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ABSTRACT

Lubricants are important components of almost all air conditioning and refrigeration systems. Their primary function is to lubricate the compressor, provide sealing of clearances between low and high pressure sides of the compressor and remove frictional heat. But the lubricant is in contact with refrigerant at all times and plays a thermo-fluidic role in the air conditioning system that can impact both system capacity and coefficient of performance (COP). Lubricants can influence capacity by altering the refrigerant-side heat transfer coefficients, and increasing pressure drop required to maintain set point temperatures. Lubricants can also affect the isentropic efficiency of the compressor.

This paper presents the results of a bench test study of the solution phase behavior and lubricating performance of several commercial and new developmental polyol ester (POE) lubricants with low GWP R-410A replacement refrigerants. The results suggest that POE lubricants used today with R-410A may not be acceptable for use with R-32 or related HFC/HFO blends. An undesirable miscibility "gap" is observed in mixtures of traditional POEs with R-32 in the concentration range of 10-40 wt% lubricant in refrigerant. In addition, attempts to resolve the miscibility issues by modification of traditional POE chemical structure lead to lubricants with diminished lubricity and load carrying properties. Studies conducted with a new class of advanced polyol esters (APOEs) show that it is possible to design synthetic lubricants optimized for R-32, combining good refrigerant miscibility and excellent lubricity and load carrying performance.

1. INTRODUCTION

The transition to lower global warming potential (GWP) alternative refrigerants is critical to the realization of environmentally sustainable and more energy efficient refrigeration technologies (Ritter, 2013). Leading candidates to replace R-22 and R-410A in air conditioning and heat pump applications include R-32 (difluoromethane) and a plethora of HFC/hydrofluoro-olefin blends with GWPs in the range of 400-650. Considerable data has been generated comparing R-410A with various low GWP alternative refrigerants in full system tests. Most notable is the work sponsored by AHRI under the Alternative Refrigerant Evaluation Program (AREP)(Wang and Amrane, 2013). But these studies have either been refrigerant "drop in" tests to commercial R-410A systems, or "soft optimized" tests where minor component modifications were made to better adapt a system to the properties of the new refrigerants. In all cases, the lubricants used for these studies were the commercial polyol ester (POE) lubricants used today with R-410A. But commercial POE lubricants used today are much less compatible with R-32 and HFC/HFO blends. There is concern that issues may arise with long term reliability of compressors due to inadequate lubrication, poor oil return to the compressor and undesirable lubricant hold up in the system; problems that would not be observed in the short term capacity and energy efficiency tests conducted within the AREP program. But regardless, there is also interest in understanding if properly optimized lubricants can improve the overall performance of low GWP-based systems.

2. EXPERIMENTAL

2.1 Refrigerant/Lubricant Miscibility Measurements
Glass tubes were charged with predetermined volumes of lubricant having a moisture content of less than 25 ppm. The tubes were then attached to a gas manifold of known volume and evacuated to < 13 Pa. The tubes were then cooled using liquid nitrogen and individually charged with predetermined amounts of refrigerant using pressure

change to accurately control the amount of refrigerant added. Each tube was then flame sealed and slowly warmed to room temperature. The total volume of lubricant/refrigerant in each tube was fixed at 2.0 mL regardless of the concentration of lubricant in refrigerant. The tubes were then secured in a temperature controlled bath. The bath temperature was then changed at a rate of 1 °C per minute. The temperature change was always made starting at room temperature and either going up or down in temperature until the first signs of incompatibility were observed. Both upper and lower critical solution temperatures were taken as the first point when a haze was observed. Measurements were conducted in the temperature range of -50 to 70 °C.

