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Oil Structure Influence on the Solubility of Carbon Dioxide in POE Lubricants

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ABSTRACT

A better knowledge of the transport and thermodynamic properties for the refrigerant+lubricant system is required to properly design the refrigeration circuit. This is essential also to develop proper models able to predict the behavior of the mixture refrigerant+lubricant depending on the working conditions. However, the experimental data available in literature are insufficient to build dedicated models, being frequently related to commercial lubricants with undefined structure.

Recently, a series of measurements have been performed at isothermal conditions with a static method to evaluate the solubility of carbon dioxide in commercial POE lubricants and pure pentaerythritol tetraalkyl esters (both linear and branched) as POE precursors. Parallely, the PRSV EoS, with the Huron-Vidal mixing rules has been selected for the correlation of the solubility data.

The paper presents a discussion on the solubility data obtained and their correlation with the selected model, with particular reference to the influence of the lubricant structure.

1. INTRODUCTION

The revolution in the field of refrigeration and air conditioning driven by the necessity to find environmentally benign substitutes for the traditional chlorinated refrigerants has lead also to a strong research effort to find proper lubricants for the new working fluids (*i.e.* hydrofluorocarbons (HFCs) and carbon dioxide (CO₂)), that are not compatible with the mineral oils generally used in the past. This research is quite complicated, since there are several features to be satisfied by a lubricant to be suitable to the various refrigerants and applications (ASHRAE Handbook, 2001). Moreover, it is more and more recognized the importance to design the components of the refrigerating systems taking into account the unavoidable presence of lubricant in solution with the refrigerant along the circuit of the refrigerating system. Since the thermophysical properties of the mixture refrigerant+lubricant depend on the working conditions (*i.e.* pressure and temperature), a proper design of the system requires an extensive knowledge of these properties. In particular, the comprehension of the phase behavior, namely the mutual solubility of refrigerant and lubricant, is essential because it influences both the return of oil to the crankcase of the compressor and the viscosity and then the lubricity of the mixture refrigerant+lubricant. In the last decades, several families of new lubricants have been identified (polyalkylene glycol (PAG), polyol ester (POE), alkylbenzenes (AB), etc.), but we are still far from the selection of lubricants optimized in relation to the various refrigerants and applications. The knowledge of the thermophysical properties of the mixture refrigerant+lubricant is still scarce (Marsh and Kandil, 2002), even though, as refer the solubility, several papers have been published in the literature in the last years (e.g. Short and Cavestri (1992), Takaishi and Oguchi (1995), Martz et al. (1996), Burton et al. (1999), Wahlstrom and Vamling (1999), Wahlstrom and Vamling (2000), Takigawa et al. (2002), Poot and De Loos (2003),

Tsuji et al. (2004), Poot and De Loos (2004)). Most of these paper refer to HFCs as refrigerants and the lubricants considered are frequently commercial oils not defined from the structural point of view, because they are quite complex mixtures of several components belonging to one of the different families. *Vice versa*, the possibility to develop predictive methods to describe the phase and viscosity behavior of lubricants and their mixtures with refrigerants relies on the identification and the knowledge of the properties of the components used to formulate the commercial lubricant (Fandiño et al., 2005). In particular, while in the last years CO₂ is emerging as one of the most promising alternative refrigerants, little is known about its solubility in lubricants.

With these premises, our group decided to start a research program to study the solubility of CO₂ in commercial blends and their precursors, with the aim to understand the influence of the structure of the oils on the mutual solubility and generate organized experimental data suitable to test both correlative and predictive models able to describe the phase behavior of these mixtures. The first results have been published on the solubility of CO₂ in linear chained pentaerythritol esters (PECs) (Bobbo et al., 2005) and in commercial oils (Bobbo et al., 2006a). Further measurements are ongoing on branched pentaerythritol esters (PEBMs) and will be published soon (Bobbo et al., 2006b). Here, a critical review of all these results with special attention to the influence of the oil structure on the solubility are presented, showing also the results of the correlation for the solubility of CO₂ in the PECs with a Peng-Robinson-Stryjek-Vera (PRSV) equation of state (EoS) applied using the Huron-Vidal (HV) mixing rules with the UNIQUAC equation for the excess Gibbs energy.

