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A NOVEL MODELLING APPROACH FOR THERMODYNAMIC DATA OF REFRIGERANT-OIL MIXTURES

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ABSTRACT

Modelling all necessary thermodynamic properties, especially density, phase behavior, specific heat capacity, entropy, enthalpy, viscosity and thermal conductivity of lubricating oils and, in addition, the vapor pressure of refrigerant-oil mixtures in chillers and heat pumps, is still a challenge today. Here we propose a new modelling approach based on the material data of the pure oil from the manufacturer's data sheet. For the temperature dependence of thermodynamic data of the pure oil, the model achieves an accuracy in the range of the measurement uncertainty. For the mixtures, the model could be extended using tabulated data of the refrigerant. With already described mathematical relationships and new approaches to the temperature-concentration behavior of the relevant thermodynamic properties of refrigerant-oil mixtures, it is possible to predict these properties.
For an example system (R290-PAG oil), the derivation of the coefficients of the equation representing the temperature-concentration behavior of the density of the refrigerant-oil system is presented. This estimation is initially made without the use of additional measurement data from the mixture. A similar approach is presented for the thermal properties of pure oils and of this mixture. The vapor pressure-viscosity behavior as a function of temperature and concentration (pvT) of a R290-PAG oil mixture can also be derived in this way and is shown in excerpts.
Keywords: Refrigerant-Oil Mixtures, Thermodynamic Properties, pvT, Propane, R290, PAG Oil, Density, Vapor Pressure, Viscosity, Heat Capacity

1. INTRODUCTION

Sales of heat pumps in Germany, especially for heating heat pumps, increased by more than 50 % in 2023 for the second year in a row (Bundesverband Wärmepumpe (2024a), Figure 1). A similar trend can be observed for industrial heat pumps. Industrial heat pumps are divided into low temperature heat pumps, standard heat pumps and high temperature heat pumps (HTHP), depending on the temperature levels required. Due to the increasing demand for higher application temperatures, the latter are further subdivided into HTHP and very high temperature heat pumps (vHTHP) (Arpagaus (2019), Figure 2). This classification of temperature levels is not yet standardised and is constantly in flux due to ongoing further developments.A study (Fraunhofer Institute IEG (2023)) shows that the environmental and waste heat available in Germany that can be utilised by heat pumps far exceeds the heat demand for buildings and industrial process heat up to 200 °C. The areas of application for industrial heat pumps are diverse (Arpagaus (2019)) and the demand will increase significantly in the coming years. However, there is still a considerable need for research, which is why numerous international and national projects are addressing some of the problems of HTHP.
The topic of lubrication and lubricants (hereafter referred to as refrigeration machine oil or oil for short) has not been considered or has been considered only marginally in the projects mentioned. In the project descriptions of the nationally funded projects (Hochschule Flensburg (2021), Energus (2022)), there is no reference to the refrigerant and the technology used, especially the compressor technology so far. This is particularly important because, in addition to the desired increased lowering temperatures (useful temperatures), the type of compressor used is decisive for the maximum temperatures within the heat pump circuit. Experience has shown that this temperature at the compressor outlet (discharge temperature) is at least 30 K above the condensation temperature,

which in turn is several Kelvin higher than the sink or useful temperature. According to Figure 2, the discharge temperature of the vHTHP (VHTWP) could therefore be up to 190 °C. To operate the compressor of a heat pump at these temperatures, knowledge of the thermodynamic behaviour of the refrigerant-oil mixtures is crucial in order to ensure high efficiency over long running times. So far, this knowledge has not been available and, above all, there is a lack of test set-ups and methods to determine the thermodynamic properties at the required temperatures. Today this data can only be estimated. None of the models currently available in the literature can be used for these incongruent liquid-liquid(gas)mixtures. Therefore, a new method is needed that can predict the required thermodynamic data up to 140 °C with only a few measuring points and that can be used in the future to predict data up to high temperatures.