2.2 Load Carrying Properties of the Lubricants

The ability of the lubricants to function under boundary lubrication conditions (i.e., metal-metal contact) was measured using the Falex Pin and Vee Block Instrument commercially available from Falex Corporation (Figure 1a). The instrument and test method are described in ASTM D 3233. For this publication, method A (continuous load) was used. In brief, a journal pin is mounted on a rotating chuck using a brass locking pin (Figure 1b). The vee blocks are inserted into holders located on a set of jaws which are then connected to a ratchet loading device. The pin and vee blocks are then submerged in 60 mL of test lubricant. The lubricant is heated to 60 °C and then the ratchet mechanism is engaged. The load on the four line contacts of the two vee blocks on the pin increases at a steady rate until the pin fails (snaps). The load at which the pin fails is taken as the load carrying capacity of the lubricant. All tests were conducted on the lubricant at atmospheric pressure in air.
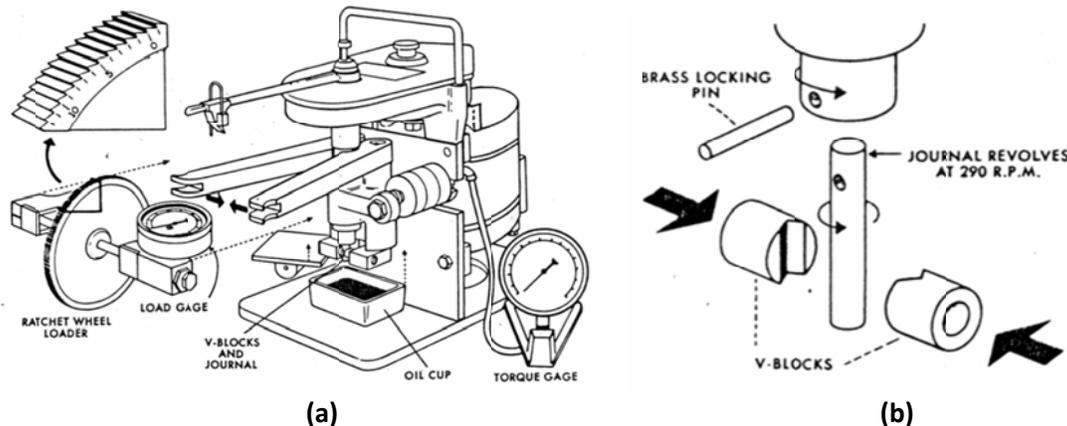

(a)   (b)

Figure 1: Diagram of (a) Falex Pin and Vee Block Test Instrument and (b) Close up of the Pin and Vee Block Contact Geometry

2.3 Lubricity Measurements

The fundamental lubricating properties of the lubricants were evaluated using the Mini Traction Machine (MTM) commercially available from PCS Instruments (Figure 2a). The MTM uses a rotating ball on rotating disk geometry (Figure 2b) to evaluate the lubricity properties of fluids under a variety of conditions. The velocity of the ball and disk can be independently controlled to model a number of different lubrication conditions. For the measurements reported in this paper, the coefficient of friction (CoF) was measured as the entrainment speed was continuously ramped from 0 to 2 meters/second at a fixed slide-roll-ratio (SRR) of 50%. The entrainment speed is defined as the mean speed of the ball and disk, (Vdisk + Vball)/2 where Vdisk is the velocity of the disk and Vball is the velocity of the ball in mm/s. The SRR is defined as [2(Vdisk-Vball)/(Vdisk+Vball)]*100 (LaFountain, et. al., 2001, Smeeth and Spikes, 1996). The load was set at 30 Newtons and tests were conducted at temperatures of 40, 80 and 120 °C.

3. RESULTS AND DISCUSSION

3.1 Polyol Ester Lubricants of the Study

A number of conventional and developmental polyol ester lubricants were included in the study. The physical properties of all POEs are reported in Table 1. The ISO viscosity grade of the lubricants varied from 32-80. The control lubricant for this study was a commercial ISO 32 POE (32 cSt POE 1) representative of premium high load
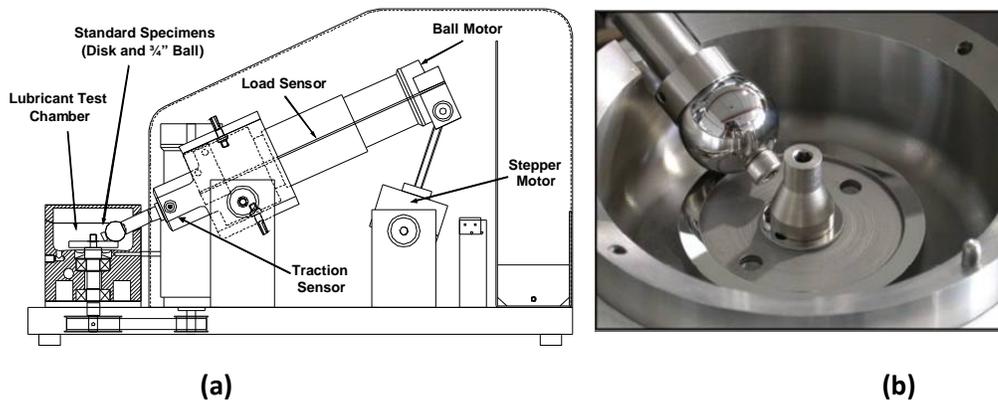
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(a)   **(b)**