2. EXPERIMENTAL

3.1 Apparatus and procedure

The solubility was measured using a static synthetic method at isothermal conditions. The measurements here considered were performed at 283.15 K. A diagram of the apparatus used is shown in Figure 1. The experimental method and procedure were already described in Bobbo *et al.* (2005). Here a brief description of the apparatus is reported only.

Equilibrium was reached in stainless steel cell with calibrated volume of around 180 cm³, endowed with glass windows for observing the mixture and with an internal helical stirrer to force the vapor through the liquid. The relationship between the level of the liquid meniscus and the volume of the liquid in the cell was calibrated with an

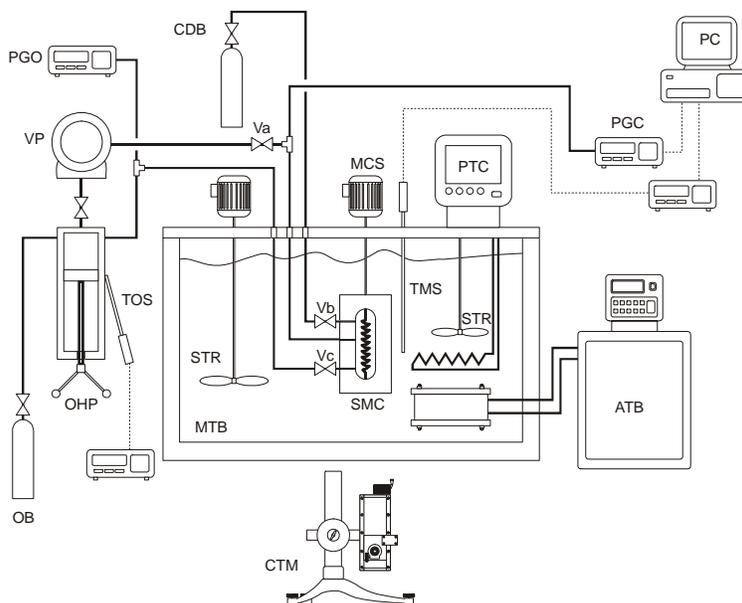


Figure 1 - Schematic Diagram of the Apparatus. ATB: Auxiliary Thermostatic Bath, CDB: Carbon Dioxide Bottle, CTM: Cathetometer, PC: Data Acquisition Computer, MCS: Measurement Cell Stirrer, MTB: Main Thermostatic Bath, OB: Oil Bottle, OHP: Oil Hand Pump, PGC: Pressure Gauge for measurement Cell, PGO: Pressure Gauge for Oil hand pump, PTC: PID Temperature Controller, SMC: Solubility Measurement Cell, STR: Stirrer, TMS: Temperature Measurement Sensor, TOS: Temperature Sensor for Oil Hand Pump, Va,b,c: Valves, VP: Vacuum Pump

estimated uncertainty of $\pm 0.5\%$. The charging of the oils into the cell was performed with a piston hand pump, while the carbon dioxide was charged by pressure difference from a stainless steel bottle.

The cell was immersed in a 100 l thermostatic bath using water as the thermostatic fluid. The temperature of the bath was kept constant by a PID-controlled heating element, which compensated for the cooling effect of an auxiliary thermostatic bath.

The temperature was measured, with an estimated total uncertainty of ± 0.03 K, by means of a 100Ω platinum resistance thermometer. The pressure was measured with a pressure gauge, with a full scale of 7000 kPa and an uncertainty of ± 2 kPa.

One of the advantages of the set-up and the measurement method is the feasibility of the measurements over a wide composition range up to a maximal pressure around 7 MPa. The pressure limitation results from the features of the pressure sensor used.

The composition of the liquid phase was established by evaluating the masses of oil and carbon dioxide dissolved in the liquid phase. The uncertainty of the liquid phase composition in mole fraction was estimated to be from ± 0.001 (high CO_2 mole fraction) to 0.015 (low CO_2 mole fraction). The mass of the oil (for hand pump calibration) and carbon dioxide (for solubility measurements) was measured with an analytical balance with an estimated uncertainty of ± 0.001 g. The level of the meniscus inside the cell, used to evaluate the liquid volume, was measured with a cathetometer with a resolution of ± 0.0001 mm, while the uncertainty in the level's measurement was estimated to be ± 0.01 mm.

