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Solubility of CO₂ in Commercial POE Oils with Different Standard Viscosity

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ABSTRACT

The selection of the optimal commercial oil to be used as lubricant in a refrigerating system with carbon dioxide (CO₂) as working fluid is not solved yet, though POE and PAG oils give acceptable results. Only a real knowledge of the oil structure and thermodynamic behavior of the oil+refrigerant mixture allows a proper selection of the lubricant. Then, a systematic study on the solubility of CO₂ in some commercial POE oils and their precursors is underway in our laboratory, and several measurements have been performed till now. Here, an investigation on the solubility of CO₂ in commercial POE lubricants with different ISO standard viscosity is presented on the base of measurements performed at temperatures from 283 K and 343 K. The results are discussed and compared with the solubility of precursors in view of the development of thermodynamic models able to predict the properties of the mixture oil+refrigerant.

1. INTRODUCTION

Natural fluids are amongst the most promising refrigerants due to their zero global warming potential (GWP) when directly emitted into the atmosphere. Among them, great attention is put on carbon dioxide (CO₂) as alternative to synthetic hydrofluorocarbons (HFC) in the refrigeration systems. However, its employment still presents different technical unsolved problems: one of them is the proper choice of the lubricant for each application. Though polyol ester oils (POE) and polyalkylene glycol oils (PAG) are widely used with carbon dioxide with acceptable results, several troubles can appear in the refrigerating machine depending on the working conditions due to undesired thermophysical behavior of the mixture oil+refrigerant, that is the actual working fluid circulating in the machine. The unavoidable solution of CO₂ into the oil, present in the compressor and the circuits, can determine, depending on temperature and pressure, phenomena such as the formation of two liquid phases due to immiscibility, the buoyancy of lubricant rich liquid on the refrigerant rich liquid due to barotropic behaviour, a strong reduction in oil viscosity etc.. These phenomena can provoke damages to the compressors because of reduced oil return or reduced lubricating power of the oil, but also negatively influence the heat transfer efficiency in evaporator and condenser. A good knowledge of the thermodynamic behavior of the CO₂ + lubricant systems is then essential for the selection of the proper oil. Numerous thermophysical properties need to be considered, but understanding phase behavior of the CO₂+lubricant mixture, with particular reference to solubility, is of special importance. The extensive production of accurate experimental data on solubility is essential to support the development of both predictive and correlative thermodynamic models, as already proposed in the literature (e.g. Yokozeki, 1994, Elvassore et al., 1999, Mermond et al., 1999, Hauk and Weidner, 2000, Huber et al., 2002, Takigawa et al., 2002, Fleming and Yan, 2003, Teodorescu et al., 2003, Youbi-Idrissi et al., 2003, Tsuji et al., 2004, Ikeda et al., 2004, Garcia et al., 2004, Quiñones-Cisnerosa et al., 2005, Marcelino Neto et al., 2007, Youbi-Idrissi and Bonjour, 2008), to enable the proper calculation of the mixtures properties and the consequent proper design of HVAC system components. In the last years, a project on the study of solubility of CO₂ in lubricants has been started at our laboratory, and several data on both commercial oils and precursors belonging to two homologous series of pentaerythritol tetralkyl...
esters (n-alkyl esters and 2-methyl alkyl esters), have been produced (Bobbo et al., 2005, Bobbo et al., 2006a, Bobbo et al., 2006b, Bobbo et al., 2007a, Bobbo et al., 2007b, Bobbo et al., 2008, Fedele et al., 2008a, Pernechele et al., 2008a, Pernechele et al., 2008b, Fedele et al., 2008b).

In this paper, solubility measurements of CO₂ in three different commercial POE oils, produced by the same company but with different ISO standard viscosity, are presented in the range between 283 K and 343 K, with the aim to evaluate the possible correlation of solubility and standard viscosity of the lubricant.

The results are then compared to those referring to some POE precursors, to derive some information on the influence of oil molar mass and structure. The data have been also successfully correlated with a model already applied in previous works.

## 2. EXPERIMENTAL SECTION

### 2.1 Materials

Carbon dioxide (CO₂), with 99.95% purity, was supplied by Air Liquide.

