} = \sum_{i=1}^{N} x_i B_i \tag{14}$$

$$\ell_{\text{mix}} = \sum_{i=1}^{N} x_i \ell_i \tag{15}$$

where the subscripts i and mix represent pure compound i and the mixture, respectively. The dilute-gas term contribution of the mixture has been considered linearly dependent on the mole fraction of the refrigerant due to the low concentration of the lubricant in the gas phase, which can be satisfactorily described with a simple linear model. The three

Table 6. Self-Referencing Method

Parameters		
a = −0.2918	d = −5.8241	g = 107.8121
b = −0.6057	e = 33.0901	h = 470.7402
c = 0.4803	f = 154.2265	i = 1321.0258

	AAD (%)	MD (%)	Bias (%)
0.9942 CO_2 + 0.0058 PEB8	1.9	6.7	0.7
0.9919 CO_2 + 0.0081 PEC5	2.8	5.6	2.1
0.9831 CO_2 + 0.0169 PEC5	7.6	7.6	−0.9
0.9934 CO_2 + 0.0066 PEC7	3.2	20	−0.9
0.9872 CO_2 + 0.0128 PEC7	1.9	7.4	−0.7
0.9947 CO_2 + 0.0053 PEC9	4.4	8.5	8.5
0.9879 CO_2 + 0.0121 PEC9	8.6	22	−6.9

Obtained results for the mixtures refrigerant + lubricant with the parameters determined by fitting the experimental viscosity data of seven CO_2 + lubricant mixtures.

Table 7. Parameters and Deviations with the Free-Volume Model for Pure Compounds

Pure Fluid	α (m^5 mol^{-1} s^{-2})	B	10^{10} ℓ (m)
PEB8	818.135	0.00142	0.0277
PEC5	449.026	0.00219	0.1544
PEC7	606.147	0.00154	0.1384
PEC9	769.557	0.00118	0.1342
Carbon dioxide	20.341	0.0157	0.5739
	AAD (%)	MD (%)	Bias (%)
PEC8	2.2	5.8	0.1
PEC5	1.3	3.8	0.07
PEC7	1.9	5.5	0.4
PEC9	2.3	6.1	0.2
Carbon dioxide	0.3	1.7	0.2

parameters (ℓ, α, and B) for each pure compound (POE lubricants and carbon dioxide) have been adjusted considering the experimental viscosity data previously measured.[17,22,23] The viscosity of the pure compounds is described satisfactorily with AADs ranging from 0.3% for CO_2 to 2.3% for PEC9. The parameters for pure CO_2 and POE lubricants are reported in Table 7, together with the deviations with which this model represents the dynamic viscosities of these compounds. Taking into account these parameter values and the mixing rules of Eqs. 13–15, the dynamic viscosities of CO_2 + POE lubricant mixtures can be predicted. The values calculated with the free-volume model agree with the experimental data within AADs ranging from 6 to 37%, whereas the MD ranges from 17 to 44%. These results contrast with those obtained for mixtures of POE lubricants,[24] for which the free volume model can predict the viscosity values with an AAD lower than 4.4%. If the ℓ_{mix}, α_{mix}, and B_{mix} values are fitted against the experimental viscosities of the mixtures, these deviations are much lower (AAD $< 3\%$) but then, the model is not predictive.

Hard-sphere model. This model has been developed[36,37,39] for the simultaneous correlation of self-diffusion, viscosity, and thermal conductivity of dense fluids. The transport coefficients of real dense fluids expressed in terms of $V_r = V/V_0$, with V_0 the close-packed volume and V the molar volume, are assumed to be directly proportional to the values given by the exact hard-sphere theory. The proportionality factor, described as a roughness coefficient R_η, reflect the degree of coupling between translational and rotational motions of the molecules and, in general, empirically accounts for deviations from the behavior of smooth hard spheres as well as the departure from molecular sphericity. Universal curves for the viscosity were established and expressed as:

$$\ln\left(\frac{\eta^*_{exp}}{R_\eta}\right) = \sum_{i=0}^{7} a_{\eta i}(1/V_r)^i$$

with

$$\eta^*_{exp} = 6.035 \times 10^8 \left(\frac{1}{MRT}\right)^{1/2} \eta_{exp} V^{2/3} \qquad (16)$$