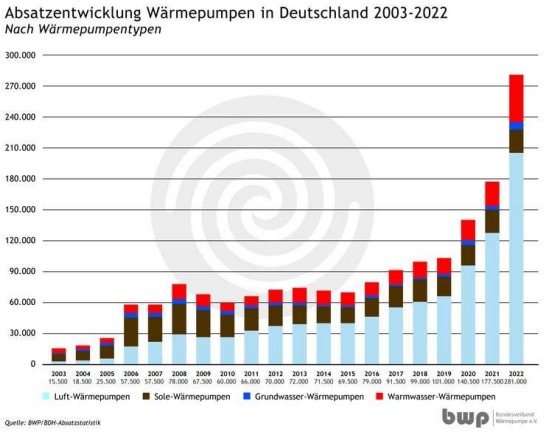

Figure 1: Sales of heat pumps for heating in Germany 2004-2023 (Bundesverband Wärmpumpen (2024))

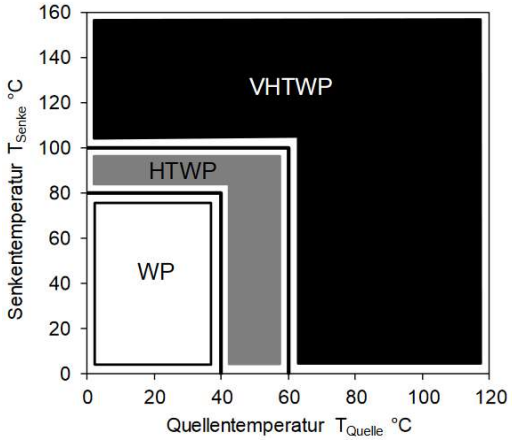

Figure 2: Development of temperature levels for compression heat pumps (Arpagaus (2019))

2. METHODOLOGY

2.1. Estimation of the temperature dependency of the density of pure oils

The density of liquids is the first physical quantity to be considered. It is an important basic variable for converting and determining of other variables. For example, it is used to calculate the kinematic viscosity or as a basis for estimating the heat capacity of the oil.

The density of an oil is generally specified by the oil manufacturers at a certain temperature, usually 15 °C. If the density of an oil is not specified or the temperature dependence is not available, it must be estimated. One method of estimating the density of liquids is by calculating the molar volume according to Elbro (Poling et al. (2001)). This method can be used to estimate the temperature dependence of the density between the triple point and the boiling point (Schmieder (2023)). For example, the density of bis(2-ethylhexyl)adipate (B(EH)A) estimated by this approach, deviates from the literature value only by 2.5 % @ 20 °C (Figure 3). At high temperatures, the model deviates more strongly from the measured values and underestimates most of the values.

The prerequisite for an estimation according Elbro is the knowledge of the molecular structure and molar mass (chain length) of the main component of the oil under consideration. For all polymers, at least the repeating group in the polymer is known. So the molar mass of the repeating group could be used to calculate the density with the method according to Elbro. However, an oil is a mixture of different polymers and length of polymers and may also contain additives. The exact composition of the oil is known only to the oil manufacturer.

In the following, the densities of Polyethylene glycol (PEG) and Polypropylene glycol (PPG) are considered as examples with their repeating groups EG and PG, respectively. The estimated densities are compared with the measured values determined by Fahl (2002) (Figure 4). The density-temperature behaviour of the example Polyalkylene glycol (PAG) oils can be estimated with an accuricy in the range of ± 5 %. However, in both cases, this method reaches its limits when the exact composition of the PAGs is not known.

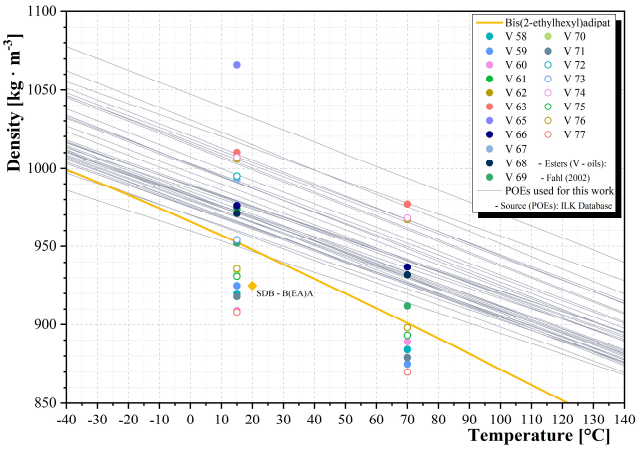

Figure 3: Comparison of estimated density of B(EH)A with reference values (Fahl (2001)) and used POE

