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THE EVALUATION OF EXISTING AND NEW REFRIGERANTS IN THE PRESENCE OF OIL

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ABSTRACT

Accurate and simple methods capable of predicting the properties of refrigerant-oil mixtures are of importance in refrigeration plant design, particularly evaporator design. This article addresses transport properties and pressure-temperature relationships. The calculation of pressure drop in the evaporator is demonstrated as part of an investigative program having experimental and mathematical parts. Results are reported for R22, R134a and two zeotropic blends "Mix1" and "Mix2", all paired with a polyolester oil.

NOMENCLATURE

C_p	specific heat in J/kgK	$\Delta\lambda$	binary interactive parameter
f	fugacity	σ	surface tension in N/m
MW	molecular weight	ϕ	fugacity coefficient
R_m	universal gas constant, 8.3143 J/(mol K)	ρ	density in kg/m ³
S	specific gravity	μ	dynamic viscosity in Nm/s ²
T	temperature in K	<u>Subscripts and Superscripts</u>	
t	temperature in °C	i	component i in a mixture
v	specific volume	L	in the liquid phase
w_{oil}	oil concentration (weight fraction)	m	mixture
x	liquid molar fraction	o, oil	oil
	<u>Greek Letters</u>	R, r	refrigerant
ν	kinematics viscosity in mm ² /s	s	in saturated state
λ	thermal conductivity in W/mK	V	in the vapor phase

INTRODUCTION

This paper reports progress to date and a future plan for a program of work having two objectives, which, though different in nature, have investigative techniques in common:

1. The discovery and evaluation of new refrigerants which are at least the equal of the HFCs in technical performance but lower in both global warming potential (GWP) and total equivalent warming impact (TEWI);
2. The investigation of the behavior of existing HFC refrigerants in the presence of oil.

Objective 1 has been inspired by the threat to the availability of the HFCs posed by Kyoto and by the statements of certain governments, such as those of the UK which has declared that

the HFC are NOT a long term solution, much to the consternation of UK industry (ACR Today, April 2000).

Objective 2 is needed due to the incompleteness of current knowledge of the behavior of HFC-oil pairings and (in some circumstances) the inconvenient behavior of these pairings in service. The authors expect the HFCs to remain in use for many years in many countries, albeit with restrictions in some.

The work has both experimental and mathematical modeling elements, described here in outline.

OVERVIEW

In most refrigeration systems and in virtually all small systems, the oil essential to the lubrication of the compressor sliding parts mixes with the refrigerant. Oil separators of differing levels of sophistication and cost have been used in compressor discharge lines to separate and return the oil to the compressor. None are perfect. All allow some of the oil to pass with the refrigerant around the circuit.

The behavior of refrigerant-oil mixtures is different from that of pure refrigerant. The presence of the oil has its greatest influence in the evaporator due to the refrigerant-oil mixture having its highest viscosity at the lowest temperatures, which of course occur in the evaporator and to the maximum values of oil to liquid refrigerant mass ratio which also occur in the evaporator, due to the evaporation of the liquid refrigerant leaving (in the later stages of the evaporator) a reduced mass of liquid refrigerant to mix with the oil. Eventually the oil is returned to the suction of the compressor by the scouring effect of the rapidly moving refrigerant gas.

The HFC blend-synthetic oil combinations, which have become the mainstay of industrial refrigeration, are considerably more complex in their behavior than the (mainly) single fluid-mineral oil combinations which they replaced. Plant designers would welcome easy-to-use calculation methods of sufficient accuracy for evaporator design. For this, vapor-liquid equilibrium relations and liquid density and viscosity data etc. are required.

This paper is a contribution to this work and to the need to discover new refrigerants, given the threat to HFC availability posed by Kyoto and certain governments.

EXPERIMENTAL WORK

The test equipment (figure 1), described in detail elsewhere (Fleming 1999), is a secondary refrigerant calorimeter which permits the determination of the following for test refrigerants: (1) refrigerating effect, (2) compressor shaft power, (3) COP, (4) refrigerant and associated wall temperatures through the evaporator, (5) the pressure drop through the evaporator and (6) the mass ratio of oil to refrigerant at entry to the expansion valve.