The coefficients $a_{\eta i}$ are universal,[37] independent of the chemical nature of the compound and V_0 and R_η are adjustable parameters. R_η is independent of pressure and temperature, whereas V_0 depends on temperature. In this model the viscosity is not an explicit function of pressure. Thus, the viscosity is only a function of volume and temperature, $\eta(V,T)$. This approach can be applied to mixtures, once known V_0 and R_η parameters for each compound, using the following mixing rules in order to determine these parameters for mixtures:

$$V_{0\,mix}(T) = \sum_{i=1}^{N} x_i V_{0i}(T) \qquad (17)$$

$$R_{\eta\,mix} = \sum_{i=1}^{N} x_i R_{\eta i} \qquad (18)$$

where the subscripts i and mix are used for pure compounds and mixture, respectively. The V_0 and R_η parameters for the pure lubricants have been taken from a work of Pensado et al.,[23] and for pure carbon dioxide they were determined by fitting the viscosity data previously reported.[17] The hard-sphere model represents the viscosity of pure CO_2 with an AAD of 0.1%, a MD of 0.5%, and a Bias of -0.001%. Considering the mixing rules given by Eqs. 17 and 18 and the parameters values for pure POEs and CO_2, the dynamic viscosities of CO_2 + PEC5, CO_2 + PEC7, CO_2 + PEC9, and CO_2 + PEB8 can be predicted. The temperature dependence of the V_0 parameters of mixtures CO_2 + PEB8, CO_2 + PEC7, and pure compounds can be observed in Figure 5. The hard-sphere model predicts the viscosity values of the mixtures with AADs ranging from 6.0 to 16%, whereas the MD ranges from 8.3 to 25%. If V_0 and R_η are fitted against the experimental viscosities of the mixtures, these deviations become much lower (AADs ranging from 3 to 11%) but in this case, the model is not predictive.

Comparisons among the models

The results obtained for the dynamic viscosity predictions for CO_2 + POE lubricant mixtures with the six different models tested, namely, Katti and Chaudhri[32] and Grunberg and Nissan[31] mixing laws, self-referencing method, hard-sphere model, and free-volume model, are compared in Figure 6. We should point out that, in most cases, the dynamic viscosity values predicted with the two models having stronger physical backgrounds, i.e., the free-volume model and the hard-sphere model, are lower than the experimental values over the entire temperature and pressure ranges, except for the free-volume model for the mixture 0.9919 CO_2 + 0.0081 PEC5 for which the predicted values are higher than the experimental data. Additionally, in most cases, we obtain AAD = Bias, i.e., all of the points are on the same side of the theoretical curve (predicted viscosities lower than the experimental values). The self-referencing method and the hard-sphere model are the best approaches among those tested to predict the viscosities of CO_2 + POE mixtures, at low concentrations of lubricant. It is interesting to point out that self-referencing method need a viscosity value at a given temperature and pressure, whereas the hard-sphere model need the composition and the density of the mixture.

