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Viscosity Behavior of Two Mixtures of CO$_2$ and Lubricant Oil

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ABSTRACT

Experimental data on the viscosity of mixtures of CO$_2$ and lubricant oil were acquired and correlated using an excess-property approach based on the classical Eyring liquid viscosity model. Two oils of different types and viscosity grades (AB ISO 32 and mineral ISO 50) were evaluated at temperatures ranging from 40 to 82°C. The excess activation energy for viscous flow was successfully correlated as a function of temperature and concentration using Redlich-Kister polynomial expansions with up to three terms. Large departures from the ideal solution viscosity behavior have been identified in both mixtures. The nature of the observed deviations has been explored in the light of their dependence on temperature, refrigerant concentration and oil type.

1. INTRODUCTION

There are several refrigeration applications where R-744 (CO$_2$) is well suited as a primary refrigerant (Pettersen, 1999). It is the only non-flammable, non-toxic natural refrigerant that is capable of operating in a vapor compression cycle at temperatures lower than 0°C. It is also widely available at a relatively low cost.

One of the main issues in the CO$_2$ compressor design is related to the performance and reliability of the bearings system. It is of utmost importance that the variation of the physical properties of the lubricant mixture with respect to temperature and refrigerant concentration are taken into account during all stages of the system design. Despite the increasing number of publications dealing with the determination of physical properties of mixtures of CO$_2$ and lubricant oils, more research is still needed before the most suitable lubricants for a variety of CO$_2$ applications are finally selected.

Recent appraisals of the experimental and theoretical work on the determination of the physical properties of mixtures of CO$_2$ and lubricant oil have been presented by Seeton and Hrnjak (2006), Bobbo *et al.* (2006), Marcelino Neto and Barbosa (2007) and Yokozeki (2007). Undoubtedly, in the open literature, the most extensively studied mixtures of CO$_2$ and oil are those involving Polyolesters (POE) and Polyalkyleneglycols (PAG). Significantly less work has been devoted to characterizing mixtures of CO$_2$ and other oil types, such as mineral (MN), Polyalphaolefin (PAO) and Alkylbenzene (AB). Moreover, the number of works in which the viscosity behavior of CO$_2$-lubricant mixtures is investigated in detail is still rather limited.

The objective of this paper is to present experimental data on the liquid viscosity of mixtures of CO$_2$ and two lubricants, namely, a mineral (MN) oil ISO 50 and an alkylbenzene (AB) ISO 32. The data points were obtained at pressures between 0.9 and 5.6 MPa and temperatures between 40 and 82°C. The liquid mixture viscosity was correlated with the Grunberg and Nissan (1949), Katti and Chaudry (1964) and McAllister (1960) correlations. The best agreement between model and experimental data was obtained with a special form of the Grunberg and Nissan (1949) equation.

