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VISCOSITY, DENSITY, AND GAS SOLUBILITY OF REFRIGERANT BLENDS AND AZEOTROPES IN SELECTED REFRIGERANT LUBRICANTS

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ABSTRACT

Data is presented for the vapor liquid equilibrium viscosity reduction of lubricants with two refrigerant blends at two temperatures. The lubricants tested were a 32 ISO VG mixed acid polyolester and a 32 ISO VG branched acid polyolester. The refrigerant blends used were HFC-125/143a/134a (44/52/4% w/w), and HFC-125/143a (50/50% w/w).

INTRODUCTION

This experiment determined the vapor liquid equilibrium viscosity reduction of two lubricants with two refrigerant blends. The lubricants tested were a 32 ISO VG mixed acid polyolester and a 32 ISO VG branched acid polyolester The refrigerant blends used were HFC-125/143a/134a (44/52/4% w/w), and HFC-125/143a (50/50% w/w). The mixtures were prepared and tested in an oscillating body viscometer, and the ratio of gases at each viscosity data point was determined by gas chromatography.

METHODS

The viscosity determination method used in this study is similar to the gas equilibrium approach described by Parmlee (1964), Albright (1956-59) and Little (1956). This study uses temperature and pressure limitations to determine refrigerant gas concentrations.

Viscosity and density are determined accurately by a fourth generation viscometer (Cavestri, 1993) taken from a report by Nissen (1981). This instrument consists of a solid cylindrical bob made of highly polished stainless steel, which is enclosed in a stainless steel pressure tube. The bob is connected to a precisely thermostatted spring inside the tube. An external electromagnet causes the bob to oscillate inside the solution-filled tube. The rate at which the bob's motion slows and stops is called the *decrement*.

The viscosity of the solution can be determined from the decrement and density. The same bob used to measure the decrement can be used for density measurements. Observations of changes in the position of the bob can determine density to within .0005 g/ml. Accurate density measurements allow the calculation of centistokes (cSt) from centipoise (cP).

The readability of the viscometer is 0.06 cP. The wide temperature range of various calibration oils results in a significant overlap that serves as an internal standard and self check. For low viscosity solutions, the difference between standards is $\pm 0.1\%$; this increases to $\pm 1.5\%$ for high viscosity solutions. The density range of the instrument is calibrated with known, readily available pure fluids that are dried over a molecular sieve prior to use; this provides a straight calibration line for density at specified temperatures. The precision of this determination is $\pm 0.3\%$

The fluid refrigerant mixture is pumped from the bottom of the viscometer and sprayed into the refrigerant vapor space at specific pressures and temperatures. The fluid sample is then drawn through a very low volume capillary line (380μ l) into a deeply evacuated, lightweight glass sampling bulb with a stopcock. A total charge is retained in the bulb. The ratio of gas to liquid oil (percentage by weight) may then be measured. The concentration measurement is reproducible within $\pm 0.5\%$ by weight at a given isothermal pressure test point. Directly sampling the refrigerant lubricant mixture at each isothermal pressure test point is essential to the measurement technique used in this study.

If there is any void space in a pressurized viscometer cell, the refrigerant-oil pair combinations will change. Single and blended refrigerants are added as liquid until the desired equilibrium pressure is reached. Blends are purged through the lubricant at a constant back pressure at the specified temperature. The fractionation of the mixed gases is determined at every temperature and pressure. Samples of the fluid/refrigerant mixture are collected to determine the percent refrigerant by weight in the fluid. The ratio of gases is determined by gas chromatography.

Pressure is measured with a Bourdon tube gauge; the double helix design of this gauge allows the needle to rotate through almost two complete revolutions (660 degrees). This temperaturecompensated gauge is calibrated with both gas and liquid, is accurate to ± 0.2 psia, and is traceable to NIST standards. Vapor pressure is measured at equilibrium, when the soluble gases are responsible for the fluid properties. Since the gas content of the fluid is measured, the amount of gas contained in the Bourdon tube is irrelevant.

Density, viscosity, and vapor pressure are always measured under isothermal conditions. The viscometer temperature is maintained by a circulating constant temperature glycol bath controlled by a Platinum RTD ($\pm 0.1^{\circ}$ C) microprocessor. The RTD probe is mounted at the surface of the viscometer tube inside the liquid bath. The other temperature zones are controlled by electric heaters, using a microprocessor controller ($\pm 0.1^{\circ}$ C) with type "J" thermocouples.

After refrigerant/lubricant samples are obtained from the viscometer, the evacuated glass bulb is weighed. The gas contained in the bulb is let into an evacuated chamber (20-30 millitorr), which pulls the refrigerant out of the sample in the glass bulb. To separate the refrigerant from the lubricant, the glass bulb is warmed carefully with a propane torch. One minute is allowed for equilibrium to occur.