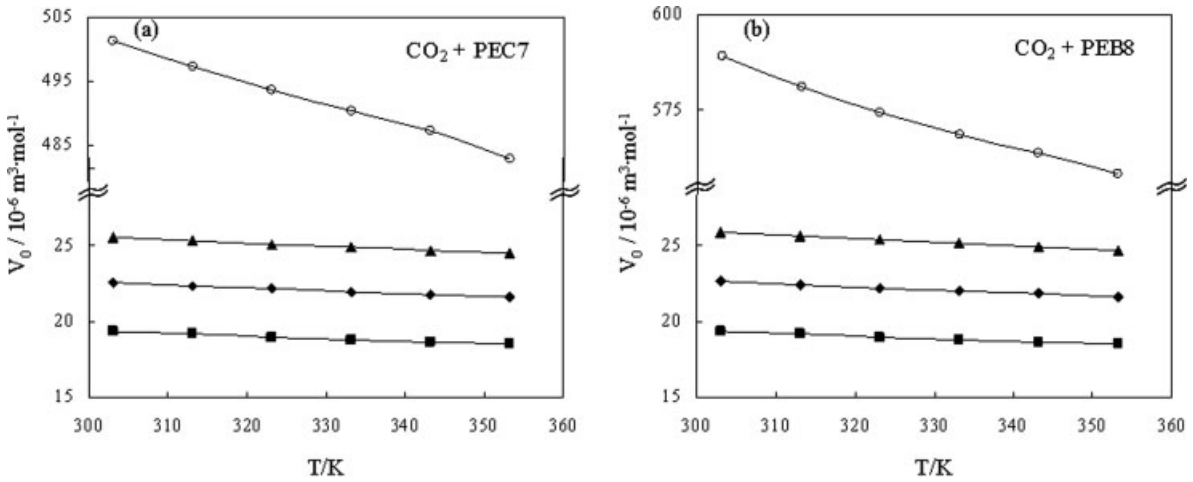

Figure 5. Hard-sphere parameters V_0 (T) vs. temperature for the mixtures CO_2 + PEC7 and CO_2 + PEB8.

(a) $xCO_2 + (1 - x)$ PEC7, (○) $x = 0$; (▲) $x = 0.9872$; (◆) $x = 0.9934$; (■) $x = 1$. (b) $xCO_2 + (1 - x)$ PEB8, (○) $x = 0$; (▲) $x = 0.9885$; (◆) $x = 0.9942$; (■) $x = 1$.