Work relating to items 1,2,3 and 4 has been reported (Fleming 1999) including a comparison of measured and calculated evaporator heat transfer coefficients for four refrigerants, two of which are zeotropes. At the time of writing item 5 and 6 are under development.

The refrigerants tested experimentally and investigated by mathematical modeling, all operating with polyoester oil Castrol SW46, are as follows: R134a, R22, Mix1 (R22/R142b, 60/40 wt%), and Mix2 (R22/R142b, 40/60 wt%).

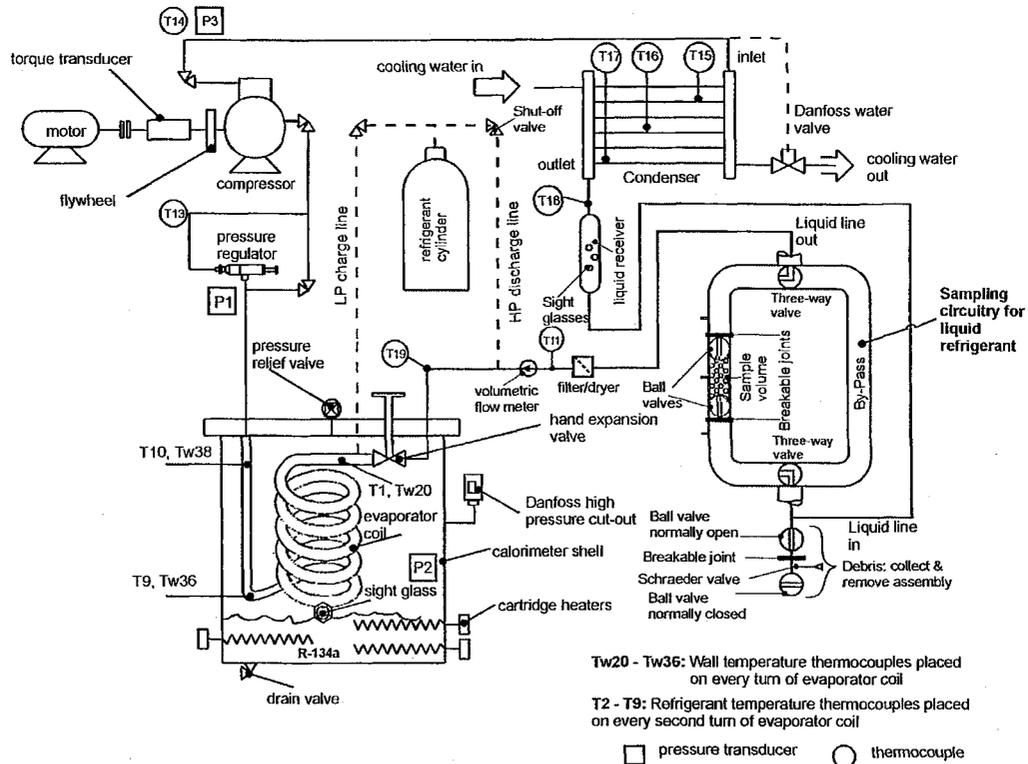


Figure 1 Schematic of the test calorimeters

MATHEMATICAL MODELLING

Transport properties of tested refrigerants and oil mixtures

1. Density

The density of most oils changes linearly with temperature. For the oil SW46 $\rho_{oL} = -0.7703 \cdot t + 999.93$, where ρ_{oL} in kg/m^3 and t in $^\circ\text{C}$.

