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H. M. L. Kang
Iowa State University

S. C. Zoz
Iowa State University

M. B. Pate
Iowa State University

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SOLUBILITY OF HFC-32, HFC-125, AND HFC-134A WITH THREE POTENTIAL LUBRICANTS

H.M. Lee Kang, S.C. Zoz, and M.B. Pate
Iowa State University
Department of Mechanical Engineering
Ames, Iowa 50011

ABSTRACT

This paper presents solubility data for three different HFC refrigerants, HFC-32, HFC-125, and HFC-134a mixed with three different lubricants, namely polypropylene glycol diol, pentaerythritol ester mixed acid, and pentaerythritol ester branched acid. These three refrigerants are important because when combined, either in groups of two or three, they form refrigerant mixtures which have been identified as potential replacement fluids for R-22. The solubility tests were performed in a test facility consisting of a series of miniature test cells submerged in a constant temperature bath. The bath temperature was precisely controlled over a temperature range of -30 C to 60 C (-22 F to 140 F). The contents of each cell were monitored by pressure and temperature sensors. In addition, each cell was charged with a known refrigerant/lubricant concentration, so that, along with temperature and pressure data, the solubility (P, T, C) could be determined. The test cells were constructed to allow for complete visibility of refrigerant/lubricant mixtures under all test conditions.

INTRODUCTION

The solubility data obtained in this study were for three different pure refrigerants, HFC-32, HFC-125, and HFC-134a with three different lubricants. These refrigerants are hereafter designated as R-32, R-125, and R-134a, respectively. Each of the three HFCs was tested for solubility (namely, pressure, temperature, and concentration), when mixed with three different lubricants. which were polypropylene glycol diol (hereafter called polypropylene glycol), pentaerythritol ester mixed acid (hereafter called mixed acid ester), and pentaerythritol ester branched acid (hereafter called branched acid ester). The viscosity for these three lubricants was ISO 32.

The solubility data was obtained for refrigerant/lubricant mixtures subjected to the following conditions:

1. Composition: 0 to 100 weight percent refrigerant
2. Temperature: -30°C to 60°C (-22°F to 140°F)
3. Pressure: 0 to 3.5 MPa (0 to 500 Psia)

The following sections describe the methodology for a new approach to measuring the solubility of refrigerant/lubricant mixtures. This new approach was developed to allow for the faster measurement of solubility, which is important considering the urgency of developing alternative refrigerant systems to replace existing CFC and HCFC systems. The solubility results for the refrigerant/lubricant pairs studied are presented in the form of graphs and equations. During the solubility tests. the contents of each cell were observed for miscibility.

Solubility data for other refrigerants and lubricants have been collected by Glova (1984), Thomas and Pham (1992), and Van Gaalen et al (1990) by using testing methods different than that used in this study. However, there are no reports in the open literature of solubility data for the refrigerant/lubricant pairs reported herein.

EXPERIMENTAL METHODS AND TEST FACILITY DESCRIPTION

Each test cell consists of a double-port, seal-cap type liquid indicator, which is essentially a 31.75 mm (1.25 inch) pipe cross with sight windows screwed into opposing ports. A valve for charging the refrigerant into the cell was screwed into one of the two remaining ports. An 1/8 inch by 8.89 mm (3 1/2 inch) length copper tube was attached into the other port, and then this tube was attached to a pressure transducer for the purpose of measuring pressure inside of the cell during the test. The use of a copper tube was to avoid contact between the pressure transducer and fluids when the cells are submersed in the bath, while simultaneously preventing condensation during the heating operation and

minimizing overall volume of the each cell. The pressure transducers were calibrated with the use of a dead weight pressure tester, and the pressure data uncertainty is ±2.97 kPa (0.43 psia).

The temperatures of the cells were controlled by placing them in one of two constant temperature baths. A hot bath was used to maintain temperatures from 10°C (50°F) to 60°C (140°F), while a cold bath was used to maintain temperatures in the range of 10°C (50°F) to -30°C (-22°F). The precise temperatures of the baths were measured by two internal resistance temperature detectors (RTD). These RTDs were calibrated, and the temperature measurements had an uncertainty of ±0.1°C (0.2°F). Thermal equilibrium conditions were usually obtained about thirty minutes after a temperature change.

