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INTERCATIONS OF HYDROFLUOROCARBONS AND POYOLESTER LUBRICANTS

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ABSTRACT

A variety of hydrofluorocarbon (HFC) compounds, both as pure substances and mixtures, are being developed as alternative refrigerants to replace the existing chlorofluorocarbons and hydrofluorocarbons which have been linked to stratospheric ozone depletion.

The use of HFC's in refrigeration systems will require new lubricants, and polyolesters are being widely promoted as the lubricant of choice for HFC refrigerants. Understanding the chemical and physical properties of mixtures of the new lubricants and proposed HFCs is of utmost importance for applying the alternatives to existing or new equipment.

Recently, we have developed a new theoretical model for oil/refrigerant interactions (solubility and viscosity). In the present report, experimental data are compared with the model. In addition, a new method to determine the miscibility gap of refrigerant/oil mixtures has been developed and tested.

INTRODUCTION

Various physical and chemical properties of HFC-lubricant mixtures are needed to develop useful products as alternative refrigerants for new and existing equipment. The chemical stability of HFC's in the presence of oil is one concern, as are the thermodynamic/thermophysical properties such as mutual solubility (miscibility and immiscibility) and viscosity of mixtures. Since HFCs are soluble (or at least partially miscible) with polyolester oils, the oil will act as another component of the refrigerant. This means the refrigerant (pure or mixture) contains an additional compound, and all thermodynamic properties such as vapor pressure, compositions of vapor/liquid phases, etc. will be affected due to the extra component.

In this report, we are particularly interested in the thermodynamic aspects of HFC/polyolester oil mixtures. A recent development of our theoretical modeling on the oil/refrigerant interactions⁽¹⁾ will be further examined. The model is constructed using the vapor-liquid equilibrium (VLE) data of binary systems (oil/refrigerant). Since it is based on thermodynamic theory, it should be able to predict all thermodynamic properties, including the vapor-liquid-liquid equilibrium (VLLE) of mixtures. The VLLE prediction is known to be a severe test for the validity of such a model, while the experimental method used commonly to obtain such data is tedious and often contains large uncertainties. Therefore, we have developed a new experimental method to obtain such data to test the model prediction. Another test for the validity of the model is to compare predicted vapor compositions of oil/refrigerant mixtures with data obtained from Gas Chromatography (GC) experiments.

EXPERIMENTS

1) VLLE measurments

When two partially miscible fluids are mixed and allowed to reach equilibrium, one can visually observe the formation of two separate liquid phases. In the case where the oil density is heavier than that of the refrigerant at the experimental temperature (T), an oil-rich layer forms on the bottom and a refrigerant-rich layer on the top. Traditional

methods require the preparation and visual observation of miscibility or non-miscibility for numerous compositions of components over a wide range of closely controlled T in order to establish a VLE or miscibility diagram such as shown in Fig.1. Often, the vapor phase weight was ignored, although it could contribute significant errors in estimating the miscibility gap in Fig. 1. The inaccuracy in the T control and no corrections for the vapor phase are often major sources of uncertainty in miscibility data.