The three commercial POE lubricants object of the analysis are Icematic SW 32, Icematic SW 46 and Icematic SW 68. To eliminate the non-condensable gases, each sample was put under vacuum and then used with no further purification. An elementary analysis was performed for the three commercial oils with the aim to estimate their molar mass assuming they are formed by mixtures of pure linear or branched pentaerythritol tetraalkyl esters. These pure esters, as demonstrated in Bobbo et al. (2006b), are present in Icematic SW 32 and are generally indicated as precursors of the commercial POE lubricants. The relation between the results of the elementary analysis (i.e. the determination of the amount of C, H and O in the oil sample) and the molar mass of the sample analysed was calibrated on two mixtures of pure pentaerythritol tetraalkyl esters prepared at our laboratories: one composed by a series of linear chained compounds (PECs) and the other by a series of branched chained compounds (PEBMs) with different molar masses. Since the molar mass of these compounds is known, it was possible to calculate the molar masses of the two known mixtures and then to compare the calculated values to the results obtained from the elementary analysis, getting an agreement within 1% and confirming the reliability of the method. The estimated molar masses of the three commercial lubricants are reported in Table 1.

<table>
<thead>
<tr>
<th>Molar mass (kg kmol⁻¹)</th>
<th>SW 32</th>
<th>SW 46</th>
<th>SW 68</th>
<th>PEC4</th>
<th>PEC6</th>
<th>PEC8</th>
<th>PEBM5</th>
<th>PEBM7</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>554</td>
<td>593</td>
<td>634</td>
<td>416.5</td>
<td>528.7</td>
<td>640.9</td>
<td>472.6</td>
<td>584.8</td>
</tr>
</tbody>
</table>

### 2.2 Experimental apparatus and procedure

A specifically built apparatus, based on the static synthetic method, was used to perform the isothermal solubility measurements. It was already described by Bobbo et al. (2005), even if slightly modified as explained in Bobbo et al. (2008), and here only the main outlines are given.

The equilibrium was reached in a stainless steel cell, with a calibrated volume of about 180 cm³, endowed with glass windows for observing the mixture and with an internal helical stirrer to force the vapor through the liquid. The cell was immersed in a water thermostatic bath, in which 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. Temperature was measured by means of a 100 Ω platinum resistance thermometer with an uncertainty of about 0.02 K, while pressure was measured by means of a Druck DPI 145 with a full scale of 35000 kPa and an uncertainty of 20 kPa. A calibration was performed to find a relationship between the level of a calibration liquid inside the cell, measured by means of a cathetometer (Gaertner Scientific M940LE), and its known volume. During the measurements, the liquid volume inside the cell is then obtained through this relationship by measuring the level of the meniscus separating the vapor and the liquid phases. Oil was directly charged in the cell by means of a glass syringe after opening the upper side of the cell, with an estimated mass uncertainty of 0.001 g. After this, the cell was closed, connected to the measurement circuit and evacuated. Then, a known amount of CO₂ was transferred in the cell from the sample bottle simply by exploiting the pressure difference. The CO₂ charged mass was measured gravimetrically. At constant temperature, the equilibrium was reached and the level of the liquid phase into the equilibrium cell was measured by means of the cathetometer, with a resolution of 0.001 mm and an estimated uncertainty in the level’s measurement of 0.05 mm. The liquid volume was calculated with the meniscus
Figure 1: Solubility of CO₂ in commercial lubricants Icematic SW 32, SW 46 and SW 68 expressed in terms of mass fraction (left) and molar fraction (right).

Level by means of the calibration equation and subtracted from the total one of the cell, obtaining the vapor phase volume and then the CO₂ mass in vapor phase, through the density calculated with Refprop 8.0 database (Lemmon International Refrigeration and Air Conditioning Conference at Purdue, July 14-17, 2008.)
et al., 2007). Considering the vapor phase formed by pure CO₂ only, due to the low oil vapor pressure, the mass of CO₂ solved in the liquid was calculated by a simple subtraction from the total mass charged. So, the uncertainty in the liquid composition measurements was estimated to be from 0.002 (high CO₂ mole fraction) to 0.02 (low CO₂ mole fraction).

### 3. RESULTS AND DISCUSSION

#### 3.1 Experimental data

Four isotherms at 283.15, 303.15, 323.15, and 343.15 K were measured for each of the three systems CO₂ + SW 32, CO₂ + SW 46, and CO₂ + SW 68. An average of 12 points per isotherms was measured, for a total of 143 experimental data. All the experimental data are shown in Figure 1 in terms of mass (left side) and molar fraction (right side). It is useful to underline that the isotherms at 283.15 K and 303.15 K are below the critical temperature of carbon dioxide and the maximum pressure for these isotherms corresponds to the saturation pressure of carbon dioxide. The isotherms at 323.15 K and 343.15 K are over the critical temperature of carbon dioxide and then the maximum pressure (and the corresponding mass/molar fraction) is limited by the maximum acceptable pressure inside the measurement cell, i.e. 10000 kPa. For each oil, the molar fractions were calculated from the experimental mass fractions through the molar mass evaluated as explained in paragraph 2.1.