After charging a known amount of oil by means of the hand pump, the carbon dioxide was transferred to the cell simply by the pressure difference between the sample bottle and the cell. The exact mass charged was measured by weighing with the analytical balance. Then the mixture of oil and CO_2 was stirred rapidly until a constant pressure was observed. When equilibrium was achieved, the level of the meniscus was measured with the cathetometer and the volume of the liquid phase in the cell was calculated. Said volume was subtracted from the total volume of the cell to obtain the volume of the vapor phase. Given the very low saturation pressure of oil, the vapor phase was assumed to be pure carbon dioxide. The mass of the CO_2 dissolved in the liquid phase was obtained by subtracting the mass of the vapor phase from the total mass charged. The procedure is repeated by adding of further amounts of CO_2 to get new equilibrium points till the completion of the isotherm.

3.2 Oils structure

As precursors of POE lubricants, six different pentaerythritol tetraalkyl esters were used. These molecules consist of a nucleus of pentaerythritol esterified by various carboxylic acids. Each ester is then characterized by a different alkyl

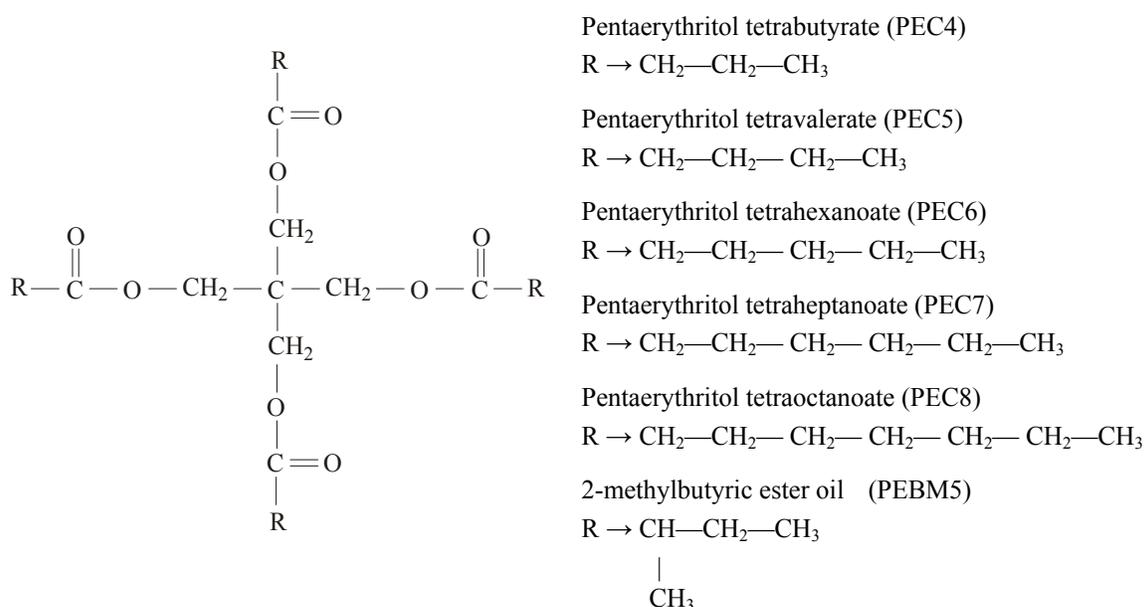


Figure 2 – Chemical Structure of the pure Pentaerythritol Tetraalkyl Esters.

chain: five are linear (*i.e.* pentaerythritol tetrabutyrate (PEC4), pentaerythritol tetravalerate (PEC5), pentaerythritol

tetrahexanoate (PEC6), pentaerythritol tetraheptanoate (PEC7), and pentaerythritol tetraoctanoate (PEC8)) and one is branched (2-methylbutyric ester (PEBM5)). The chemical structures of the pure precursors are shown in Figure 2. The Castrol Icematic SW32 polyolester oil was used as a commercial oil. No information about the oil composition were available from the producer. For this reason a gas chromatographic analysis was performed as shown in Figure 3. Four main components were clearly identified by the analysis. To get further information on the components, a MALDI (Matrix Assited Laser Desorption Ionisation) analysis was performed. This spectrometric technique allows to define the molar mass of each component of the oil. The presence of PEC6 or PEB6 (the isomers have the same molar mass), PEC7 or PEB7 and PEC8 or PEB8 was clearly stated (PEB means that the alkyl chain of the ester is branched). However, it was not possible to distinguish between the isomers (*e.g.* PEC6 or PEB6) and to identify the other main compound. Further investigation is needed and will be performed in the near future.