Computerized data acquisition methods were used to obtain the temperature and pressure data. A microcomputer, along with data acquisition hardware and software, monitored and recorded all signals generated by the installed sensors

Experimental Procedure
The charging of lubricant into each test cell was done with the use of syringe through the front window space. Then, the window was replaced and tightened. A vacuum pump was hooked up to the valve, and a vacuum was pulled to remove any dissolved moisture or air from the lubricant inside the cell. The vacuum process took approximately 2 to 3 hours to be completed.

A refrigerant was then injected into the cells from a refrigerant canister with the use of a manifold that allowed for the evacuation of the connecting lines. The cells were weighed on a scale, which has an uncertainty of ±0.01 gram, before and after the injection of the lubricant and refrigerant. During cell charging, each cell was filled with the mixture of refrigerant/lubricant so that the vapor space was less than 15% of the total volume. In addition, since temperature and pressure data are available, changes in the liquid concentration due to the refrigerant present in the vapor space could be calculated.

The pressure and temperature were measured for each test point. These data allowed for the calculation of the refrigerant concentration at each test condition to be calculated. In addition to calculations of the actual liquid concentration, correlating equations that fit the solubility data, including pressure, temperature, and concentration, were derived.

Six test cells were placed in the frame assembly, and then they were submersed, excluding the top portion of the cells where the pressure transducers are attached, in one of the two 20 x 12 x 12 inch glass baths. The glass allowed for visibility of the test cells so that one could observe various phenomena inside of the cell, such as miscibility due to temperature changes occurring throughout the tests.

Data Reduction
After the data had been taken and reduced for each refrigerant/lubricant combination, a multi-linear regression analysis was performed. Thus, an equation for pressure as function of temperature and concentration was obtained. This equation was used to graphically plot results, and interpolate results at intermediate states for which the data were not directly obtained. The linear regression was performed using SAS (Statistical Analysis and System, 1993), which allows for the determination of the set of coefficients for the following empirical equation.

$$P = P_{sat}(A_0 + A_1C + A_2T + A_3CT + A_4C^2 + A_5C^2T + A_6CT^2 + A_7T^2 + A_8C^2T^2 + A_9C^3)$$

where   P = the absolute pressure, MPa
        C = the mass fraction of refrigerant in the liquid
        T = the temperature in °K divided by a reference temperature of 293°K
        P_{sat} = reference saturation pressure at temperature T
Pure refrigerant properties were obtained with use of REFPROP (NIST, 1993)

The above equation is non-linear, but it is linearized by using the following variable substitutions:

$$X_1 = C; \quad X_2 = T; \quad X_3 = CT; \quad X_4 = C^2; \quad X_5 = C^2T; \quad X_6 = CT^2; \quad X_7 = T^2; \quad X_8 = C^2T^2; \quad X_9 = C^3$$

After these substitutions the equation can be linearized in the nine variables, X_1 through X_9. Table 1 lists the coefficients for the empirical correlations of solubility for refrigerant/lubricant mixtures. The resulting equations are empirical fits of the data, and thus not based on any theoretical consideration. Also, some of the coefficients do not significantly contribute to the correlation. The correlations for the pressure of refrigerants/lubricant mixtures are well fit to the test data, being within ±5%.

Table 1. Coefficients for Empirical Correlation of Solubility Data for Refrigerant/Lubricant Mixtures

Term	R-32			R-125			R-134a		
	propylene glycol	mixed acid ester	branched acid ester	propylene glycol	mixed acid ester	branched acid ester	propylene glycol	mixed acid ester	branched acid ester
A_0	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
C	4.3604	4.3440	4.6133	0.0000	1.7585	2.8598	1.9304	1.0157	0.0000
T	0.1542	0.2567	0.1197	0.0000	0.0000	0.0000	0.1123	0.0000	0.0000
CT	0.0000	0.2671	0.0000	2.5158	0.0000	0.0000	10.563	9.3640	7.7127
C^2	6.4446	7.0375	6.9716	0.5355	0.5883	2.9163	0.0000	0.0000	1.4575
C^2T	0.1440	0.0000	0.0000	2.0182	1.5540	0.0000	9.2971	9.3226	6.9599
CT^2	0.0000	0.0000	0.0000	0.2942	0.8116	0.0000	4.8830	4.7213	4.0372
T^2	0.1466	0.2391	0.1077	0.0000	0.0000	0.0045	0.1144	0.0000	0.0000
C^2T^2	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	4.3102	4.7176	3.6877
C^3	2.9460	3.4292	3.3584	0.2581	0.5600	1.0554	2.2542	1.9804	2.0625