2. EXPERIMENTAL WORK

2.1 Experimental Apparatus and Procedure

The experimental facility is schematically illustrated in Fig. 1 (Marcelino Neto and Barbosa, 2007). A specified amount of lubricant oil is placed in the 4L equilibrium cell (2). A vacuum of 0.04 mbar is generated in the apparatus to remove moisture and dissolved gases. An initial amount of refrigerant is fed into the cell. The system temperature is set by a thermostatic bath (1) that circulates service water through a tank (6) in which the equilibrium cell is fully immersed. In the present experiments, the pressure of the oil-refrigerant mixture is, therefore, the dependent variable. The equilibrium cell is instrumented for absolute pressure, P, and the temperature of the fluids in the cell is recorded by three type-T thermocouples (T_1, T_2, T_3) located at three distinct heights to measure the temperatures of the liquid and vapor phases. A gear pump (5) moves the liquid oil-refrigerant mixture through the experimental facility. The speed of the electrical motor is set at its minimum value (12 Hz). The mixture first flows through a Coriolis-type mass flow transducer (4) that records flow rate, temperature and liquid density. Then, an oscillating piston viscometer (3) registers temperature and dynamic viscosity of the liquid mixture. The solubility of the mixture is measured gravimetrically using a liquid mixture sample collected in a 150 mL cylinder (7). The experimental apparatus is integrated with a signal conditioning module (8) and a computerized system for data acquisition and treatment (9). The tank (top, sides and bottom), connection tubing and instrumentation (Coriolis flow meter, pump and sampling cylinder) are thermally insulated to prevent heat losses. The temperature variation between the viscometer, the mass flow/density meter and test cell were within the uncertainty level set during the calibration of the thermocouples. The experimental procedure for obtaining the mixture solubility has been outlined in Marcelino Neto and Barbosa (2007).
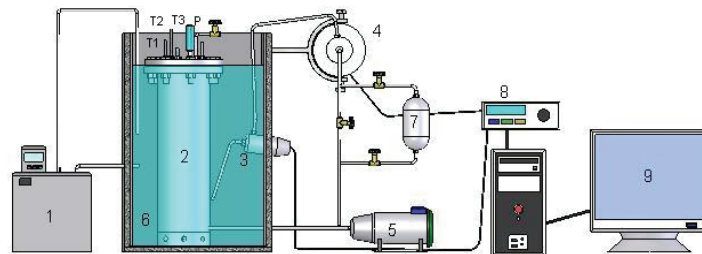

Figure 1. Schematic representation of the experimental rig.

The temperature measurement uncertainty was estimated at ±0.2°C (68% confidence level). The uncertainty of the density measurements (estimated from the manufacturer specifications) was ±1% of the absolute reading (95% confidence level). The uncertainty of the viscosity measurements (estimated from the manufacturer specifications) was ±1% of the full scale (68% confidence level). It should be observed that, because of interchangeable pistons, the uncertainty is ±0.1 cP for the 0.1-10 cP piston, and ±1 cP for the 1-100 cP piston. The uncertainty of the pressure transducer (estimated from the manufacturer specifications) was ±0.15% FS (0.3 bar) and that of the balance was ±0.3 g. After an error propagation analysis (Marcelino Neto, 2006), the uncertainty in the solubility measurement was determined at ±0.5 g/kg. The experimental procedure was validated with vapor pressure and density measurements of pure CO_2 and with density and viscosity of an ISO 10 lubricant oil, whose properties have been made available from its manufacturer (Marcelino Neto and Barbosa, 2007).

2.2. Experimental Conditions

The experimental conditions of the present experiments are as follows. Solubility, liquid density and viscosity of CO_2/MN ISO 50 and CO_2/AB ISO 32 oil mixtures were measured at temperatures between 40 and 82°C. R-744 was supplied by AGA (99.9% pure) and the lubricants were supplied by Embraco. The exact chemical composition of the lubricants is a proprietary information.

3. VISCOSITY MODELING

3.1. Liquid Viscosity Models

The Eyring theory (Glasstone *et al.*, 1941) for the viscosity of pure liquids can be extended for binary mixtures as follows (Oswal and Desai, 2001)

$$\eta V = N_a h \exp\left(\frac{x_1 G_1^+ + x_2 G_2^+ + G^{E+}}{RT}\right) \tag{1}$$

or, in a more suitable form

$$\ln(\eta V) = x_1 \ln(\eta_1 V_1) + x_2 \ln(\eta_2 V_2) + \frac{G^{E+}}{RT} \tag{2}$$

Katti and Chaudry (1964) modeled the activation energy for viscous flow in Eq. (2) using a polynomial Redlich-Kister type expansion given by

$$\frac{G^{E+}}{RT} = \frac{D_0 x_1 x_2}{RT} + \frac{D_1(2x_1 - 1)(x_1 - x_1^2)}{RT} + \frac{D_2(2x_1 - 1)^2(x_1 - x_1^2)}{RT} + \cdots \tag{3}$$

where D_i are fitting parameters with $i = 0,1,2,...N$. In the present work, the Katti and Chaudry expansion was truncated in the third term.