Figure 2: Schematic of (a) the Mini Traction Machine and (b) the Ball-on-Disk Contact Geometry

carrying polyol esters used today with R-410A and other HFC refrigerants (the current state of technology). Traditional polyol esters used commercially today are typically of the general structures shown in Figure 3. They are prepared by the reaction of either pentaerythritol or dipentaerythritol with carboxylic acids to produce a thermally stable lubricant with good miscibility in HFC refrigerants. The exact chemical structure of the starting carboxylic acids can be selected to produce a lubricant with a wide variation in physical properties that includes viscosity and cohesive properties such as solubility with other substances. For refrigeration applications, the mixture of acids is selected that provides a lubricant with properties optimized to a particular refrigerant class or even a specific refrigerant. The advanced polyol esters (APOE) of the study are prepared by selective polymerization of traditional pentaerythritol esters. The technology has been used for many years to prepare high viscosity polyol esters for industrial lubrication but has only recently been refined to prepare HFC miscible refrigeration lubricants (Carr, *et al.*, 2014, Liebfried, 1972)

Table 1: Physical Properties of the POE Lubricants Included in the Study

Lubricant	32 cSt POE 1	32 cSt POE 2	68 cSt POE 1	68 cSt APOE	80 cSt APOE
KV @ 40 °C	31	31	72	64.1	80.3
KV @ 100 °C	5.8	5.6	9.8	9.4	10.1
Viscosity Index	129	120	120	126	107
Density (Kg/L)	0.998	0.996	0.987	1.036	0.999
Pour Point (°C)	-60	-54	-44	-45	-42
Flash Point (°C)	260	249	277	243	285
Critical Solution Temperature in R-32					
10 vol% Oil in Refrigerant	+2	-32	+10	-7	-18
30 vol% Oil in Refrigerant	Not Miscible	-20	Not Miscible	-23	-6

3.2 Miscibility of POE Lubricants with R-32 Refrigerant

Polyol ester lubricants were the oil of choice to replace mineral oils in stationary applications during the major conversion from CFCs and HCFCs to HFCs starting in the 1990s. Figure 4a shows the miscibility profile of 32 cSt POE 1 with R-410A refrigerant. The figure shows how the phase behavior of the refrigerant/lubricant mixture varies as a function of both the concentration of lubricant in refrigerant and temperature. HFC/POE mixtures typically have two distinct phase separation temperatures at any given concentration of lubricant between -60 and +70 °C. But an important trait of any good refrigerant lubricant is that a single phase exists over the entire range of relative concentrations between -20 to 60 °C. Such phase behavior provides confidence that the R-410A/ISO 32 POE 1 mixture will remain as a single phase over the entire temperature operating range of the refrigeration system. In contrast, the miscibility profile of the same 32 cSt POE 1 with R-32 is shown in Figure 4b. The profile contains
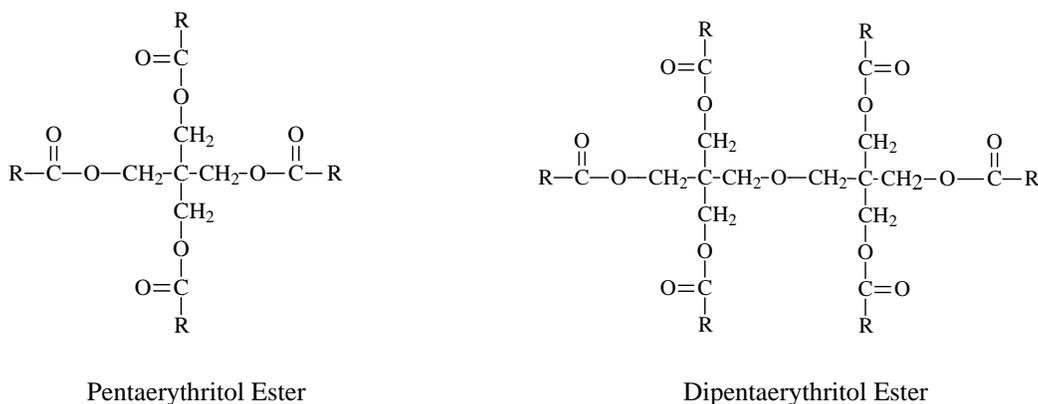
R
|
O=C
|
O
| R   R
O   CH₂   O | |
‖ | ‖   O=C   C=O
R—C—O—CH₂-C-CH₂-O—C—R | |
| O   O
CH₂   O   CH₂   CH₂   O
| ‖ | | ‖
O   R—C—O—CH₂-C-CH₂-O—CH₂-C-CH₂-O—C—R
| | |
O=C   CH₂   CH₂
| | |
R   O   O
| |
O=C   C=O
| |
R   R