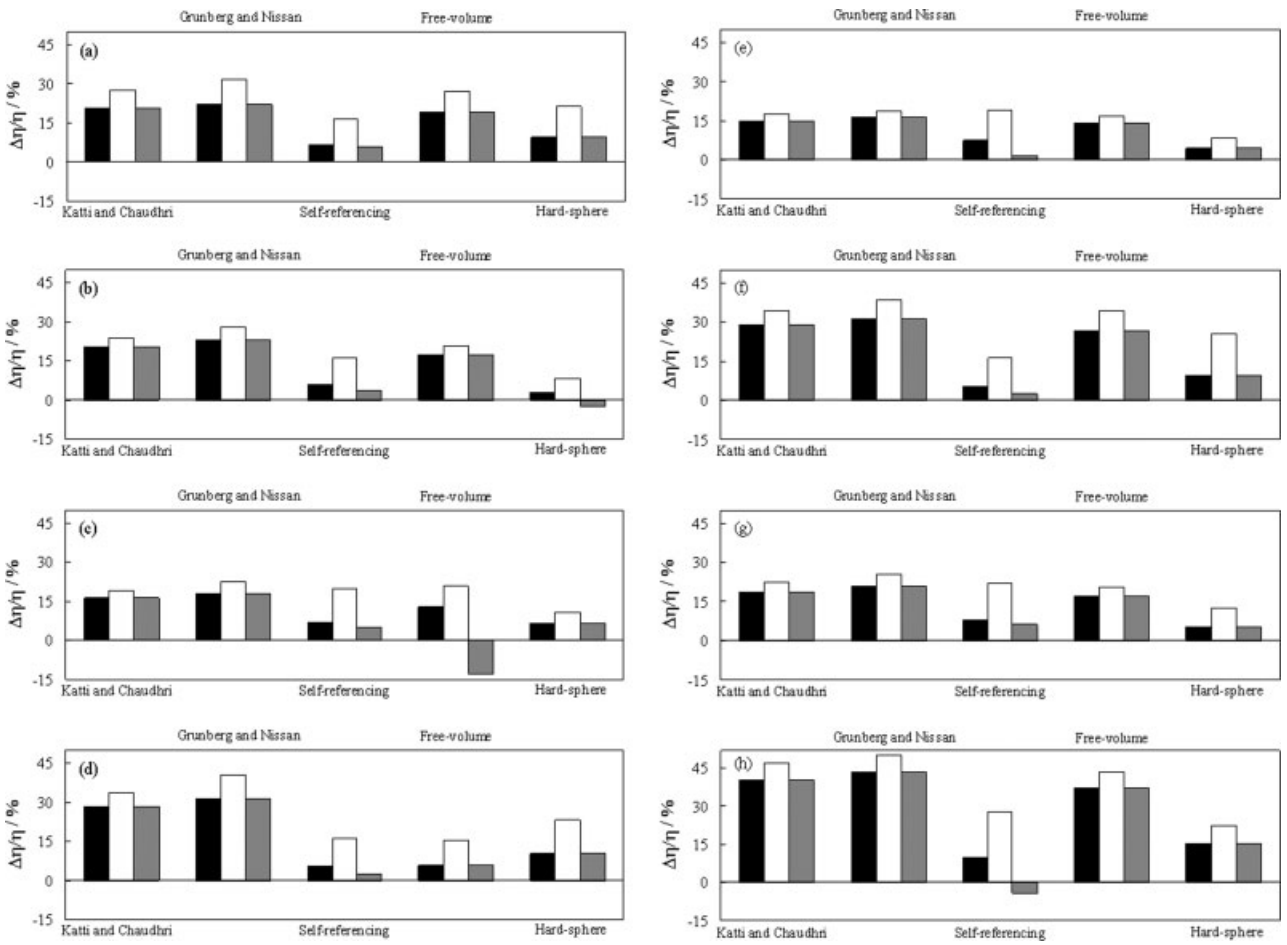

Figure 6. Deviations between the experimental values and the predicted data for the analyzed models: (black) AAD, (white) MD, and (gray) Bias.

(a) 0.9942 CO_2 + 0.0058 PEB8, (b) 0.9885 CO_2 + 0.0115 PEB8, (c) 0.9919 CO_2 + 0.0081 PEC5, (d) 0.9831 CO_2 + 0.0169 PEC5, (e) 0.9934 CO_2 + 0.0066 PEC7, (f) 0.9872 CO_2 + 0.0128 PEC7, (g) 0.9947 CO_2 + 0.0053 PEC9, (h) 0.9879 CO_2 + 0.0121 PEC9.

Conclusions

The density and viscosity data for two binary mixtures of carbon dioxide with pentaerythritol tetra-2-ethylhexanoate, with 7.8% and 14.4% mass fraction of lubricant have been measured between 303.15 and 353.15 K and up to 60 MPa with a specially designed vibrating wire sensor. From the density data we have determined the excess molar volumes, finding that this property is negative for both mixtures. The viscosity of the mixtures increases drastically with lubricant concentration. The mixture with a concentration ~15% in mass of lubricant has viscosity values around twice those of pure carbon dioxide.

In general, it is not possible to predict the viscosity mixtures CO_2 + POE lubricants with average deviations smaller than 10% using either the self-referencing model, the hard-sphere scheme, the free-volume model, or the mixing rules of Katti and Chaudhri and of Grunberg and Nissan. It is interesting to point out that the hard-sphere model and the self-referencing model are the more adequate to predict the viscosity of this type of mixtures. For the self-referencing model we have obtained an optimized set of parameters that allows the prediction of the viscosity of mixtures of carbon dioxide with real lubricants (at low lubricant concentrations), if the viscosity at a given temperature and pressure is known. New experimental measurements over wide temperature, pressure, and composition ranges are needed to complete this study.