Some refrigerant/oil mixtures exhibit ideality, some do not. Experimental data for mixtures R22/SW46 and R134a/SW46 shows good agreement with both Equation (1) and (2). Equation (2) is more accurate in the temperature range $-35^\circ\text{C} \sim 20^\circ\text{C}$, but above 20°C , both equations underpredict mixture density

$$\frac{1}{\rho_{mL}} = \frac{w_{oil}}{\rho_{oL}} + \frac{1-w_{oil}}{\rho_{RL}} \quad (1) \quad , \quad \rho_{mL} = w_{oil}\rho_{oL} + (1-w_{oil})\rho_{RL} \quad (2)$$

2. Viscosity

Very few refrigerant-oil mixtures exhibit ideal behavior in viscosity. For the purpose of the present work, the authors fitted the following equation to experimental data for R134a/SW46 ($-35^\circ\text{C} \sim 20^\circ\text{C}$) and R22/SW46 ($-20^\circ\text{C} \sim 40^\circ\text{C}$):

$$\nu_{mL} = C1 \cdot e^{-C2 \cdot t} \quad (3)$$

where ν_{mL} is the kinematic viscosity of the mixtures in mm^2/s and t is temperature in $^\circ\text{C}$. $C1$, $C2$ are empirical constants.

3. Surface tension, Specific heat and Thermal conductivity

Experimental data for surface tension, specific heat and thermal conductivity for the mixtures studied here are not available, hence use was made of equations in the open literature.

Jensen and Jackman (1984) measured the surface tension of R113/oil and presented equation (4), which has an average deviation of 1.6% from its experimental data,

$$\sigma_{mL} = \sigma_{RL} + (\sigma_{oL} - \sigma_{RL})\sqrt{w_{oil}} \quad (4)$$

For specific heat, both Thome (1995) and Jensen and Jackman (1984) recommended equation (5). Thome (1995) also recommended equation (6) for the specific heat of oils:

$$C_{PmL} = (1 - w_{oil})C_{PRL} + w_{oil}C_{PoL} \quad (5)$$

$$C_{PoL} = 4.186 \frac{0.388 + 0.00045(1.8 \cdot t + 32)}{\sqrt{s}} \quad (6)$$

where the oil liquid specific heat C_{PoL} is in kJ/(kg.K), the temperature t in °C (-18°C < t < 204°C) and s is the specific gravity of the liquid at 15.6 °C (valid for 0.75 < s < 1.05).

For the thermal conductivity of refrigerant-oil mixtures the Filipov equation is available.

$$\lambda_{mL} = \lambda_{RL}(1 - w_{oil}) + \lambda_{oL}w_{oil} - 0.72(\lambda_{oL} - \lambda_{RL})(1 - w_{oil})w_{oil} \quad (7)$$

Vapour liquid equilibrium

1. Equilibrium condition for mixtures of refrigerant(s) with oil

The vapor pressure of refrigeration oils is far less than that of refrigerants. As a result the vapor phase of mixtures may be considered to be composed only of refrigerants. Therefore the equilibrium condition for refrigerant-oil mixtures at a constant temperature and pressure could be explained via the concept of fugacity and quantitatively expressed by fugacity coefficients: i.e. $f_{r,i}^V = f_{r,i}^L$ or $\phi_{r,i}P = \gamma_{r,i}x_{r,i}f_{r,i}^0$. With a knowledge of the vapor phase fugacity coefficient $\phi_{r,i}$, standard state fugacity $f_{r,i}^0$, and activity coefficient $\gamma_{r,i}$, the vapor pressure (bubble point pressure) P could be determined at a given molar fraction of refrigerants in the liquid phase.

The fugacity coefficient in the vapor phase can be found from an equation of state. Given of the accuracy of Peng-Robinson equation demonstrated by Lin and Daubert (1980) and Moshfeghian, Shariat et al. (1992), this equation was used. Details of the equation are available in textbooks such as that of Elliott and Lira (1999).