To express the solubility in terms of mole fraction, the molecular mass of the Castrol Icematic SW32 was evaluated by performing an ESI (Electron Spray Ionisation) analysis. The obtained value, used in the calculation of the mole fraction from the experimental mass fraction, is equal to 568. However, the estimated uncertainty of this value is around 10%, that is significantly influencing the derived solubility in terms of mole fraction, especially considering that the solubility of the various oils is quite similar. This is why we undertook further study, at moment in progress, to evaluate more precisely the average molecular mass.

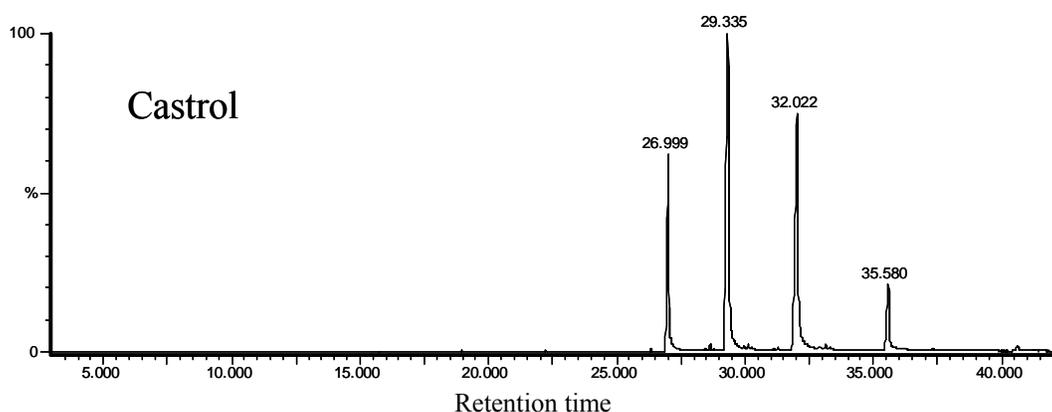


Figure 3 - GC analysis for the Castrol Icematic SW32 oil

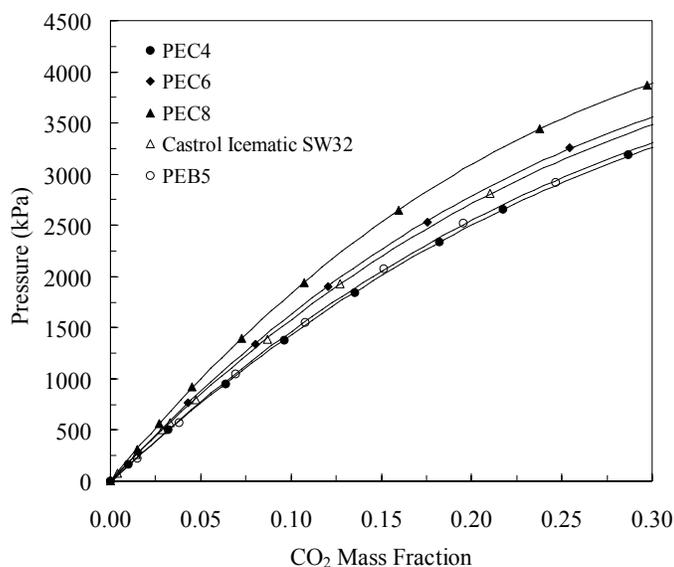


Figure 4 - Solubility in mass fraction of CO₂ in ester oils at 283 K

3.3 Solubility

The solubility of CO₂ in the various oils here considered was measured along isotherms at 283.15 K. A total of 82 points were measured. Figure 4 shows the solubility in terms of mass fraction of CO₂ dissolved in the liquid phase. For clarity, the curves corresponding to only three PECs (*i.e.* PEC4, PEC6 and PEC8) have been reported.

Figure 5 shows the solubility in terms of mole fraction of CO₂ in the liquid phase. The low and the high CO₂ concentration region have been enlarged for a better comprehension of the behavior (Figure 6). The representation in terms of mole fraction is more significant than the previous one from the point of view of the thermodynamic behavior and modeling. A discussion of the results is reported here below.