Pentaerythritol Ester   Dipentaerythritol Ester

Figure 3: Some Chemical Structures of Conventional POEs Used as Refrigeration Lubricants

a two phase region between the concentration range of 20-35 vol% lubricant. Such phase behavior for this refrigerant/lubricant mixture is cause for concern since it is possible that a separate lubricant rich phase can form in select areas of the refrigeration system; resulting in poor oil return to the compressor as well as unacceptable system pressure drops. In addition it is possible that lubricant hold up in select locations in the system can result in less than optimum heat exchanger efficiency.
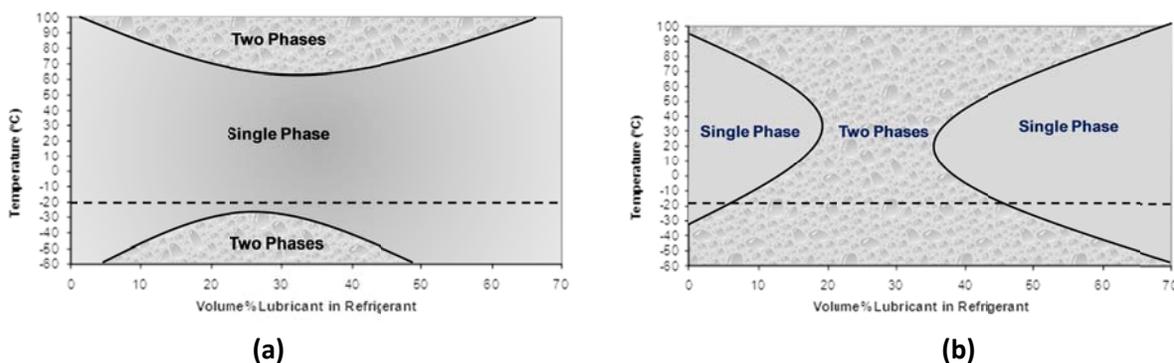

Figure 4: Miscibility Profile of (a) 32 cSt POE 1 with R-410A (control) and (b) 32 cSt POE 1 with R-32

However, Figure 5a shows the miscibility profile for 32 cSt APOE with R-32; demonstrating that it is possible to synthesize POE lubricants with the preferred phase behavior with R-32 through selective modification of the POE chemical structure. But as will be discussed in other papers in this series, other factors suggest that higher viscosity lubricants are recommended for compressors using R-32 refrigerant (Urrego, *et al.*, 2014).