The Grunberg and Nissan (1949) model assumes an ideal solution behavior ($V = x_1 V_1 + x_2 V_2$) in which the mixture viscosity is correlated from

$$\ln(\eta) = x_1 \ln(\eta_1) + x_2 \ln(\eta_2) + G_0 x_1 x_2 + G_1(2x_1 - 1)(x_1 - x_1^2) + \\ G_2(2x_1 - 1)^2(x_1 - x_1^2) + \cdots \tag{4}$$

In the present paper, the Grunberg and Nissan correlation has been employed in two different ways. In the first approach, henceforth referred to as the G-N approach, G_0 is correlated as a linear function of the CO_2 mole fraction for each temperature (Tomida *et al.*, 2007)

$$G_0 = \Gamma_0(T) + \Gamma_1(T)x_1 \tag{5}$$

and the remaining coefficients G_i are assumed equal to zero. In the second approach, the G-N2 approach, the series in truncated in the third term and the coefficients G_0, G_1 and G_2 are assumed independent of temperature and are determined from a best-fit to the experimental data.

The McAllister (1960) liquid mixture viscosity model is based on Eyring's theory of absolute reaction rates. For a binary mixture, the McAllister semi-theoretical equation is written as

$$\ln \nu = x_1^4 \ln \nu_1 + 4x_1^3 x_2 \ln \nu_{1112} + 6x_1^2 x_2^2 \ln \nu_{1122} + 4x_1 x_2^3 \ln \nu_{2221} x_2^4 \ln \nu_2 \\ - \ln\left[x_1 + x_2 \frac{M_2}{M_1}\right] + 4x_1^3 x_2 \ln\left[\frac{3}{4} + \frac{M_2}{4M_1}\right] + 6x_1^2 x_2^2 \ln\left[\frac{1}{2} + \frac{M_2}{2M_1}\right] \\ + 4x_1 x_2^3 \ln\left[\frac{1}{4} + \frac{3M_2}{4M_1}\right] + x_2^4 \ln\left[\frac{M_2}{M_1}\right] \tag{6}$$

where ν is the kinematic viscosity of mixture, ν_i is the kinetic viscosity of pure component i at the same temperature and pressure as the mixture, and M_i is the molar mass. $\nu_{1112}, \nu_{1122}, \nu_{2221}$ are fitting coefficients calculated from a best-fit to the experimental data.

3.2. Implementation
The models were implemented in the Engineering Equation Solver – EES (Klein, 2007), and the genetic algorithm

routines available in EES were employed in the determination of the models' coefficients. The physical properties of pure CO_2 were obtained from EES and the properties of the pure lubricants (density and viscosity) were derived from polynomial fittings to our own experimental data. To evaluate the prediction ability of the correlations, the following quantities can be defined

$$\text{RMS} = \frac{100}{n} \sqrt{\sum_{i=1}^{n} \frac{\left(\eta_{cal,i} - \eta_{exp,i}\right)^2}{\eta^2_{exp,i}}} \tag{7}$$

$$\text{AAD} = \frac{100}{n} \sum_{i=1}^{n} \left| \frac{\eta_{cal,i} - \eta_{exp,i}}{\eta_{exp,i}} \right| \tag{8}$$

$$\text{Bias} = \frac{100}{n} \sum_{i=1}^{n} \frac{\eta_{cal,i} - \eta_{exp,i}}{\eta_{exp,i}} \tag{9}$$

where, in the McAllister (1960) model, η is substituted by ν in the above equations.