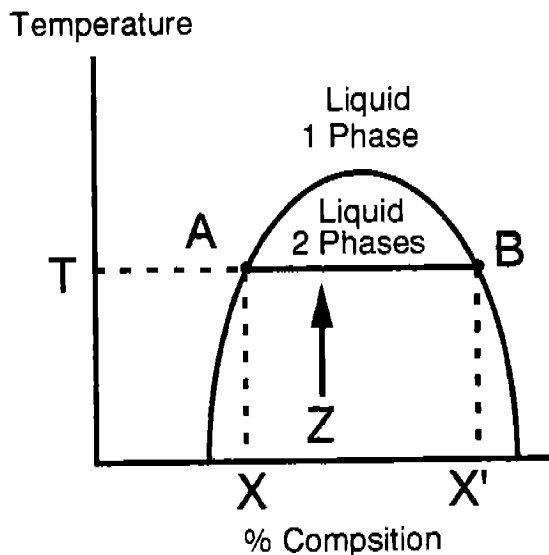


Fig. 1 Miscibility diagram

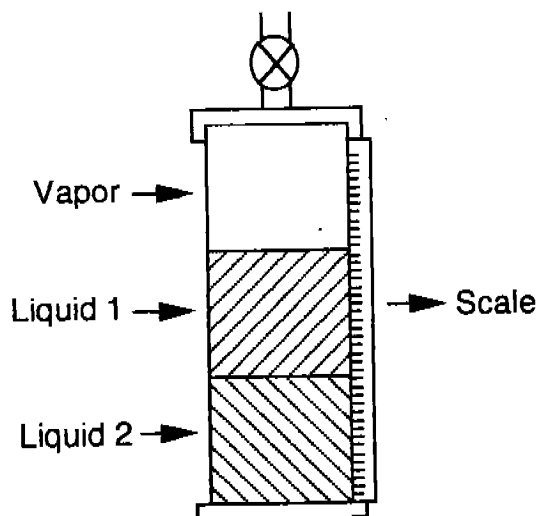


Fig. 2 Experimental Apparatus

A novel/simple method has been developed to obtain miscibility data for oil/refrigerant mixtures based on the thermodynamic principle of Gibbs phase rule⁽²⁾. When a binary oil/refrigerant mixture forms three phases (two liquids and vapor), the thermodynamic freedom is one. At a given T, the intensive variables such as pressure, compositions, and densities of the system are fixed, and only the extensive variables like total weight and volume can be changed. To illustrate, suppose that a sample is prepared with a total charge of Z in Fig.1 in a sealed container and that at a given T it forms vapor space and two liquids (A and B) with compositions of X and X'. Then, if we change the total weight by leaking vapor, the compositions of X, X', and the vapor phase, as well as their densities, will remain the same at the given T, and only the volume of each phase will vary. These constant properties (densities and compositions) can be determined from simple volumetric measurements.

Let Wt be the initial total charge of refrigerant and oil (weight: Wo) in a sealed container (volume: Vt). Then, assume it forms three phases: one liquid phase (density: D; volume: V; oil weight fraction: Xo; refrigerant weight fraction: Xr), another liquid phase (D', V', Xo' and Xr') and vapor phase (D''). From the material balance, the following equations hold:

$$W_t = DV + D'V' + D''(V_t - V - V') \quad (1)$$

$$W_o = DVX_o + D'V'X_o' \quad (2)$$

$$X_r = 1 - X_o, \quad X_r' = 1 - X_o' \quad (3)$$

In Eq.(2), the concentration of oil in the vapor phase is assumed to be zero. Here, the constant properties to be determined at a given T are D, D', D'', Xo, Xr, Xo', and Xr', while Wt, Wo, Vt, V, and V' are obtained by weight/volume measurements. After Wt is varied by leaking the vapor, only V and V' in Eq.(1) will change. Two sets of vapor leak experiments provide three sets of Eq.(1) with the three unknowns (D, D' and D''), which will be determined by solving the linear simultaneous equations. Using the determined D and D' with Eq.(2), Xo and Xo' will be similarly determined with the data from the same vapor leaks. Then, Eq.(3) simply gives Xr and Xr'.

Based on the above model, a simple apparatus was built, as shown in Fig.2 schematically. The container is made of Teflon[®] PFA tubing (3/8" OD and 1/16" thick), and the meniscus of phase boundaries can be viewed from the outside. It is strong enough to hold pressures up to 395 psia without significant deformations. This has been tested using R-11 (15 psia) and R-143a (183 psia) at room temperature. The total volume (10.70 cc) and cylinder cross-section (0.3354 cm²) were calibrated by using these compounds and water, as well as a small dead volume correction for the bottom of the container. The volumes of the liquid layers (V and V') were determined simply by measuring the height of the individual layer and multiplying by the cylinder cross-section. The experimental procedure is to prepare the container at an initial composition and measure the total weight (typically several grams) and the liquid volumes (heights) after equilibration at a fixed T. A small amount of vapor (refrigerant only) is then allowed to leak off the top of the container. After equilibration at the same T, new weight and volume measurements are made. This process can be repeated as many times as desired. For safety reasons, temperatures higher than room temperature were not studied in this apparatus.