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Literature Cited

1. Bobbo S, Fedele L, Scattolini M, Camporese R, Stryjek R. Solubility of carbon dioxide in 2-methylbutyric, 2-methylvaleric and 2-methylhexanoic ester oils. *Fluid Phase Equilib*. 2007;256:81–85.
2. Huber ML, Holcomb CD, Outcalt SL, Elliott JR. Vapor-liquid equilibria for an R134a/lubricant mixture: measurements and equation-of-state modeling. *ASHRAE Trans*. 2000;106:768–773.
3. Marsh KN, Kandil M. Review of thermodynamic properties of refrigerants + lubricant oils. *Fluid Phase Equilib*. 2002;199:319–334.
4. Yokozeki A. Solubility of refrigerants in various lubricants. *Int J Thermophys*. 2001;22:1057–1071.
5. Yokozeki A. Solubility correlation and phase behaviors of carbon dioxide and lubricant oil mixtures. *Appl Energy*. 2007;84:159–175.
6. Youbi-Idrissi M, Bonjour J, Terrier MF, Meunier F, Marvillet C, Solubility of CO_2 in a synthetic oil. Presented at International Congress of Refrigeration, Washington, 2003.
7. Takigawa K, Sandler SI, Yokozeki A. Solubility and viscosity of refrigerant/lubricant mixtures: hydrofluorocarbon/alkylbenzene systems. *Int J Refrig*. 2002;25:1014–1024.
8. Seeton C, Fahl J, Henderson D. Solubility, viscosity, boundary lubrication and miscibility of CO_2 and synthetic lubricants. Presented at 4th IIR-Gustav Lorentzen Conference on Natural Working Fluids at Purdue, 2000.
9. Monsalvo MA, Baylaucq A, Reghem P, Quiñones-Cisneros SE, Boned C. Viscosity measurements and correlations of binary mixtures. 1,1,1,2-Tetrafluoroethane (HFC-134a) + tetraethylene glycol dimethylether (TEGDME). *Fluid Phase Equilib*. 2005;233:1–8.
10. Monsalvo MA, Baylaucq A, Quiñones-Cisneros SE, Boned C. High-pressure viscosity behavior of x 1,1,1,2-tetrafluoroethane (HFC-134a) + (1 − *x*) triethylene glycol dimethylether (TriEGDME) mixtures. Measurements and modeling. *Fluid Phase Equilib*. 2006; 247:70–79.
11. Li H, Rajewski TE. Experimental study of lubricant candidates for the CO_2 refrigeration system. Presented at Final Proceedings of the 4th IIR-Gustav Lorentzen Conference on Natural Working Fluids at Purdue, West Lafayette, IN, 2000.
12. Comuñas MJP, Baylaucq A, Boned C, Canet X, Fernández J. High-pressure volumetric behavior of x 1,1,1,2-tetrafluoroethane + (1 − x) 2,5,8,11,14-pentaoxapentadecane (TEGDME) mixtures. *J Chem Eng Data*. 2002;47:233–238.
13. Comuñas MJP, Fernández J, Baylaucq A, Canet X, Boned C. PρTx measurements for HFC-134a + triethylene glycol dimethylether system. *Fluid Phase Equilib*. 2002;199:185–195.
14. Comuñas MJP, Baylaucq A, Boned C, Fernández J. Dynamic viscosity for HFC-134a + polyether mixtures up to 373.15K and 140 MPa at low polyether concentration. Measurements and modeling. *Ind Eng Chem Res*. 2004;43:804–814.
15. Wahlstrom A, Vamling I. Viscosity for mixtures of HFCs and pentaerythritol esters. Presented at Twentieth International Congress of Refrigeration, Sydney, Australia, 1999.