The ratio of the gases can be determined from the sample of gases drawn off the top oil. A second gas sample is obtained to determine if equilibrium has been established and whether the ratio of gases has changed. Gas chromatography is used to analyze the refrigerant sample. Separate measurement studies indicate that more than 80% of the refrigerant contained in the liquid sampling bulb has been removed. Finally, all remaining traces of refrigerant are removed by heating the bulb to constant weight under vacuum. This was then used for the final measurements of net percentage by weight.

RESULTS

Viscosity reduction evaluations were performed with fluids and gases at isothermal conditions. The solubility of each refrigerant blend with each test lubricant was different, so the lubricants were purged with liquid refrigerant gas at constant pressure. The isothermal measurements of refrigerant/lubricant mixtures presented in figures 1-8 were taken with this technique. These figures show the concentration of the blend components as shaded areas, which are cumulative rather than overlapped. For example, in figure 1, the concentration in the lubricant of HFC-125 at 1 MPa is

approximately ten percent. The concentration of HFC-143a is approximately seven percent, and the concentration of HFC-134a is approximately three percent. The concentration of the blend is represented by the top line, approximately twenty percent.

The ratio of the blend components in the vapor space above the liquid mixture was maintained equal to that of the pure refrigerant blend, although any arbitrary ratio (such as that for a given temperature) could have been selected. The ratio of components in the vapor space is very close to that actually observed in the solution, especially at higher pressures.

The refrigerant blends were more soluble in the tested branched acid polyolester than in the mixed acid polyolester. The concentrations of gas in these two lubricants at any given pressure (such as 1 MPa) are remarkably different; however, the viscosities of the solutions are quite similar.

Composite viscosity and pressure data at constant refrigerant concentrations is presented in figures 9 through 12. This is smoothed data obtained from individual isothermal measurements. Although the experiment is not yet complete, definite trends in solubility and operating pressures are evident. With both tested blends, the mixed acid polyolester (figures 10 and 12) exhibited higher operating pressures than the branched acid polyolester (figures 9 and 11). This may suggest that mixed acid polyolester would experience less outgassing due to refrigerant insolubility when used as a bearing lubricant.

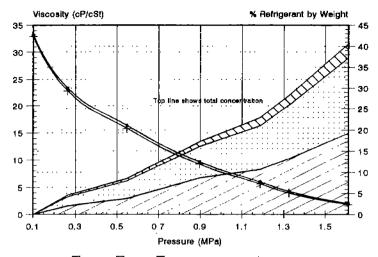
In conclusion, both tested refrigerant blends seemed to have similar effects on the viscosity of the tested lubricants. The similar compositions of the blends may be responsible for this. If this is the case, the one blend that remains to be tested -- HFC-32-125-134a (23/25/52% w/w) -- may show significantly different results due to differences in gas solubility and pressure. This blend contains a greater percentage of HFC-134a than those already tested, which could improve gas solubility.

ACKNOWLEDGEMENTS

This project was supported by the Air-Conditioning and Refrigeration Technology Institute under ARTI MCLR PRoject Number 650-51400: Blends, and by the United States Department of Energy.

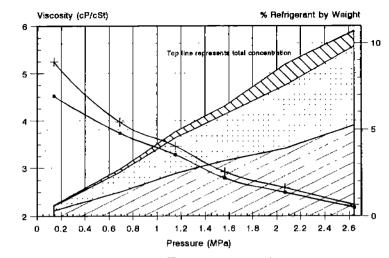
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🖸 % R-143a 🖸 % R-125 🖾 %R-134a 🛨 Viscosity, cP + Viscosity, cSt

Figure 1. Viscosity, solubility and gas fractionation at 40°C. HFC-125/143a/134a (44/52/4% w/w) and 32 ISO VG branched acid polyclester.





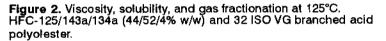
Top line replesents

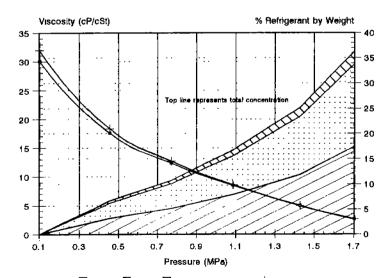
% Refrigerant by Weight

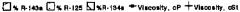
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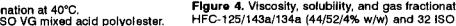
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Viscosity (cP/cSt)

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2

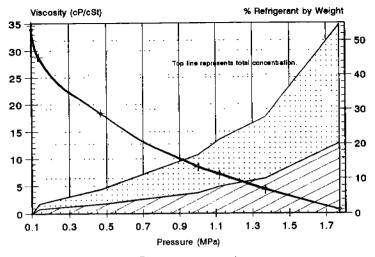
Figure 4. Viscosity, solubility, and gas fractionation at 125°C. HFC-125/143a/134a (44/52/4% w/w) and 32 ISO VG mixed acid polyolester.