2) Vapor Compositions of HFC-Lubricant Mixtures

As mixtures of HFC's are being considered as replacement refrigerants, concern has been expressed over the potential to separate or fractionate during various use, handling and service scenarios. The introduction of polyolester lubricants into a refrigeration system using a blend of HFC's further complicates the issue by adding an extra variable which may cause shifts in vapor phase compositions in addition to those of the refrigerant-only cases. There is variation among the individual HFC compounds with respect to their solubility in a common ester oil. In addition, their solubility in different oils can be quite different. To illustrate this point, vapor compositions for an oil-HFC mixture (R125/R143a at 50/50% mixture in oil) was calculated as a function of percentage oil for several different commercial polyolester oils, and two cases are shown in Fig. 3. It should be noted that this mixture, which is known as a near-azeotropic blend, does change the vapor compositions significantly as the percentage of oil increases, and also the magnitude of the change strongly depends on the kinds of oils.

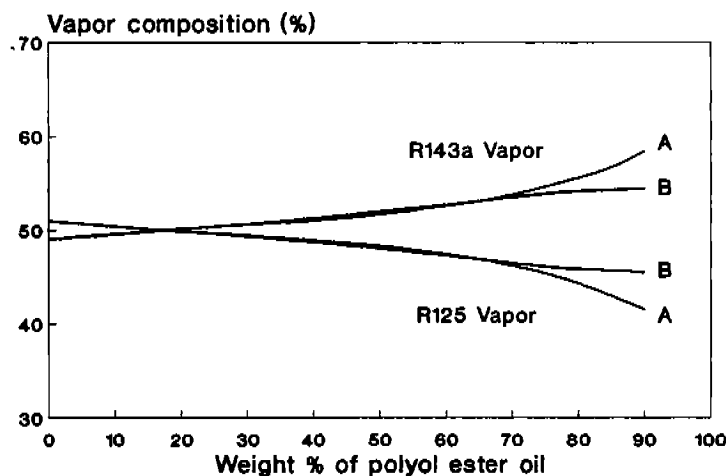


Fig. 3 Vapor compositions vs. % oils for R125/R143a (50/50 %) mixtures in different polyol ester oils (A,B) Calculated based on the theoretical model⁽¹⁾ at T of 75 F.

In order to confirm such theoretical calculations, we have conducted the following experiments for systems of near-azeotropic and zeotropic refrigerants with a polyolester oil. Samples were prepared gravimetrically and allowed to equilibrate at room temperature. Vapor samples were removed and analyzed on 30 m PoraPlotQ[®] GC column using a flame ionization detector.

RESULTS AND DISCUSSIONS

1) Miscibility gap

Fig. 4 shows a miscibility diagram for HFC-32 and a 22cSt polyolester lubricant. The solid line is the VLLE curve calculated based on the theoretical model⁽¹⁾. The solid points are experimentally determined in the present study. The excellent agreement between the theory and experiment allow one to have high confidence in the predicted curves, and one need only experimentally verify several points rather than determine the entire curve.

The VLLE for HFC-143a is shown in Fig. 5. For the HFC-143a with the same oil as above, measurements were made at room temperature and at -10 C conditions. Again, excellent agreement is found between the theoretically predicted miscibility curves and the points based on the present work.