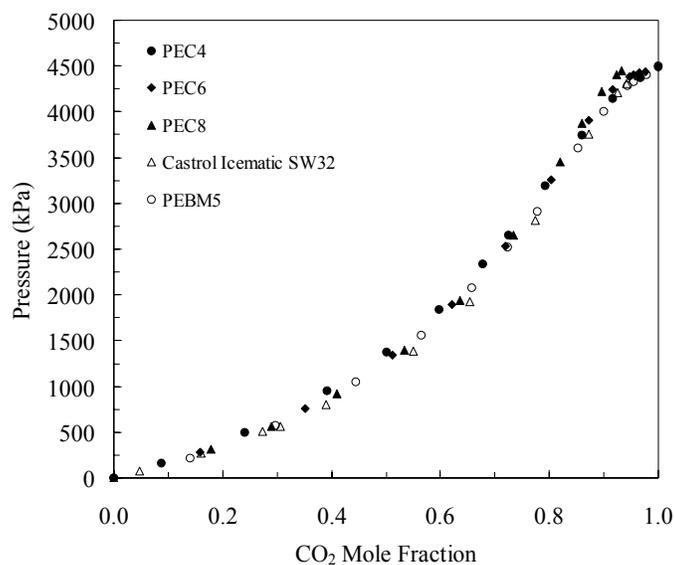


Figure 5 - Solubility in mole fraction of CO₂ in ester oils at 283 K

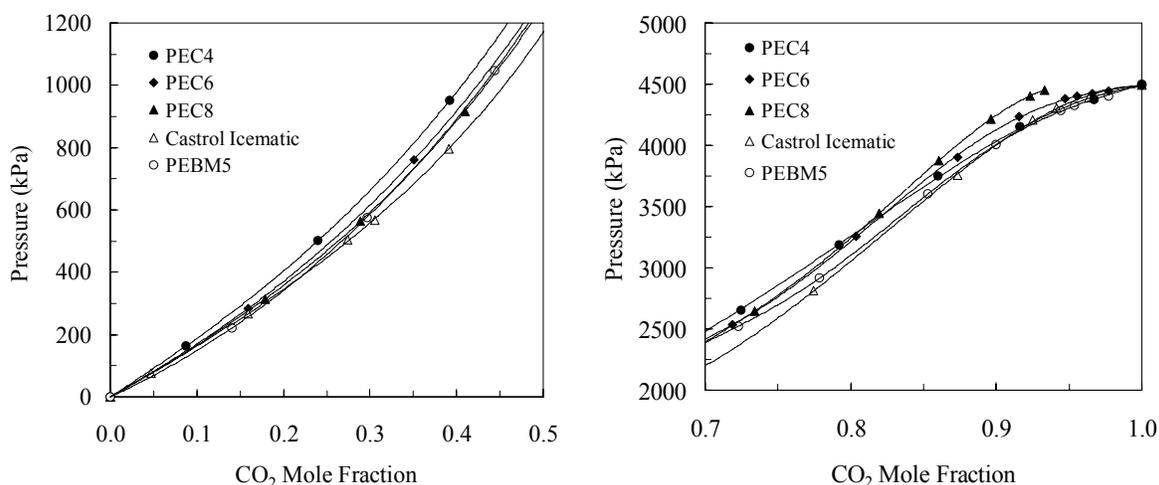


Figure 6 – Mole fraction solubility enlargement at the low and the high CO₂ concentration

3. DATA CORRELATION

The solubility data, for PECs only at moment, were correlated by means of the PRSV EoS with the Huron-Vidal mixing rules and the UNIQUAC equation for the excess Gibbs energy. The model has been adapted so to overcome the lacking of basic information (*e.g.* critical properties) for the components considered (PECs). The details of the methodology will be described in a dedicated paper due to the limited space of the present paper. Hence, here, the correlation results are simply summarized in terms of deviations between experimental and calculated pressures as shown in Figure 7. The absolute average percentage deviations in pressure are below $\pm 0.5\%$ for every system. The deviations are well within the estimated experimental uncertainty, but a small S-shaped trend of deviation has to be noted. The model used has the advantage to give the possibility to easily extend its application to the correlation (or prediction) of the solubility of refrigerant mixtures, provided the parameters for the respective binaries are available.