The standard state fugacity is taken as the pure refrigerant fugacity at the system pressure and temperature, therefore

$$f_{r,i}^0 = P_{r,s,i} \cdot \phi_{r,s,i} \cdot Pe_i \quad (8)$$

where $P_{r,s,i}$ is the saturation pressure of the pure refrigerant component i at the system temperature; $\phi_{r,s,i}$ is the fugacity coefficient of the pure saturated refrigerant i , which could also be found from Peng-Robinson equation at the system temperature and the corresponding saturation pressure. The Poynting effect (Pe) makes allowance for the influence of pressure on the liquid fugacity, which, if liquid compressibility is insignificant, will be given by

$$Pe_i = \exp\left[v_{r,i}^L(P - P_{r,s,i})/RT\right]$$

2. Activity coefficient correlation

The physical principles governing the behavior of multicomponent mixtures are not well understood, especially when large molecules are present. Since an experimental approach requires an impractically large number of experiments, an alternative is to estimate activity coefficients from correlations suitable for sparse measured data. Local composition theories such as the Heil model and NRTL model are very attractive for refrigerant-oil mixtures (Martz, Burton et al. 1996) and have been chosen for this study. Details of these correlations are given by Reid (1977) etc.

2.1 Heil and NRTL models for mixtures of a single refrigerant with oil

Figure 2 and Figure 3 compare the experimental data with calculated results for R134a/SW46 (Heil model) and R22/SW46 (NRTL model) and show good agreement. Both figures show clearly the decreased vapor pressure which results from an increased oil concentration.

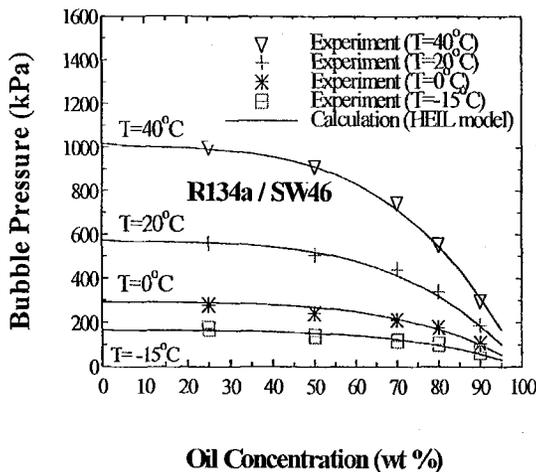


Figure 2 Bubble pressure, temperature, and oil concentration for R134a/SW46

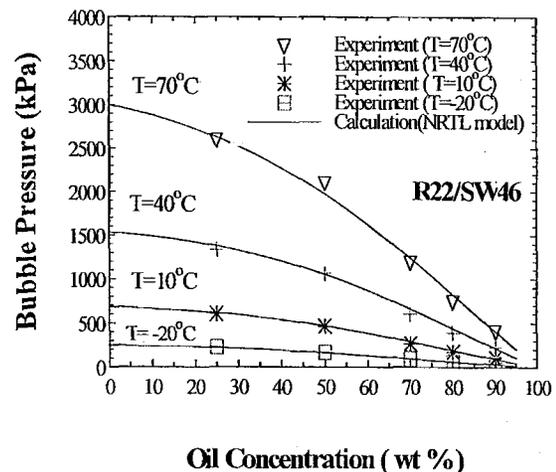


Figure 3 Bubble pressure, temperature, and oil concentration for R22/SW46

2.2 NRTL model for refrigerant blends with oil

Efforts were made to model the behavior of two binary refrigerant blends "Mix1" and "Mix2" in the presence of oil. NRTL was used because it gives the best results of all the models for R22 with oil (Martz, Burton et al. 1996). The difficulty lies in the lack of information about R142b with oil. This problem was dealt with relating the binary parameters required by the NRTL model with some basic characteristics of refrigerant and oil. From the literature (Martz, Burton et al. 1996; Burton, Jacobi et al. 1999) and data supplied by Castrol for this study for R22/SW46 and R134a/SW46, the authors found the deviation from Raoult's law depends on the molecular weight ratio of oil to refrigerant, thus it was selected as a determining factor. Another factor was the critical temperature of refrigerant multiplied by the universal gas constant because the ratio $\Delta\lambda / R_m T$ gives a meaningful dimensionless number. From these considerations, the binary parameters were implicitly related as follows