16. Wahlström A, Vamling L. Solubility of HFCs in pentaerythritol tetraalkyl esters. *J Chem Eng Data*. 2000;45:97–103.
17. Pensado AS, Pádua AAH, Comuñas MJP, Fernández J. Viscosity and density measurements for carbon dioxide + pentaerythritol ester lubricant mixtures at low lubricant concentration. *J Supercrit Fluids*. 2008;44:172–185.
18. Hauk A, Weidner E. Thermodynamic and fluid-dynamic properties of carbon dioxide with different lubricants in cooling circuits for automobile application. *Ind Eng Chem Res*. 2000;39:4646–4651.
19. Fandiño O, Comuñas MJP, Lugo L, López ER, Fernández J. Density measurements under pressure for mixtures of pentaerythritol ester lubricants. Analysis of a density–viscosity relationship. *J Chem Eng Data*. 2007;52:1429–1436.
20. Fandiño O, García J, Comuñas MJP, López ER, Fernández J. PρT measurements and EoS predictions of ester lubricants up to 45 MPa. *Ind Eng Chem Res*. 2006;45:1172–1182.
21. Fandiño O, Pensado AS, Lugo L, Comuñas MJP, Fernández F. Compressed liquid densities of squalane and pentaerythritol tetra(2-ethylhexanoate). *J Chem Eng Data*. 2005;50:939–946.
22. Pensado AS, Comuñas MJP, Lugo L, Fernández J. High pressure characterization of dynamic viscosity and derived properties for squalane and two pentaerythritol ester lubricants: pentaerythritol tetra-2-ethylhexanoate and pentaerythritol tetranonanoate. *Ind Eng Chem Res*. 2006;45:2394–2404.
23. Pensado AS, Comuñas MJP, Fernández J. Relationship between viscosity coefficients and volumetric properties: measurements and modeling for pentaerythritol esters. *Ind Eng Chem Res*. 2006;45: 9171–9183.
24. Lugo L, Canet X, Comuñas MJP, Pensado AS, Fernández J. Dynamic viscosity under pressure for mixtures of pentaerythritol ester lubricants with 32 viscosity grade. Measurements and modelling. *Ind Eng Chem Res*. 2007;46:1826–1835.
25. Fandiño O, López ER, Lugo L, Fernández J. Solubility of carbon dioxide in pentaerythritol ester oils. Presented at International Conference on Chemical Thermodynamics, Boulder, 2006.
26. Audonnet F, Pádua AAH. Density and viscosity of mixtures of *n*-hexane and *1*-hexanol from 303 to 423 K up to 50 MPa. *Int J Thermophys*. 2002;23:1537–1550.
27. Audonnet F, Pádua AAH. Viscosity and density of mixtures of methane and *n*-decane from 298 to 393 K and up to 75 MPa. *Fluid Phase Equilib*. 2004;216:235–244.
28. Audonnet F, Pádua AAH. Simultaneous measurement of density and viscosity of *n*-pentane from 298 to 383 K and up to 100 MPa using a vibrating-wire instrument. *Fluid Phase Equilib*. 2001;181:147–161.
29. McMullan JT, Hewitt NJ, Masson AJ, Murphy NE. The influence of oil viscosity and refrigerant quality on evaporator performance. *Int J Energ Res*. 1992;16:567–581.
30. Kim MH, Pettersen J, Bullard CW. Fundamental process and system desing issues in CO_2 vapor compression systems. *Prog Energ Combust*. 2004;31:119–174.