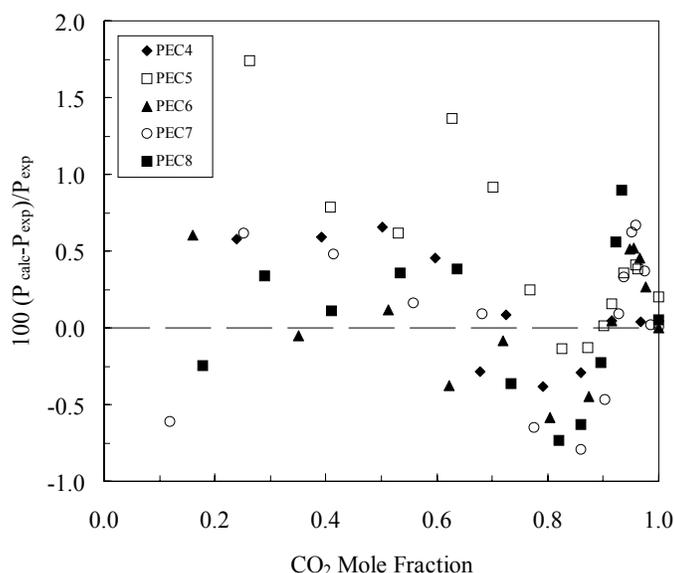


Figure 7 – Deviations between the pressure calculated with the PRSV-HV EoS and the experimental data.
(P_{exp} : experimental pressure; P_{calc} : calculated pressure)

4. DISCUSSION

The solubility may be discussed both in terms of mass and mole fraction of CO_2 dissolved in oil in the liquid phase. The former has more technical interest, and is more easily applied when commercial oils are considered as far as accurate data on the molecular mass are not easily accessible. The latter is more suitable when the data are used for the interpretation of the thermodynamic behavior and correlation or prediction with proper models. The behavior of the systems here analysed are clearly different depending on the different representation of the solubility: this is related in particular to the quite different molecular masses of the various oils.

In terms of mass fraction, the solubility of PECs decreases from the lowest to the highest molecular mass, that means the longer the linear chain of the carboxylic acid, the lower the solubility in terms of mass fraction. Though not shown in Figure 4, the solubility of PEC5 is between those of PEC4 and PEC6, while that of PEC 7 is between those of PEC6 and PEC8. The PEBM5, that is characterized by a branched chain of the carboxylic acid, is an isomer of PEC5 and then has the same molecular mass. However, its solubility is higher than that of PEC5, being close to that of PEC8. Finally, the solubility of the commercial oil Castrol Icematic SW32 is within the solubilities of PEC6 and PEC7.

While the solubility of CO_2 in terms of mass fraction is quite significantly different in the various oils, the solubility expressed in terms of mole fraction are quite similar for all systems with PECs and the PEBM5. Thus we can conclude that solubility shows slightly dependence only on the size of the PECs and structure (isomerism). Notwithstanding the similar behaviour, some observations can be done on the base of Figures 5 and 6.

In the lower mole fraction region, the solubility of PECs increases from PEC4 to PEC8. Then, the longer the carboxylic acid chain, the higher the solubility, that is the contrary than in terms of mass fraction. The pressure is lower than the one given by the Raoult's law, meaning that the solubility is higher than the ideal one. The PEBM5 has a solubility close to that of PEC8 and higher than that of its isomer PEC5. The commercial POE has the highest solubility.

At mole fractions higher than roughly 0.8 the solubility inverses in relation to both the Raoult's law and the structure of the PECs, decreasing from PEC4 to PEC8; PEC8 shows an immiscibility region (two liquid phases) at mole fractions higher than 0.94. The solubility of PEBM5 becomes very similar to that of the commercial POE and, at mole fraction higher than 0.9, they are very similar to that of PEC8.

5. CONCLUSIONS

The results of the first series of solubility measurements at 283.15 K for CO₂ in some ester oils, both pure pentaerythritol esters and a commercial POE (Castrol Icematic SW32), are presented and discussed. The solubility in PECs has been effectively correlated with the PRSV EoS implemented with the HV mixing rules and the UNIQUAC equation for the excess Gibbs energy with overall deviation in pressures below $\pm 0.5\%$.