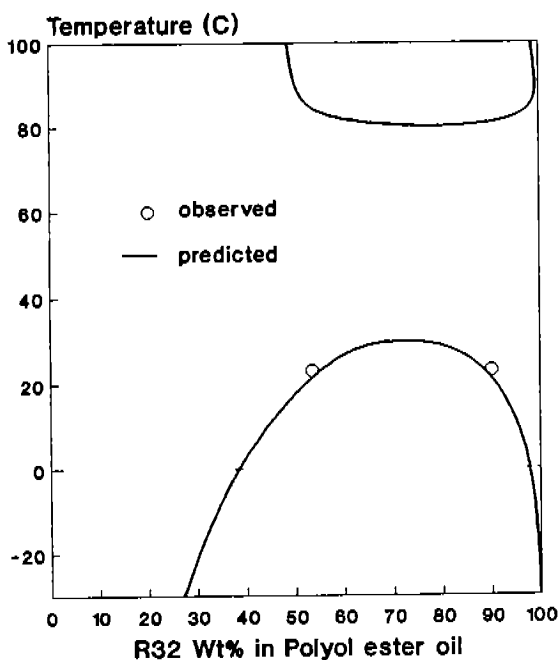


Fig.4 Miscibility diagram of R32

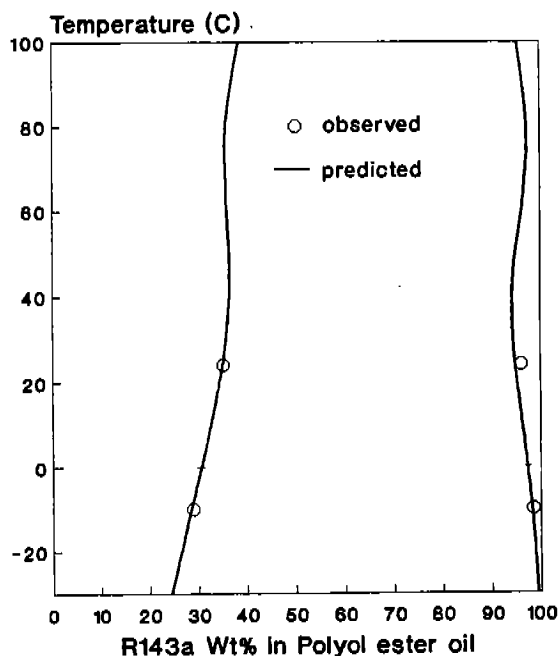


Fig.5 Miscibility diagram of R143a

The accuracy in the measured weight % with the present apparatus and procedure is about 2-3 %. It can be reduced to less than 1%, since the present method depends only on weight and volumetric measurements, which are generally regarded as the most accurate analytical techniques. The temperature control and establishment of equilibrium conditions should be more carefully done to improve accuracy. However, it is encouraging to see that the initial simple and quick experiments are accurate enough to meet our present purposes.

The methodology presented here should also be applicable to more complex mixtures of oil and refrigerants such as ternary mixtures (binary refrigerant blend with oil) and multicomponent oil mixtures with pure refrigerant. Current work is under way to evaluate the present technique for measuring VLLE of such complex mixtures.

2) Vapor compositions

Figs. 6, 7 and 8 show the experimental results. A similar behavior shown in Fig. 3 has been observed for the system of HFC-125/HFC-143a (50/50%) with a polyolester oil (Fig. 6). As mentioned earlier, this binary refrigerant blend is

known to be near-azeotropic. It is observed that the azeotropic nature is now completely destroyed by the addition of the oil. Another such an example is the case of Fig. 7. Again, the blend of HFC-125/HFC-32 (52.1/47.9%), which is known to be near azeotropic, does separate from the azeotropic compositions with oil addition, although the degree of change seems smaller than that of HFC-125/HFC-143a case. On the contrary, a blend of HFC-125 and HFC-134a (47.4/52.6%), which is a zeotropic mixture, shows nearly constant vapor compositions with those of the pure refrigerant mixture: the oil effect is very small in this case. These rather odd behaviors are explained by the relative solubility differences of each compound in the oil. The relative order of the solubility in polyol ester oils is generally: HFC-125 > or = HFC-134a > HFC-32 > HFC-143a as measured⁽³⁾.