31. Grunberg L, Nissan AH. Mixture law for viscosity. *Nature*. 1949; 164:799–800.
32. Katti PK, Chaudhri MM. Viscosities of binary mixtures of benzyl acetate with dioxane, aniline, and *m*-cresol. *J Chem Eng Data*. 1964; 9:442–443.
33. Allal A, Moha-Ouchane M, Boned C. A new free volume model for dynamic viscosity and density of dense fluids versus pressure and temperature. *Phys Chem Liq*. 2001;39:1–30.
34. Allal A, Boned C, Baylaucq A. Free-volume viscosity model for fluids in the dense and gaseous states. *Phys Rev E*. 2001;64:011203/011201-011203/011210.
35. Boned C, Allal A, Baylaucq A, Zéberg-Mikkelsen CK, Bessieres D, Quiñones-Cisneros SE. Simultaneous free-volume modeling of the self-diffusion coefficient and dynamic viscosity at high pressure. *Phys Rev E*. 2004;69:031203/031201-031203-031206.
36. Assael MJ, Dymond JH, Tselekidou V. Correlation of high-pressure thermal conductivity, viscosity, and diffusion coefficients for *n*-alkanes. *Int J Thermophys*. 1990;11:863–873.
37. Assael MJ, Dymond JH, Papadaki M, Patterson PM. Correlation and prediction of dense fluid transport coefficients. I. *n*-alkanes. *Int J Thermophys*. 1992;13:269–281.
38. Dymond JH, Awan MA. Correlation of high-pressure diffusion and viscosity coefficients for *n*-alkanes. *Int J Thermophys*. 1989;10:941–951.
39. Dymond JH. Hard-sphere theories of transport-properties. *Chem Soc Rev*. 1985;14:317–356.
40. Glasstone S, Laidler K, Eyring H. *The Theory of Rate Processes*. New York: McGraw-Hill, 1941.
41. Quiñones-Cisneros SE, Zéberg-Mikkelsen CK, Fernández J, García J. General friction theory viscosity model for the PC-SAFT equation of state. *AIChE J*. 2006;52:1600–1610.
42. Quiñones-Cisneros SE, Zéberg-Mikkelsen CK, Stenby EH. The friction theory (f-theory) for viscosity modeling. *Fluid Phase Equilib*. 2000;169:249–276.
43. Rey-Castro C, Vega LF. Transport properties of the ionic liquid 1-ethyl-3-methylimidazolium chloride from equilibrium molecular dynamics simulation. The effect of temperature. *J Phys Chem B*. 2006;110:14426–14435.
44. McCabe C, Cui S, Cummings PT. Characterizing the viscosity-temperature dependence of lubricants by molecular simulation. *Fluid Phase Equilib*. 2001;183/184:363–370.
45. Cholakov GS, Stateva RP, Shacham M, Brauner N. Prediction of properties in homologous series with a shortcut QS2PR method. *AIChE J*. 2007;53:150–159.
46. Bhatia SK, Nocholson D. Transport of simple fluids in nanopores: theory and simulation. *AIChE J*. 2006;52:29–38.
47. Annaland MVS, Dijkhuizen W, Deen NG, Kuipers JAM. Numerical simulation of behavior of gas bubbles using a 3-D front-tracking method. *AIChE J*. 2006;51:99–110.
48. Suzuki T, Ebert R-U, Schueuermann G. Application of neural networks to modeling and estimating temperature-dependent liquid viscosity of organic compounds. *J Chem Inf Comput Sci*. 2001;41:776–790.
49. Span R, Wagner W. A new equation of state for carbon dioxide covering the fluid region from the triple-point temperature to 1100 K at pressures up to 800 MPa. *J Phys Chem Ref Data*. 1996;25:1509–1596.
50. Marquardt DW. An algorithm for least-squares estimation of nonlinear parameters. *J Soc Ind Appl Math*. 1963;11:431–441.
51. Cibulka I, Hnedkovsky L. Liquid densities at elevated pressures of *n*-alkanes from C_5 to C_{16}: a critical evaluation of experimental data. *J Chem Eng Data*. 1996;41:657–668.
52. Cibulka I, Takagi T. pρT data of liquids: summarization and evaluation. V. Aromatic hydrocarbons. *J Chem Eng Data*. 1999;44:411–429.
53. Cibulka I, Takagi T. pρT data of liquids: summarization and evaluation. VI. Nonaromatic hydrocarbons (C_n, $n \geq 5$) except n-alkanes C_5 to C_{16}. *J Chem Eng Data*. 1999;44:1105–1128.
54. Cibulka I, Zikova M. Liquid densities at elevated pressures of 1-alkanols from C_1 to C_{10}: a critical evaluation of experimental data. *J Chem Eng Data*. 1994;39:876–886.