The figure shows a similar trend for the solubility of CO₂ in the different oils, both in terms of mass fraction and molar fraction. It is clear, as it could be expected, that the solubility increases when the temperature decreases. The solubility in terms of molar fraction shows a clear negative deviation from the ideal behavior (i.e. pressures are lower than predicted by the Raoult’s law), showing a prevalence of attractive forces between carbon dioxide and oil molecules. However, at temperatures below the CO₂ critical temperature (304.1 K) and at high molar fractions, the deviation is positive, showing a prevalence of repulsive intermolecular forces.

The solubility of CO₂ in the three oils is quite similar at every temperature, but has not trend related to the standard oil viscosity. At a given pressure, the solubility in SW 32, i.e. the less viscous oil, is the highest, but the solubility in SW 68, i.e. the most viscous oil, is higher than in SW 46. This could suggest that the viscosity of the three oils is different due to a different mix of pure precursors.

A direct comparison among the solubility of CO₂ in the three commercial oils and some precursors belonging to pentaerythritol tetraalkyl esters linear (PECs) and branched (PEBMs) chained series (Bobbo et al., 2005, Bobbo et al., 2006b, Bobbo et al., 2007a, Bobbo et al., 2007b, Bobbo et al., 2008, Fedele et al., 2008a, Pernechele et al., 2008b, Fedele et al., 2008b) is presented in Figures 2 and 3, where the solubility expressed in terms of mass and molar fraction is shown for the different oils at the temperature of 283.15 K (similar considerations could be done at other temperatures).

As shown in figure 2, in terms of mass fraction PECs have a wider range of solubility than commercial oils. PEC6 has a solubility similar to the average solubility of commercial oils, while PEC8 has a lower solubility and PEC4 a higher solubility. A different situation arises when the solubility is expressed in terms of molar fraction: due to the effect of the different molar masses, PECs show in general a lower solubility than commercial oils and PEC8 is the precursor with the higher solubility.

A similar analysis can be performed for the PEBMs on the base of figure 3: PEBMs have higher solubility than the three commercial oils in terms of mass fraction, with PEBM5 more soluble than PEBM7, but slightly lower solubility when it is expressed in molar fraction, with PEBM7 showing slightly higher solubility than PEBM5. It must be underlined that expressing the solubility in terms of mass fraction is more useful for practical purposes, but the more rigorous and thermodynamically significant definition is in terms of molar fraction.

However, it is evident that no conclusions can be taken on the nature of the commercial oils on the base of this analysis and only the knowledge of the real compositions of the commercial oils would allow a comprehension of the relation between the properties of the precursors and those of the commercial oils.

A more complex structure of commercial oils can be deducted also from Figure 4, where the saturation pressure at 343.15 K for each oil has been expressed as a function of molar mass for several fixed molar fractions. It is evident that the dependence of solubility on molar mass is linear for the pure precursors PECs (the behaviour of PEBMs cannot be evaluated, since they are only two), while a more complex dependence is shown by the commercial oils.
Figure 2: comparison between the solubility in molar fraction and mass fraction of CO2 in commercial lubricants Icematic SW 32, SW 46 and SW 68 and the solubility in PEC precursors at 283.15 K.

Figure 3: comparison between the solubility of CO2 in molar fraction and mass fraction in commercial lubricants Icematic SW 32, SW 46 and SW 68 with the solubility in PEBM precursors at 283.15 K.

Figure 4: saturation pressure as a function of molar mass at different CO2 mole fractions for the PECs, the PEBMs and the commercial POEs lubricants.
3.2 Immiscibility
As already said, one of the potential problems in applying commercial oil in refrigerating machines is given by the possible immiscibility of the lubricant with the refrigerant (here carbon dioxide). This phenomenon can determine oil accumulation inside the heat exchanger tubes, reducing heat transfer capabilities, and lowering the oil transportation to the compressor, resulting in an overall decrement of the refrigeration cycle performance and possible damages to the compressor. For this reason we investigated also the limits of miscibility of carbon dioxide in the three POEs as a function of temperature. After charging the cell, temperature was changed till the appearance of a cloudy point in the liquid phase was observed. Changing composition by adding CO₂, it was possible to define at least part of the LLE saturation temperature at which a second liquid phase appears. A miscibility gap was found for SW 46 and SW 68 at temperatures higher than 292.2 K and 296.6 K, respectively. However, due to experimental limits, the gap could be investigated in the range of mass fraction between roughly 0.5 and 0.85. The results are summarized in Figure 5. The LLE temperature limit is lower (around 5 K at a given composition) and the miscibility gap looks wider for the SW 46 oil than for SW 68. No miscibility gap was observed for the oil SW 32.