As the viscosity of the polyol ester is increased, it becomes increasingly difficult to maintain good miscibility in HFC refrigerants as well as retain suitable lubricating properties. Changes made to chemical structure of the POE to maintain miscibility with the refrigerant for higher viscosity lubricants is often balanced by a loss of lubricant lubricity and load carrying properties. But it is possible to use advanced synthesis techniques to generate unique ester structures that have both excellent miscibility with R-32 while still maintaining good lubricity and load carrying performance. The miscibility profile for an 80 cSt APOE lubricant is shown in Figure 5b. Although the critical solution temperature for the 80 cSt APOE goes above the optimum of -20 °C, the majority of the low temperature two phase region remains below -20 °C, and there is still a continuum of a single phase region across the entire range of refrigerant/lubricant concentrations above 0 °C. The significance of being able to prepare higher
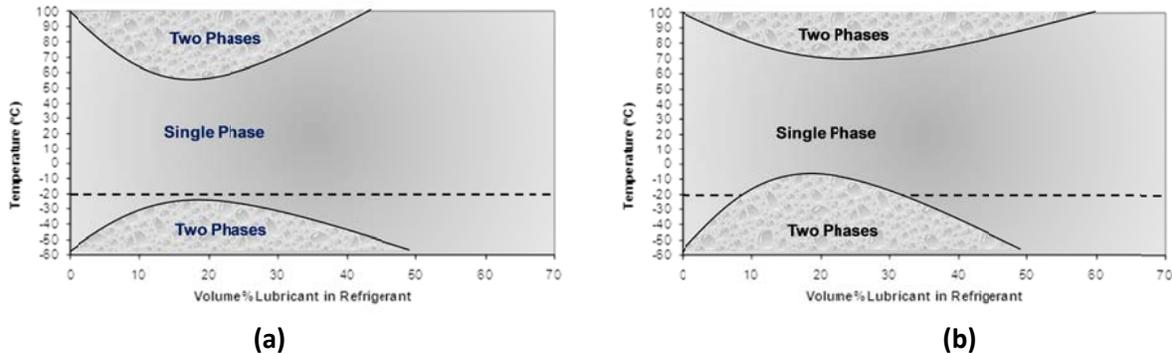
Figure 5: Miscibility Profile of (a) 32 cSt APOE with R-32 and (b) 80 cSt APOE with R-32

viscosity lubricants with good miscibility in R-32 will be explained in subsequent papers/presentations in this series (Urrego *et al.,* 2014).

3.3 Load Carrying Performance and Lubricity of the POE Lubricants
Compressors are designed to operate under steady state conditions of fluid film lubrication. In such a condition, the moving parts are completely separated by a protective hydraulically generated barrier of lubricant. The thickness of this film is a function of lubricant viscosity, the relative speed between the moving parts, surface roughness and the contact geometry of the parts. However, even the best compressor designs spend a small portion of their operating time under harsh boundary lubrication conditions (i.e., in a state where the load is sufficient to result in metal-metal contact of frictional surfaces). Boundary lubrication conditions are most often observed during start up/shut down, as well as small periods of time when the compressor operates at the fringe or outside the prescribed operating window. Without proper boundary lubrication, compressors can undergo catastrophic failure even after just a few seconds under such conditions.

A significant challenge in developing lubricants for R-32 refrigerant is to identify polyol ester structures that have the required ISO viscosity grade, are miscible with R-32 and also have the load carrying performance required to ensure long service life of the compressor. In general, the types of chemical structures that increase viscosity and provide adequate miscibility are contradictory to those structures that give good load carrying.

The ability of a lubricant to reduce friction and prevent wear under conditions of boundary lubrication can be estimated using the Falex Pin and Vee Block test. The higher the reported failure load, the better the lubricant is predicted to prevent wear; even when all fluid film lubrication has ceased. Table 6 shows the failure load for a number of POE lubricants evaluated in this study. It should be noted that none of the POE lubricants tested contained any additives. The data demonstrates that it is possible to synthesize advanced polyol esters (APOEs) that are miscible with R-32 refrigerant and have load carrying performance equivalent to, or better than, the corresponding high lubricity POEs used today with R-410A.

3.4 Lubricity Performance of the Polyol Esters
The lubricity of a lubricant can be considered as a separate property apart from load carrying performance. It is a property more related to the amount of frictional energy loss due to lubrication of parts under normal operation in either mixed film lubrication (where only the asperities on the surface of the metals are in partial contact) as well as the energy required to physically move the lubricant past itself (termed viscous drag) under fluid film lubrication. The property is more related to frictional energy losses rather than the potential wear resulting from high load (as described above)(Bovington, 1999).