55. Troncoso J, Bessières D, Cerdeiriña CA, Carballo E, Romaní L. Automated measuring device of (p, ρ, *T)* data Application to the *1*-hexanol + *n*-hexane system. *Fluid Phase Equilib*. 2003;208:141–154.
56. Canet X. Viscosité dynamique et masse volumique sous hautes pressions de mélanges binaires et ternaires d'hydrocarbures lourds et légers. PhD Thesis, Université de Pau et des Pays de l'Adour, Pau, France, 2001.
57. Marchi P, Scalabrin G, Ihmels EC, Fischer K, Gmehling J. PρTx measurements for (1,1,1,2-tetrafluoroethane + triethylene glycol dimethyl ether) at high haloalkane content. *J Chem Eng Data*. 2006; 51:992–996.
58. Fenghour A, Wakeham WA, Vesovic V. The viscosity of carbon dioxide. *J Phys Chem Ref Data*. 1998;27:31–44.
59. Siegismund V, Kauffeld M, Influence of lubricant oil on CO_2 heat transfer in minichannel tubes. Presented at Commercial Refrigeration–Thermophysical Properties and Transfer Processes of Refrigerants, IIR International Conferences, Vicenza, Italy, 2005.
60. Zingerli AP, Groll EA. Influence of refrigeration oil on the heat transfer and pressure drop of supercritical CO_2 during in-tube cooling. Presented at 4th IIR-Gustav Lorentzen Conference on Natural Working Fluids at Purdue, West Lafayette, IN, 2000.
61. Youbi-Idrissi M, Bonjour J, Marvillet C, Meunier F. Impact of refrigerant-oil solubility on an evaporator performances working with R-407C. *Int J Refrig*. 2003;26:284–292.
62. Comuñas MJP, Baylaucq A, Boned C, Fernández J. High-pressure measurements of the viscosity and density of two polyethers and two dialkyl carbonates at high pressures. *Int J Thermophys*. 2001;22: 749–768.
63. Kanti M, Zhou H, Ye S, Boned C, Lagourette B, Saint-Guirons H, Xans P, Montel F. Viscosity of liquid hydrocarbons, mixtures and petroleum cuts, as a function of pressure and temperature. *J Phys Chem*. 1989;93:3860–3864.
64. Geller VZ, Davis KE. Solubility and viscosity of refrigerant/POE lubricant mixtures. Presented at Int Congr Refrig: Refrig 19th. 1995.
65. Geller VZ, Paulaitis ME, Bivens DB, Yokozeki A. Viscosities of HFC-32 and HFC-32/lubricant mixtures. *Int J Thermophys*. 1996;17: 75–83.
66. Baylaucq A, Boned C, Canet X, Zéberg-Mikkelsen CK, Quiñones-Cisneros SE, Zhou H. Dynamic viscosity modeling of methane+*n*-decane and methane+toluene mixtures: comparative study of some representative models. *Petrol Sci Technol*. 2005;23:143–157.
67. Boned C, Zéberg-Mikkelsen CK, Baylaucq A, Dauge P. High-pressure dynamic viscosity and density of two synthetic hydrocarbon mixtures representative of some heavy petroleum distillation cuts. *Fluid Phase Equilib*. 2003;212:143–164.
68. Et-Tahir A, Boned C, Lagourette B, Xans P. Determination of the viscosity of various hydrocarbons and mixtures of hydrocarbons versus temperature and pressure. *Int J Thermophys*. 1995;16:1309–1334.
69. Boned C, Et-Tahir A, Lagourette B, Xans P, Gao J. Comparative analysis of some representative models of viscosity versus pressure in the case of various hydrocarbons and their mixtures. *J Therm Sci*. 1996;5:60–74.
70. Baylaucq A, Boned C, Daugé P, Lagourette B. Measurements of the viscosity of three hydrocarbons and the three associated binary mixtures versus pressure and temperature. *Int J Thermophys*. 1997;18:3–23.
71. Baylaucq A, Daugé P, Boned C. Viscosity and density of the ternary mixture heptane + methylcyclohexane + 1-methylnaphtalene. *Int J Thermophys*. 1997;18:1089–1107.
72. Canet X, Baylaucq A, Boned C. High-pressure (up to 140 MPa) dynamic viscosity of the methane + decane system. *Int J Thermophys*. 2002;23:1469–1486.
73. Chung TH, Ajlan M, Lee LL, Starling KE. Generalized multiparameter correlation for nonpolar and polar fluid transport properties. *Ind Eng Chem Res*. 1988;27:671–679.

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