RESULTS AND DISCUSSION

The solubility data for three different pure refrigerants, namely, R-32, R-125, and R-134a with three different lubricants, referred to as a polypropylene glycol, mixed acid ester, and branched acid ester are shown in Figures 1 through 9. Shown in each figure are ten isotherms which were produced by a partial third-order empirical multi-regression curve fit over the data for nine compositions.

These plots show that for a given nominal concentration the vapor pressure increases with increasing temperature and increasing refrigerant concentration. As a rule, lubricants which have a higher solubility for refrigerant will produce lower values of pressure over the refrigerant/lubricant mixture. Observation of Figures 1 through 9 reveal that the polypropylene glycol diol has a somewhat higher solubility than the two esters.

R-32

The solubility of R-32 in the polypropylene glycol, mixed acid ester, and branched acid ester is shown in Figures 1, 2, and 3, respectively. For all three lubricants, it can be seen that the vapor pressure of the solution increases gradually over 40 percent refrigerant. It should be mentioned that the pressure falls off rapidly when the refrigerant concentration is below 40 percent. This fall in pressure is greater at higher refrigerant concentrations and temperatures while the fall in pressure is gentler for the more soluble lubricants (e.g., polypropylene glycol).

The polypropylene glycol diol has a slightly higher solubility than the two esters based on comparing Figures 1 through 3. The order of increasing solubility of R-32 with these three lubricant mixtures is pentaerythritol ester branched acid, pentaerythritol ester mixed acid, polypropylene glycol diol

R-125

The solubility of R-125 in the polypropylene glycol, mixed acid ester, and branched acid ester is shown in Figures 4, 5, and 6, respectively. For all three lubricants, it can be seen that the solubility pressure is fairly constant at concentrations over 80 percent refrigerant. The vapor pressure then falls off rapidly when the refrigerant concentration is below 80 percent. As mentioned earlier, this fall in pressure is greater at higher refrigerant concentrations and temperatures while the fall in pressure is gentler for more soluble lubricants.

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Based on comparing Figures 4 through 6 the polypropylene glycol diol has a somewhat higher solubility than the two esters, while the pentaerythritol ester branched acid has a somewhat higher solubility than the pentaerythritol ester mixed acid. The order of increasing solubility of R-125 with these three lubricant mixtures is pentaerythritol ester mixed acid, pentaerythritol ester branched acid, and polypropylene glycol diol, which is the same order of solubility found for the R-32.

R-134a

The solubility of R-134a in the polypropylene glycol, mixed acid ester, and branched acid ester is shown in Figures 4, 5, and 6, respectively. For all three lubricants, it can be observed that the solubility pressure is fairly constant between 50 and 80 percent refrigerant, and then the pressure increases again at concentrations over 80 percent refrigerant. The pressure falls off rapidly when the refrigerant concentration is below 50 percent refrigerant. As with the other two refrigerants, this fall in pressure is greater at higher refrigerant concentrations and temperatures while the fall in pressure is gentler for more soluble lubricants

The esters have a somewhat higher solubility than the polypropylene glycol diol while the pentaerythritol ester branched acid has a somewhat higher solubility than the pentaerythritol ester mixed acid at concentrations over 40 percent refrigerant, based on comparing Figures 7 through 9. The order of increasing solubility of R-134a with these three lubricant mixtures is polypropylene glycol diol, pentaerythritol ester mixed acid, pentaerythritol ester branched acid.

CONCLUSIONS

A new method was developed for determining the solubility (pressure, temperature, and concentration) of refrigerant/lubricant mixtures. Data have been collected for mixtures of three pure HFC refrigerants, namely, R-32, R-125, and R-134a with three different lubricants, which were polypropylene glycol diol, pentaerythritol ester mixed acid, and pentaerythritol ester branched acid. These solubility data are for temperatures from -30°C (-24°F) to 60°C (140°F) and for pressures up to 3.5 MPa (500 psia). The results are presented as solubility plots showing pressure as a function of temperature and refrigerant concentration. The solubility data have been analyzed using a empirical multi-linear regression analysis and the result of empirical correlating equation developed from this data allows convenient interpolation of the data at specific property conditions. The solubility plots show that for a given nominal concentration, the pressure of the mixture increases with increasing temperature and increasing refrigerant concentration.