4. RESULTS AND DISCUSSION

The experimental data for the mixture viscosity, density and molar solubility are presented in Table 1 as a function of pressure and temperature for both mixtures. The model predictions have been summarized in Table 2, where the search intervals employed in the calculation of the fitting parameters are also presented. A direct comparison between the G-N2 model and the Katti and Chaudry (1964) correlation (both with a three-term expansion of the activation energy parameter) indicates that the latter has predicted the data with a better agreement. Although there may be several reasons for this particular result, perhaps the most apparent explanation seems to be the fact that the severe non-ideality of the mixture molar volume is not considered in the Grunberg and Nissan (1949) model. The mass density of both mixtures as a function of temperature is presented in Figs. 2 and 3, where a significant departure from the ideal mixture behavior (calculated from Eq. 10) is clearly observed. The McAllister (1960) model does not perform well under the conditions evaluated in the present work.

Table 1. Experimental data.

Mixture	$T(°C)$	P(MPa)	x_1 (kmol/kmol)	ρ (kg/m³)	η (cP)
CO$_2$ + MN ISO 50	40.5	1.0	0.2070	911.6	27.0
		3.4	0.3653	914.9	9.9
		5.5	0.5085	917.6	4.3
	59.7	1.2	0.1417	902.0	11.3
		3.4	0.3540	904.2	5.9
		5.6	0.4237	905.0	2.7
	81.5	1.2	0.1520	898.1	5.6
		3.8	0.2946	892.9	2.8
		5.5	0.4044	895.9	1.9
CO$_2$ + AB ISO 32	40.5	1.4	0.2512	873.1	19.9
		3.6	0.5173	861.4	8.7
		5.1	0.6681	869.7	4.3
	57.7	1.3	0.1942	864.2	12.4
		3.5	0.4053	856.8	5.5
		5.4	0.5286	866.6	3.6
	69.2	1.4	0.2115	859.1	7.0
		3.5	0.3611	859.1	3.8
		5.5	0.4702	858.7	2.0

Table 2. Summary of the data correlation.

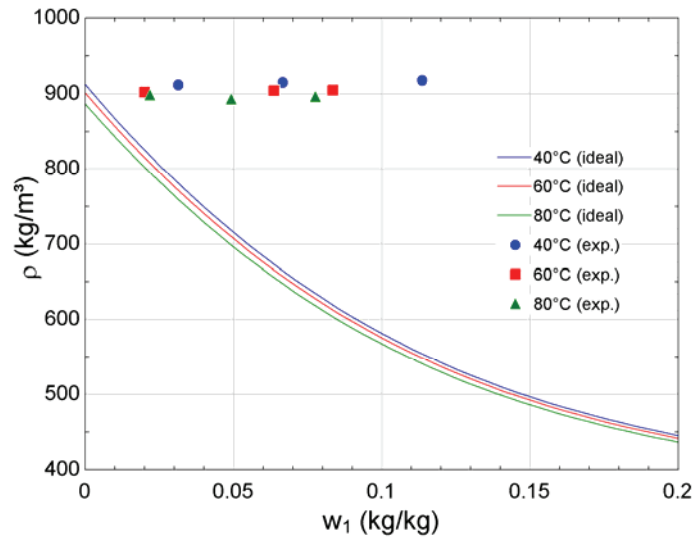| Mixture	Model	Parameter	Search interval	RMS(%)	AAD(%)	Bias(%)
CO$_2$ + MN ISO 50	G-N2	$G_0 = 8.29$ $G_1 = 2.64$ $G_2 = 4.22$	−10000 to 10000	3.6	10.2	1.4
	G-N	$G_0 = 5.35 − 1.04x_1$ $G_0 = 4.39 − 1.62x_1$ $G_0 = 7.54 − 9.84x_1$	−10000 to 10000	3.0 5.4 3.8	4.7 8.5 5.9	0.4 0.8 0.5
	Katti-Chaudry	$D_0 = 15646$ $D_1 = 4997$ $D_2 = 6543$	−100000 to 100000	3.3	6.8	1.4
	McAllister	$v_{1112} = 932$ $v_{1122} = 1$ $v_{2221} = 106.5$	−10000 to 10000	11.4	33.9	−17.8
CO$_2$ + AB ISO 32	G-N2	$G_0 = 16.75$ $G_1 = 12.16$ $G_2 = 5.03$	−10000 to 10000	6.3	16.0	−6.6
	G-N	$G_0 = 1.58 + 13.9x_1$ $G_0 = 4.71 + 3.16x_1$ $G_0 = 2.14 + 1.68x_1$	−10000 to 10000	2.6 2.3 1.2	4.0 3.6 1.9	0.5 0.3 −0.02
	Katti-Chaudry	$D_0 = 16364$ $D_1 = 30433$ $D_2 = 46503$	−100000 to 100000	4.6	10.6	1.1
	McAllister	$v_{1112} = 57.5$ $v_{1122} = 1$ $v_{2221} = 6.6$	−10000 to 10000	11.4	33.9	−17.8