The lubricating properties of the POEs in the absence of refrigerant were evaluated using the Mini Traction Machine. A plot of the coefficient of friction (CoF) as a function of entrainment speed at 40 °C (Figure 6) shows how friction varies as the rate of oil entering the contact region increases. The shape of the curves can be related to the classic

Table 2: ASTM D 3233 Load at Failure for Select POE Lubricants

POE Lubricant ID	ISO Viscosity Grade and Description	ASTM D 3233 Failure Load (Method A), (lbs. force at pin failure)
POEs Designed for R-410A		
32 cSt POE 1	ISO 32 POE designed for R-410A	950
68 cSt POE 1	ISO 68 POE designed for R-410A	875
POEs Designed for R-32		
32 cSt POE 2	ISO 32 Pentaerythritol Ester	750
68 cSt POE 2	ISO 68 Pentaerythritol Ester	700
32 cSt APOE	ISO 32 Advanced POE	>1000
46 cSt APOE	ISO 46 Advanced POE	>1000
68 cSt APOE	ISO 68 Advanced POE	>1000
80 cSt APOE	ISO 80 Advanced POE	875

Stribeck curve (LaFountain *et al.*, 2001) and provides important information on the frictional properties of the lubricants under conditions of mixed film and fluid film (hydrodynamic) lubrication. At very low entrainmentspeeds there is some direct metal-to-metal asperity contact (near boundary lubrication conditions), but as the entrainment speed increases there is a pressure buildup between the contacting surfaces due to a hydraulic effect of increasing oil suction into the contact inlet. The increasing pressure in the contact inlet results in a progression from near boundary, to mixed film, to complete fluid film (hydrodynamic) lubrication. Under conditions of near boundary and mixed film lubrication, also termed the elastohydrodynamic lubrication (EHL) regime, the high pressure in the contact produces local elastic flattening of the surfaces and increases the viscosity of the lubricant. In such contacts, the CoF is determined by the molecular structure of the lubricant and contact temperature (Gunsel *et al.*, 1999)(Smeeth and Spikes, 1996).

The 32 cSt POE 1 (designed for HFC refrigerants in 1998 to 2000) is an example of a perfectly optimized lubricant in terms of miscibility, load carrying and lubricity performance. It has the lowest CoF observed of any of the lubricants. The R-32 miscible lubricants fall into two general classes; traditional POEs and advanced POEs (APOE). The CoF traces as a function of entrainment speed illustrate two major points. First, the frictional properties of the traditional POEs deteriorate as the ISO viscosity grade is increased and changes to structure are made to improve miscibility with R-32. Second, the R-32 miscible APOE lubricants can be designed to provide nearly identical frictional properties to a premium HFC miscible ISO 32 POE while still maintaining good miscibility with R-32. However, even this class of lubricants has limits since the ISO 80 APOE sacrifices lubricity performance in order to maintain miscibility with R-32. Tests conducted at 80 °C and 120 °C (not shown) displayed a similar trend.