The order of increasing solubility of R-32 with these three lubricant mixtures is pentaerythritol ester branched acid, pentaerythritol ester mixed acid, and polypropylene glycol diol. The order of increasing solubility of R-125 with these three lubricant mixtures is pentaerythritol ester mixed acid, pentaerythritol ester branched acid, and polypropylene glycol diol. The order of increasing solubility of R-134a with these three lubricant mixtures is polypropylene glycol diol, pentaerythritol ester mixed acid, and pentaerythritol ester branched acid.

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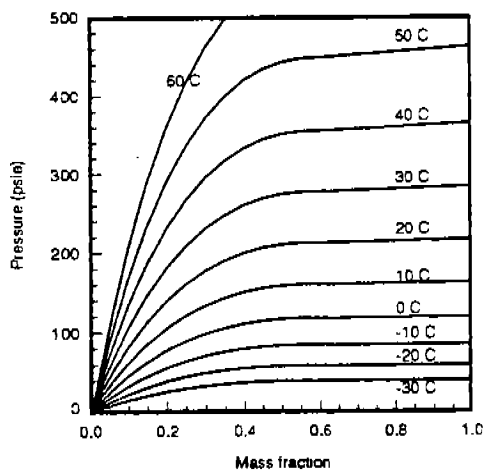
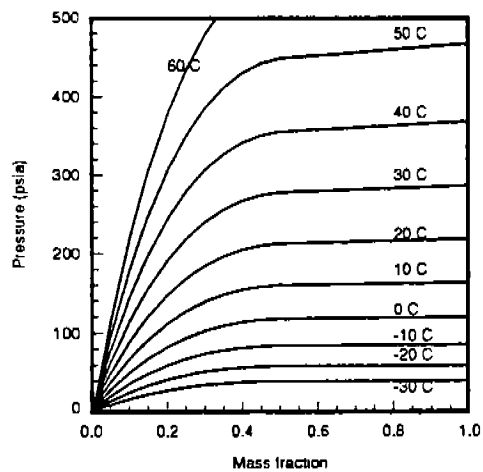**Figure 1** Solubility of R-32 in polypropylene glycol diol

Figure 2 Solubility of R-32 in pentaerythritol ester mixed acid
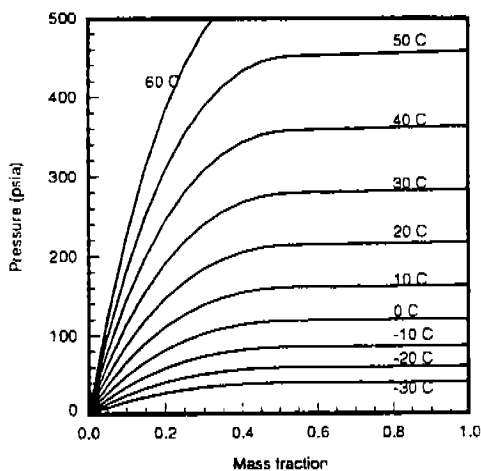

Figure 3 Solubility of R-32 in pentaerythritol ester branched acid
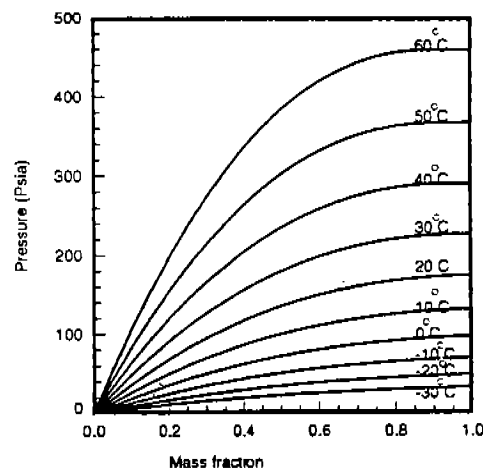