![Figure 5: limits of miscibility for CO₂ in SW 46 and SW 68.](image)

3.3 Data correlation
Data were correlated using the PR EoS (Peng and Robinson, 1976) with the Huron-Vidal mixing rules (Huron and Vidal, 1979) and the UNIQUAC equation for the $g^E$ at infinite dilution. To perform the needed correlation it is necessary to express the solubility (that corresponds actually to a vapor liquid equilibrium) for the studied systems in terms of molar fraction and approximate a model for the oils structure, considering the commercial oils are actually a mixture of pure precursors. The average molar masses used in the modeling for the studied oils are those obtained with the methodology previously described based on the elementary analysis and reported in Table 1. Considering the uncertainty in the method applied, reported results must be considered as ‘approximated’ as the data were not validated with other methodology.

The molecular parameters involved in the model were obtained assuming an average structure of the lubricants represented by the following formula:

$$\text{C-}[\text{CH}_2\text{-COO-CH(\text{CH}_3)-CH}_2\text{-CH}_3]_n$$

where the number $n$ denotes the effective number of -CH₂ group in the acid fatty part of POE. This number has been tuned to the assumed molecular mass of oils. A linear dependence on temperature was assumed for the parameters used in the model:

$$a_{22} = a_{22(0)} + a_{22(1)} T$$  \hspace{1cm} (1)

$$\tau_{12} = \tau_{12(0)} + \tau_{12(1)} T$$  \hspace{1cm} (2)

$$\tau_{21} = \tau_{21(0)} + \tau_{21(1)} T$$  \hspace{1cm} (3)
The coefficients of Equations (1-3) are reported in table 2. The correlation was performed in a classical way, i.e. assuming equal fugacities of the components in the coexisting vapor and liquid phases and, in addition, assuming that vapor phase consists of pure CO₂.

The experimental data treated in the described methodology could be well correlated with the model and methodology applied. The results of the correlation are synthetically reported in table 2. It is worth to mention, here, that the model detects the LLE equilibrium with quantitative agreement with the experimental observation of the second liquid phase. The overall deviations are within estimated experimental uncertainty; however, greater deviations were observed for concentrations close to the region of the second liquid phase appearance. More detailed results and the interpretation of the data treatment will be published soon in a separated paper.

Table 2: parameters used in the model and deviations of model from experimental data

<table>
<thead>
<tr>
<th>Oil</th>
<th>(a_{22(0)})</th>
<th>(a_{22(1)})</th>
<th>(τ_{12(0)})</th>
<th>(τ_{12(1)})</th>
<th>(ΔP) (kPa)</th>
<th>(ΔP) (%)</th>
<th>AAD (P) (kPa)</th>
<th>AAD (P) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SW 32</td>
<td>216140</td>
<td>-1137.24</td>
<td>0.489419</td>
<td>0.000368</td>
<td>0.304211</td>
<td>-0.000600</td>
<td>7.9</td>
<td>0.2</td>
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<tr>
<td>SW 46</td>
<td>240223</td>
<td>-1208.40</td>
<td>0.434181</td>
<td>0.000207</td>
<td>0.278831</td>
<td>-0.000294</td>
<td>8.4</td>
<td>0.1</td>
</tr>
<tr>
<td>SW 68</td>
<td>287473</td>
<td>-1043.25</td>
<td>0.459931</td>
<td>0.002089</td>
<td>0.276120</td>
<td>-0.000116</td>
<td>5.8</td>
<td>0.1</td>
</tr>
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</table>

4. CONCLUSIONS

This paper presents a series of measurements on the solubility of carbon dioxide in three commercial POE oils characterized by different ISO standard viscosity. The analysis of the results, and a comparison with the solubility of pure precursors (PECs and PEBs), has shown that the behaviour of commercial oils is more complex than that of precursors in relation to the standard viscosity and the molar mass. Moreover, the interpretation of the results in relation to the pure precursors properties would be possible only after determining the molecular structure and composition of the commercial oils. The immiscibility of the commercial oils was studied also, showing miscibility gaps for the SW 46 and SW 68 oils in the range of temperature explored. The solubility data were successfully correlated with a model based on Peng-Robinson equation of state and Huron-Vidal mixing rules.

NOMENCLATURE

<table>
<thead>
<tr>
<th>AAD</th>
<th>absolute average deviation</th>
<th>-</th>
<th>Δ</th>
<th>absolute deviation</th>
<th>-</th>
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<tbody>
<tr>
<td>P</td>
<td>Pressure (kPa)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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