Figure 2. Experimental liquid mixture molar volume of the CO$_2$ + MN ISO 50 mixture.

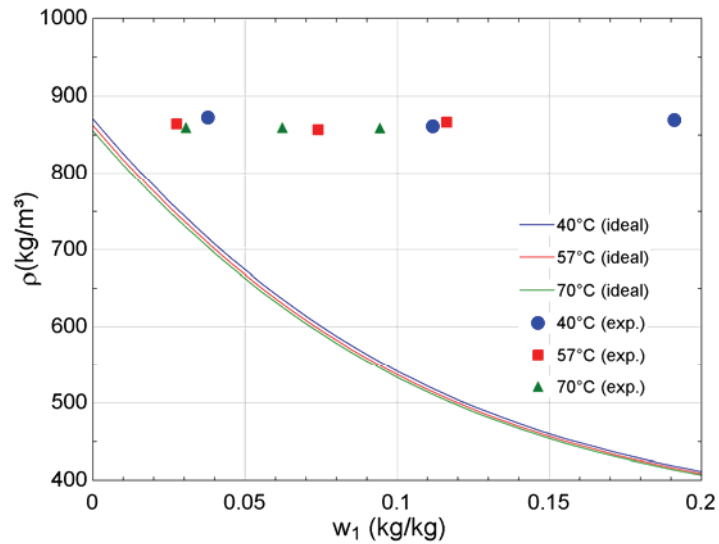$$\frac{1}{\rho^{id}} = \frac{\sum x_i V_i}{\sum x_i M_i} \tag{10}$$

Figure 3. Experimental liquid mixture molar volume of the CO_2 + AB ISO 32 mixture.

The performance of the Grunberg and Nissan (1949) correlation improves significantly when a temperature dependent approach is adopted (Tomida *et al.*, 2007). In Table 2, the correlations for G_0 as a function of temperature are presented as a function of increasing temperature from top to bottom. Figures 4 and 5 present a comparison between the Katti and Chaudry (1964) correlation and the G-N approach. Despite the better agreement of the latter model, the Katti and Chaudry model is recommended because it is easier to apply at intermediate temperatures that have not been correlated during the experiments.
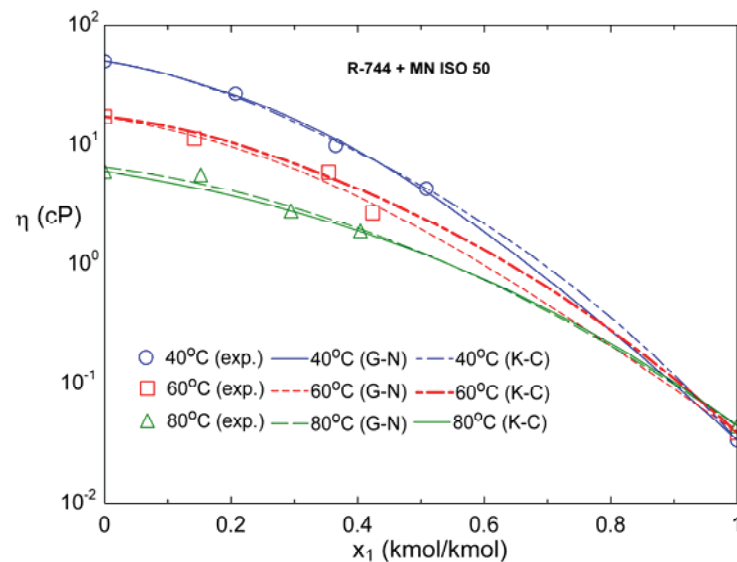