$$\left(\frac{MW_{oil}}{MW_R}\right) = 1.1502 \left(\frac{\Delta\lambda_{12}}{R_m T_{crit,R}}\right)^2 - 3.6443 \left(\frac{\Delta\lambda_{12}}{R_m T_{crit,R}}\right) + 6.96$$

$$\left(\frac{MW_{oil}}{MW_R}\right) = -3.4323 \left(\frac{\Delta\lambda_{21}}{R_m T_{crit,R}}\right)^2 - 9.7165 \left(\frac{\Delta\lambda_{21}}{R_m T_{crit,R}}\right) - 0.0832$$

where subscript 1 stands for refrigerant and 2 for oil. Both R_m and $T_{crit,R}$ (°K) are in SI units. These two equations are correlated from data of Martz (1996) and Burton (1999) for R12, R22, R134a, R125, R32 with oils including paraffinic mineral oil, naphthenic mineral oil, PAG and POE and data supplied by Castrol for R22 and R134a with Castrol SW46 (POE). The molecular weight ratio ranges from 2.9 to 8.1. Since R142b/SW46 has the molecular weight ratio of 4.78, these equations could be used as a first approximation. The binary parameters found for mixture of R22(1) – R142b(2) – SW46(3) are

$$\begin{aligned} \Delta\lambda_{12} &= 289.6 & \Delta\lambda_{13} &= 2818.2 & \Delta\lambda_{23} &= 8073.99 \\ \Delta\lambda_{21} &= 327.9 & \Delta\lambda_{31} &= -4620.2 & \Delta\lambda_{32} &= -2214.69 \end{aligned}$$

These binary parameters were used in the NRTL model to obtain activity coefficients then to find the relationship between the bubble pressure, temperature, and oil concentration (figures 4 and 5). To make this method generally useful a database of binary parameters for a range of different single refrigerant /oil pairings is needed.

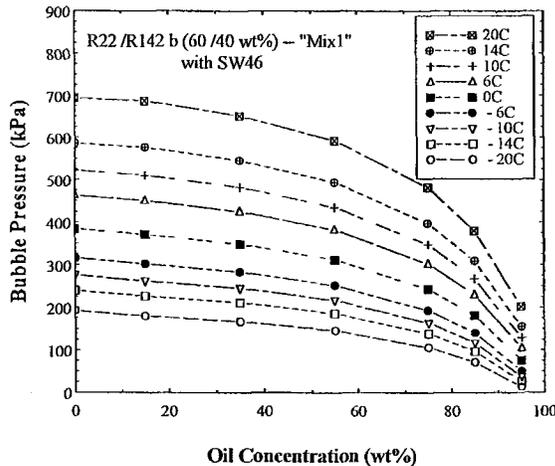


Figure 4 Bubble pressure, Temperature and Oil concentration of R22/R142b(60/40wt%) – “Mix1” with SW46

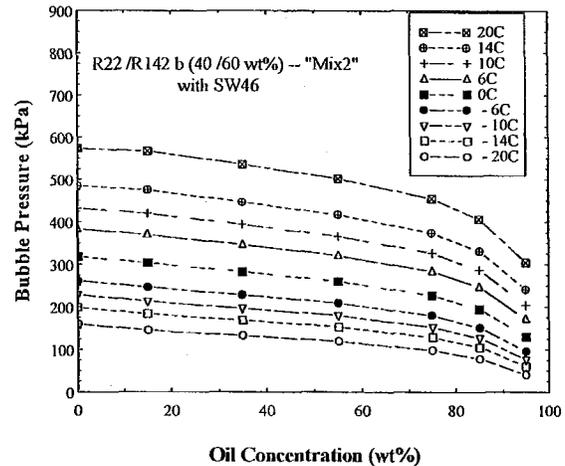


Figure 5 Bubble pressure, Temperature and Oil concentration of R22/R142b(40/60wt%) – “Mix2” with SW46

APPLICATION

Limited space in this paper permits only a short demonstration of the outcome of the calculation techniques described earlier. Pressure drop has been chosen since some attention has been given to heat transfer in earlier papers (Fleming, 1999).