0.12 0.32 0.52 0.72 0.92 1.12 1.32 1.52 1.72 1.92 2.12 2.32 2.52

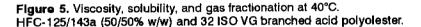
Pressure (MPa)

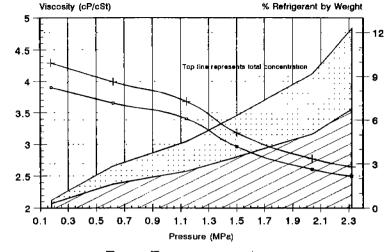
□% R-143a □% R-125 □%R-134a + Viscosity, cP + Viscosity, cSt

Figure 3. Viscosity, solubility, and gas fractionation at 40°C. HFC-125/143a/134a (44/52/4% w/w) and 32 ISO VG mixed acid polyolester.



🛛 % R-143a 🗔 % R-125 🗢 Viscosity, cP + Viscosity, cSt





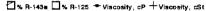
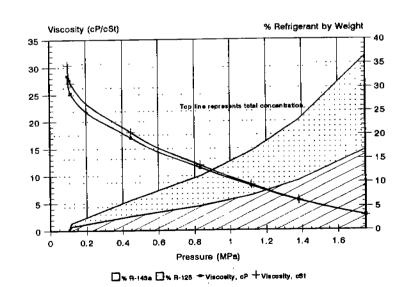
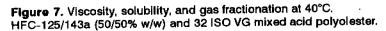
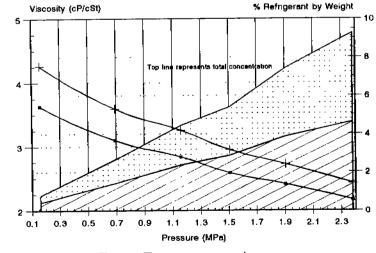


Figure 6. Viscosity, solubility, and gas fractionation at 125°C. HFC-125/143a (50/50% w/w) and 32 ISO VG branched acid polyelester.







🛛 % R-143a 🗔 % A-125 = Viscosity, cP + Viscosity, cSt

Figure 8. Viscosity, solubility, and gas fractionation at 125°C. HFC-125/143a (50/50% w/w) and 32 ISO VG mixed acid polyolester.

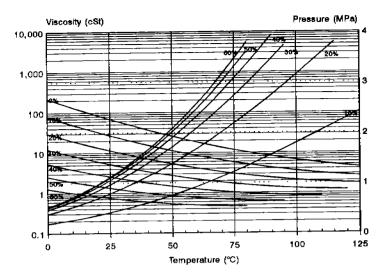


Figure 9. Viscosity and pressure at constant concentrations. HFC-125/143a/134a (44/52/4% w/w) and 32 ISO VG branched acid polyolester.

Viscosity (cSt)

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25

10 30%

Pressure (MPa)

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125

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40%

75

30%

100

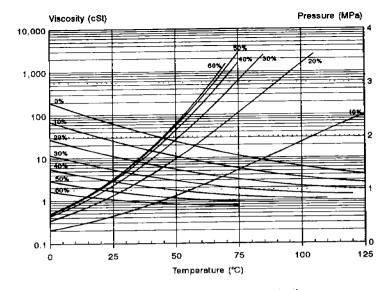


Figure 10. Viscosity and pressure at constant concentrations. HFC-125/143a/134a (44/52/4% w/w) and 32 ISO VG mixed acid polyolester.

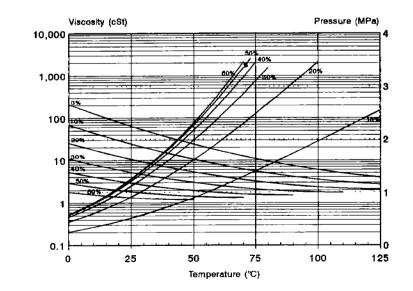


Figure 11. Viscosity and pressure at constant concentrations. HFC-125/143a (50/50% w/w) and 32 ISO VG branched acid polyolester.

50

Temperature (°C)

Figure 12. Viscosity and pressure at constant concentrations. HFC-125/143a (50/50% w/w) and 32 ISO VG mixed acid polyolester.