Figure 4. Viscosity of the CO_2 + MN ISO 50 mixture and comparison with the Katti and Chaudry (1964) and G-N models (Grunberg and Nissan, 1949).
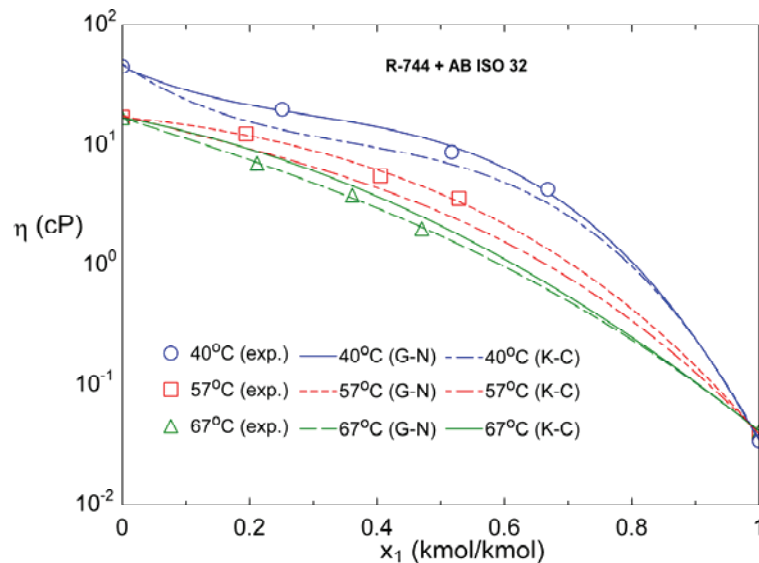
Figure 5. Viscosity of the CO_2 + AB ISO 32 mixture and comparison with the
Katti and Chaudry (1964) and G-N models (Grunberg and Nissan, 1949).

5. CONCLUSIONS

The present paper put forward new data on the viscosity of a mixture of CO_2 (R-744) and two lubricant oils (MN ISO 50 and AB ISO 32). An experimental facility that enables the simultaneous measurement of the viscosity, density and solubility has been utilized. The data were obtained at three different temperatures in the range of 40 and 82°C. The viscosity data have been correlated with the Grunberg and Nissan (1949), Katti and Chaudry (1964) and McAllister (1960) correlations. When a three-term polynomial expansion of the excess activation energy with temperature independent coefficients is employed in the Grunberg and Nissan (1949) and Katti and Chaudry (1964) models, the latter presents a better correlation of the experimental data. The performance of the Grunberg and Nissan (1949) approach is improved when temperature dependent coefficients are utilized. However, this complicates the application of the model at intermediate temperatures. The performance of the McAllister (1960) correlation has been less satisfactory than those of the other models.

NOMENCLATURE

G_i^+	Activation energy for viscous flow	(J/kmol)
G^{E+}	Excess activation energy for viscous flow	(J/kmol)
h	Planck's contant [6.626 x 10^{-34}]	(Js)
M	Molar mass	(kg/kmol)
N_a	Avogrado's number [6.023 x 10^{26}]	($kmol^{-1}$)
R	Universal gas constant [8.314]	(kJ/kmol.K)
T	Temperature	(K or °C)
V	Molar volume	(m^3/kmol)
V_i	Molar volume of component i	(m^3/kmol)
w_i	Mass fraction of component i	(kg/kg)
x_i	Molar fraction of component i	(kmol/kmol)
η	Dynamic viscosity	(cP or mPa.s)
ν	Kinematic viscosity	(m^2/s)
ρ	Mass density	(kg/m^3)

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