The pressure drop is calculated by two methods and compared. Pressure Drop 1 is determined by subtracting the measured exit (compressor suction) pressure from the pressure

at the evaporator inlet as determined by the VLE relationship developed here, for a trial value of 5% by weight of oil since at the time of writing this has not been measured. While Pressure Drop 2 refers to the results obtained from one of the three correlations:

- Pierre (1964) for pure refrigerants.
- Pierre(1964) for refrigerant/oil mixtures.
- Schlager (1990) correlation $PF = (\mu_{L,m} / \mu_{L,R})^{0.2}$

where in the correlation of Schlager(1990), PF is the pressure drop ratio of refrigerant-oil mixtures to pure refrigerant.

Pressure Drop1 and 2 correlated rather better when oil is present than when it is absent. The scatter is substantial for both R134a and R22 but greater for R22. In relation to Pressure Drop1 Pierre(1964) tends to give high values where Schlager(1990) gives low values.

A true assessment of the different calculation methods must await the acquisition of measured values for evaporator pressure drop and oil/refrigerant mass ratio at inlet to the evaporator, which are part of the next phase of the work.

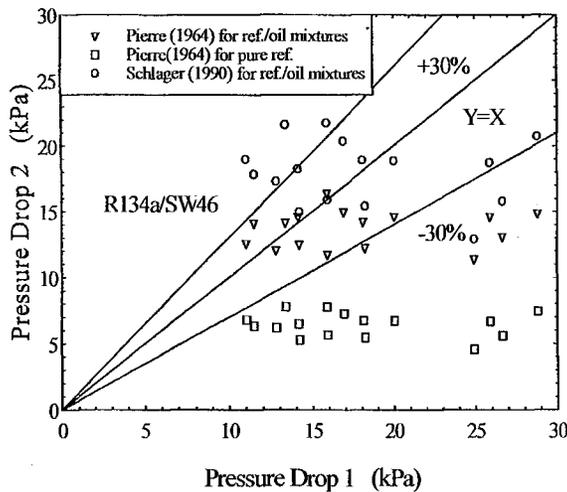


Figure 6 Pressure drop of R134a/ SW46

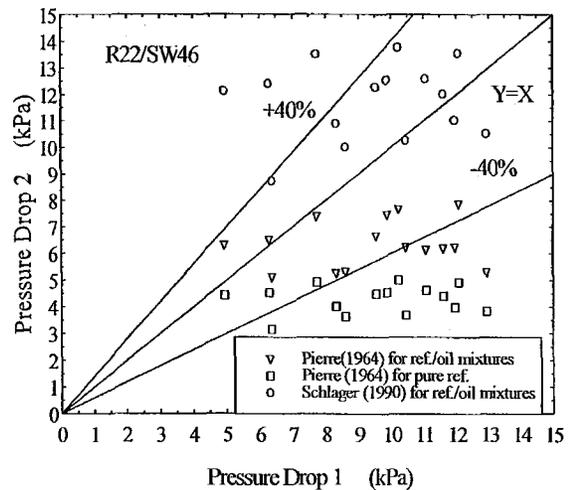


Figure 7 Pressure drop of R22/ SW46

DISCUSSION AND CONCLUSION

VLE calculation shows that for a given pressure the saturation temperature of the refrigerant-oil mixture is higher than that of the pure refrigerant. Although the increase only becomes high at high oil concentration, care must be taken in its assessment because in the later stages of the evaporator high concentrations are reached due to the diminishing presence of liquid refrigerant. In practice it is possible that a large portion of the evaporator will be influenced by the presence of oil. A mixture comprised of a single refrigerant and oil will behave like a special zeotrope at high oil concentration, and a zeotropic refrigerant blend will have its "temperature glide" increased by the presence of oil.

Phenomena influenced by oil such as pressure drop, flow regime, heat transfer etc. will require much more study if they are to be quantified. A major obstacle is the lack of measured data for refrigerant mixtures in the presence of oil. The authors have addressed this problem

by attempting to predict the binary interaction parameters in the activity coefficient correlations from basic fluid properties and a small amount of measured data.

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