The solubility in terms of mass fraction decreases from the lightest to the heaviest PEC. The solubilities of the PEBM5 and the commercial oil are between those of PEC4 and PEC6.

As refer the solubility expressed in terms of mole fraction the experimental results showed a weak dependence on the size of the molecules of PECs, with an increase from the lightest (PEC4) to the heaviest (PEC8) for mole fractions below 0.8 and viceversa at higher mole fractions. The branched oil PEBM5 shows a higher solubility than its isomer PEC5, suggesting that CO₂ is in general less soluble in linear chained oils than in the branched ones. The commercial oil Castrol Icematic SW32 shows the highest solubility among the considered oils within the full mole fractions range. The analysis of the composition and components' structure of the commercial oil does not allow at moment a conclusive interpretation of these results and further investigation will be performed to understand such behavior.

REFERENCES

ASHRAE Refrigeration Handbook. 2002. American Society of Heating, Refrigerating, and Air-Conditioning Engineers, Atlanta, GA.

Bobbo, S., Scattolini, M., Camporese, R., Fedele, L., Stryjek, R., 2005, Solubility of Carbon Dioxide in Pentaerythritol Esters, *Proc. IIR Conf. on Thermophysical Properties and Transport Processes of Refrigerants*, Vicenza, Italy, p. 193-200.

Bobbo, S., Scattolini, M., Camporese, R., Fedele, L., Stryjek, R., 2006, Solubility of Carbon Dioxide in some Commercial POE Oils, *Proc. 7th IIR Gustav Lorentzen Conference on Natural Working Fluids*, Trondheim, Norway, accepted for presentation.

Bobbo, S., Fedele, L., Scattolini, M., Camporese, R., Stryjek, R., 2006, Solubility of Carbon Dioxide in 2-methylpropionic, 2-methylbutyric, 2-methylhexanoic and 2-methylvaleric ester oils, *Proc. Sixteenth Symposium on Thermophysical Properties*, Boulder, CO, USA, accepted for presentation.

Burton, C., Jacobi, A.M. and Mehendale S.S., 1999, Vapor-liquid equilibrium for R-32 and R410A mixed with a polyol ester: non-ideality and local composition modeling, *Int. J. Refrig.*, vol. 22: p. 458-471.

Marsh, K.N., Kandil, M.E., 2002, Review of thermodynamic properties of refrigerants+lubricant oils, *Fluid Phase Equil.*, vol. 199: p. 319-334.

Martz, W.L., Burton, C.M. and Jacobi A.M., 1996, Vapor-liquid equilibria for R-22, R134a, R-125, and R-32/125 with a polyol ester lubricant: measurements and departure from ideality, *ASHRAE Trans.*, vol. 102, no.1: p. 367-374.

Poot W. and de Loos, T.W., 2004, High pressure behaviour of binary systems of refrigerants and phenylalkanes: the system 1,1,1,2-tetrafluoroethane+phenyloctane, *Fluid Phase Equil.*, vol. 222-223: p. 255-259.

Poot W. and de Loos, T.W., 2003, High pressure phase equilibria in the system 1,1,1,2-tetrafluoroethane+heptylbenzene, *Fluid Phase Equil.*, vol. 210: p. 69-75.

Short, G.D. and Cavestri, R.C., 1992, High-viscosity ester lubricants for alternative refrigerants, *ASHRAE Trans.*, vol. 98-1: p. 789-793.

Takaishi, Y. and Oguchi, K., 1995, Solubility of R-32 and polyolester lubricant mixtures, *Proc. 19th Int. Cong. of Refrigeration*, The Hague, The Netherlands, vol. IVa: p. 568-574.

Takigawa, K., Sandler, S.I., Yokozeki, Y., 2002, Solubility and viscosity of refrigerant/lubricant mixtures: hydrofluorocarbon/alkylbenzene systems, *Int. J. Refrig.*, vol. 25: p. 1014-1024.

Wahlström, Å. and Vamling, L., 1999, Solubility of HFC32, HFC125, HFC134a, and HFC 152a in a pentaerythritol tetrapentanoate ester, *J. Chem. Eng. Data*, vol. 44: p. 823-828.

Wahlström, Å. and Vamling, L., 2000, Solubility of HFCs in pentaerythritol tetraalkyl esters, *J. Chem. Eng. Data*, vol. 45: p. 97-103.

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