4. CONCLUSIONS

Commercial synthetic lubricants used today with R-410A have significantly different compatibility with many of the alternative refrigerants being considered as low GWP replacements. R-32 and related blends provide a significant lubrication challenge. It may be necessary to use higher viscosity grade lubricants which are miscible with R-32 to provide equivalent performance and system reliability. The physical properties, miscibility, load carrying properties of several types of candidate POE lubricants for use with R-32 were compared in bench tests. The results suggest that one developmental class of unique advanced POEs (APOEs) can be prepared that have suitable miscibility in R-32 while still maintaining the high load carrying and lubricity of premium POEs used today with R-410A. Subsequent papers and presentations will describe the solution properties of the APOE/R-32 working fluids (Urrego *et. al.*, 2014), energy efficiency tests in full systems (Benanti *et al.*, 2014) and lubricant mass distribution in a convertible split system residential air-conditioner (Wujek *et. al*, 2014).
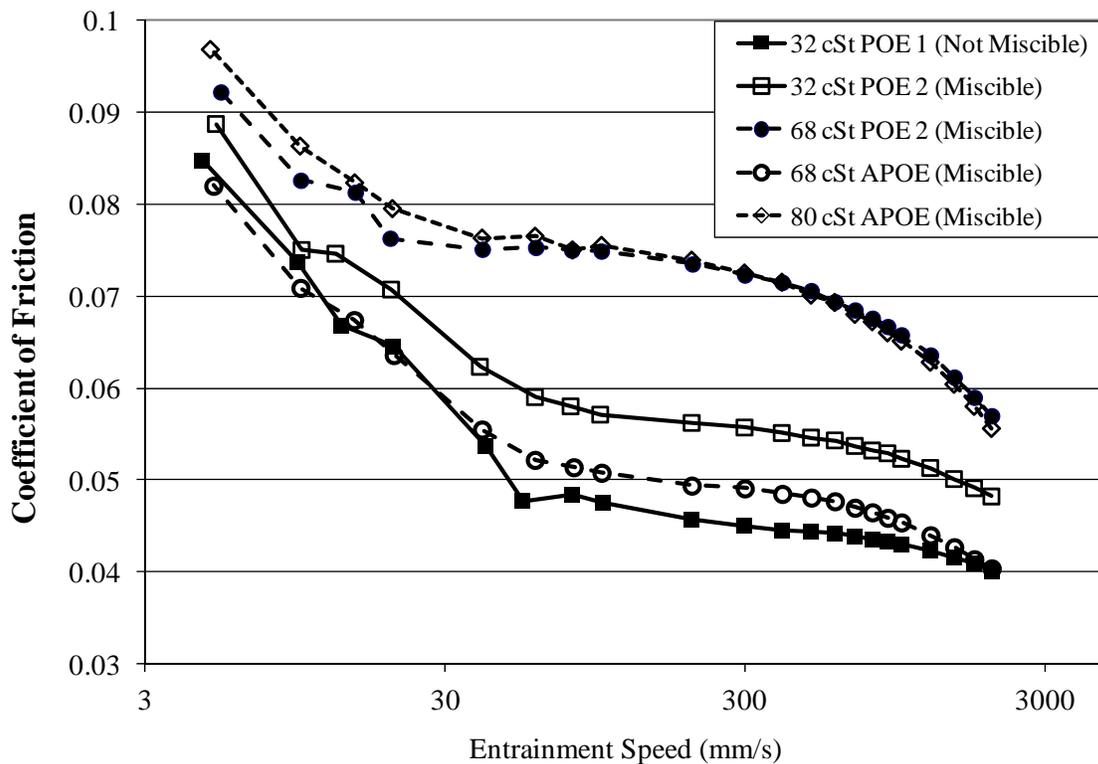
Figure 6: Coefficient of Friction as a Function of Entrainment Speed at 40 °C

NOMENCLATURE

APOE	Advance POE	(–)
AHRI	Air-Conditioner Heating and Refrigeration Institute	(–)
AREP	Alternate Refrigerant Evaluation Program	(–)
ASHRAE	American Society of Heating, Refrigerating and Air-Conditioning Engineers	(–)
ASTM	American Society for Testing and Materials	(–)
°C	Degrees Celsius	(–)
CFC	Chlorofluorocarbon	(–)
COP	Coefficient of Performance	(–)
COF	Coefficient of Friction	(–)
cSt	Centistokes (viscosity)	(millimeter/second^2)
GWP	Global Warming Potential	(–)
HCFC	Hydrochlorofluorocarbon	(–)
HFC	Hydrfluorocarbon	(–)
HFO	Hydrofluoro-olefin	(–)
KV	Kinematic Viscosity, Centistokes	(millimeter/second^2)
MTM	Mini Traction	(–)
N	Newton	(kilogram meter/second^2)
POE	Polyol Ester	(–)
ppm	parts per million	(milligrams/liter)
Pa	Pascals	(units?)
PVT	Pressure-Viscosity-Temperature	(Bar-cSt-°Centigrade)

SRR	Slide-Role-Ratio	(–)
Vdisk	Velocity of the MTM disk	(millimeter/second)
Vball	Velocity of the MTM ball	(millimeter/second)

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