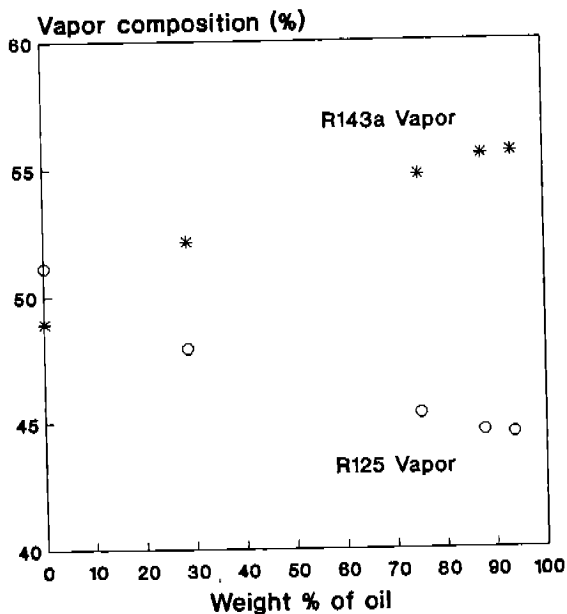


Fig.6 Vapor compositions vs. % oil: R125/R143a

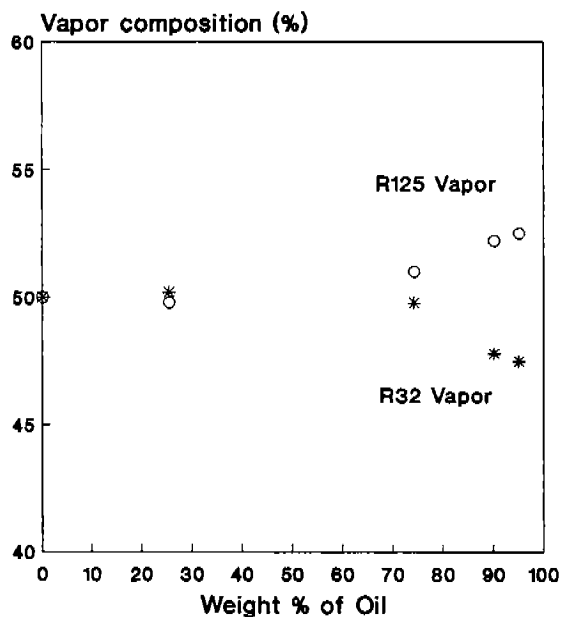


Fig.7 Vapor compositions vs. % oil: R125/R32

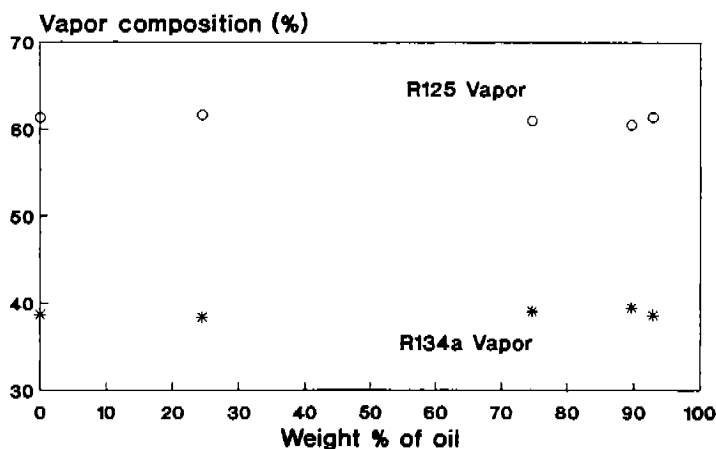


Fig.8 Vapor compositions vs. % oil: R125/R134a

The above experiments agree with the theoretical model predictions qualitatively, but can not be compared numerically with the model results, since the experiments have been done without measuring the pressure, even though the T was set to a constant (room temperature). Thermodynamics indicate that the vapor compositions depend on the system pressure in these cases. In order to rigorously test the theory with experimental data, the temperature, pressure, and compositions must be measured. Such experimental results are shown in Table 1. The theoretical results were calculated based on the experimental total charge of materials, temperature and pressure, and compared with the observed vapor compositions. The agreements between the prediction and experiment are excellent in this system.

Table 1. Comparison of theory and experiment in R143a/R125 (50.3/49.7wt%) /oil mixtures

Oil weight %	Temperature (F)	Pressure (psia)	Observed R143a %	Predicted R143a %
25.3	74.7	172.7	50.4	50.5
75.1	80.3	117.9	53.4	53.3
79.7	79.7	95.7	54.9	53.5
90.0	74.1	52.6	54.4	54.7

CONCLUSIONS

A new experimental method for the determination of VLLE of refrigerant-oil mixtures has been developed and applied to HFC/polyolester oil mixtures. In addition, vapor phase compositions of HFC's blends in the presence of a polyolester oil have been measured. The experimental results are compared with those calculated based on our recent theoretical model. The reasonable validity of the theoretical model has been established.

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