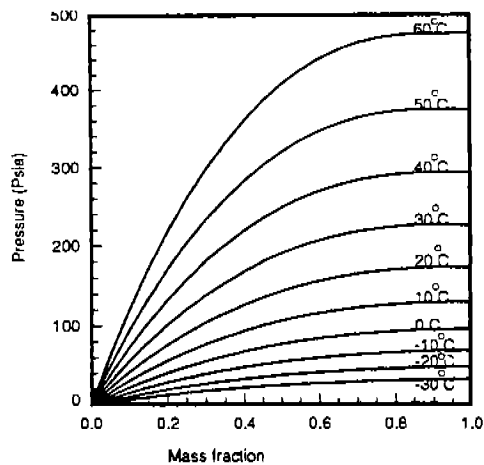**Figure 4** Solubility of R-125 in polypropylene glycol diol

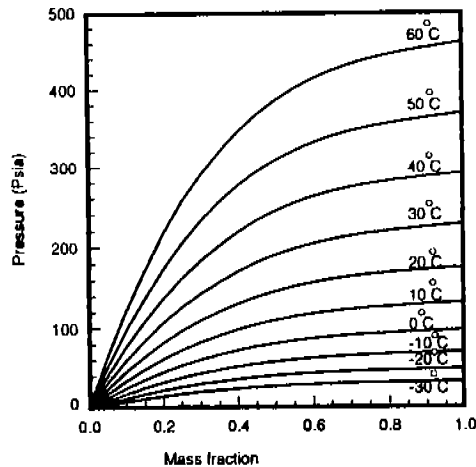**Figure 5** Solubility of R-125 in pentaerythritol ester mixed acid

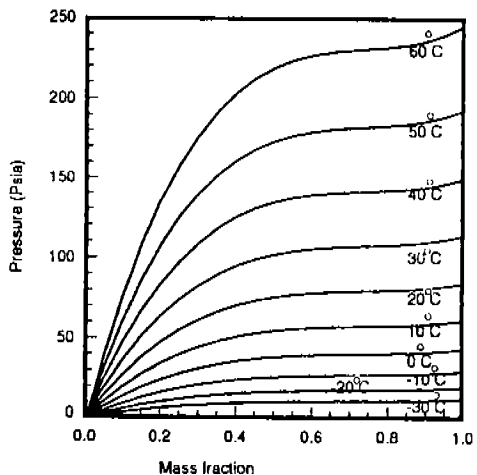**Figure 6** Solubility of R-125 in pentaerythritol ester branched acid

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Figure 7 Solubility of R-134a in polypropylene glycol diol

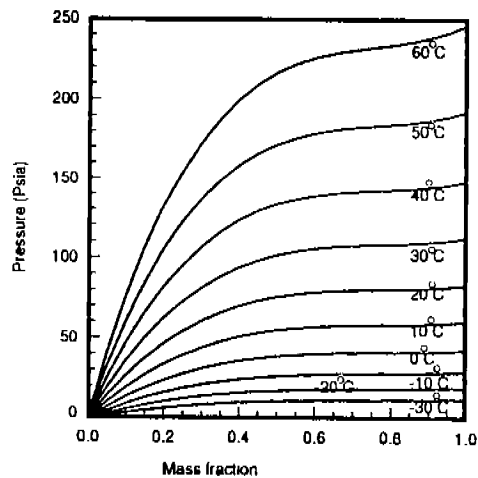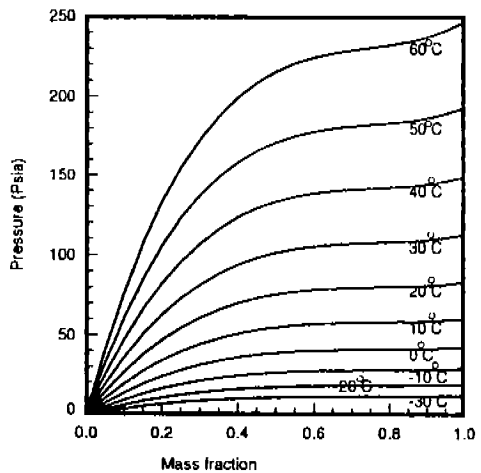**Figure 8** Solubility of R-134a in pentaerythritol ester mixed acid

Figure 9 Solubility of R-134a in pentaerythritol ester branched acid