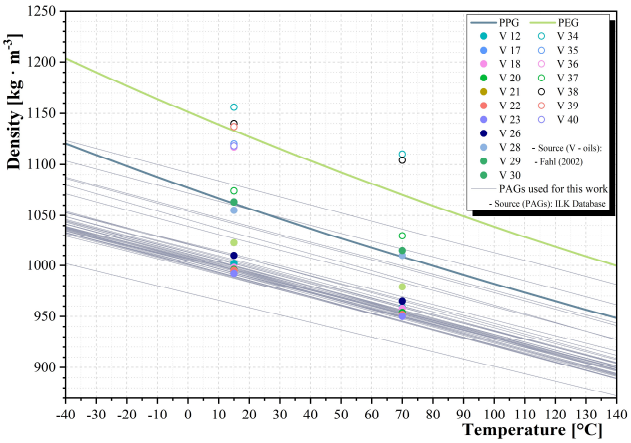

Figure 4: Comparison of estimated density PEG and PPG with reference values (Fahl (2001)) and used PAG

To obtain a realistic estimation of the temperature dependence of the density, even if the exact compostion is not known, a new, alternative statistical approach is proposed for cases where a sufficient number of measurement data is available for a "peer group". In chapter 3.1, a "mean function" for pure PAGs respectively POEs is derived and discussed. The basic idea is based on the observation, that the increase in density of all oils at given temperature intervals is - as can be seen in Figure 3 and Figure 4 - almost the same, with only a few exceptions such as oil V 38 (Fahl (2002). By knowing only the 15 °C value and shifting the mean function in parallel, all other values can be estimated.

2.2. Estimation of the heat capacity of pure refrigeration oil

The heat capacity of pure oils is rarely given in the oil manufacturers' data sheets. Knowledge of the heat capacity is crucial for calculating the enthalpy in the refrigerant-oil mixture. Thome (2011) proposed an empirical formula to estimate the specific heat capacity of mineral oils (Eq. 1). With two coefficients (a, b) and a reduced density factor, which is a coefficient of the density of the oil and the density of water at 15.6 °C. A second method has also been postulated for the specific heat capacity, which allows the heat capacity c_P of a substance to be estimated from the functional groups of the molecule. This method according to Rùzicka and Domalski (Poling et al. (2001)) is based on tabulated values for the respective groups present in the molecule.

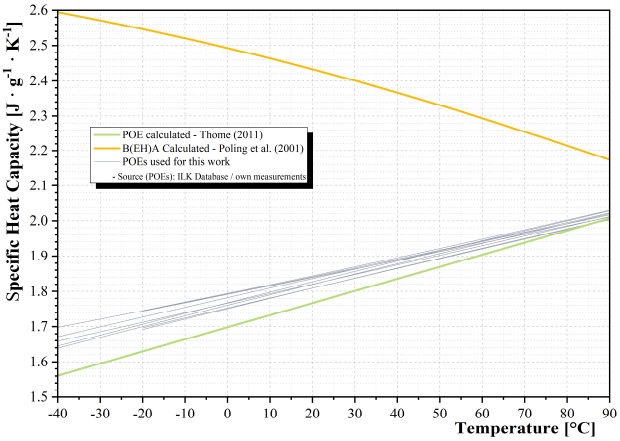

Figure 5: Specific heat capacity c_P of pure POEs measured versus calculated

$$c_{P,MO} = \frac{a+b \cdot T}{\sqrt{s}} \; with \; s = {}^{\rho_{oil,15.6\,°C}}/_{998.5\ kg/m^3} \qquad \text{Eq. (1)}$$

Using both methods, Schmieder (2023) estimated the specific heat capacity for POE oils and compared it with measured values at the ILK Dresden (Figure 5). The application of the empirical formula according to Thome (2011) shows good results with a suitable increase, but shifted to a lower heat capacity. The estimation for the POE oils according to Rùzicka and Domalski (Poling et al. (2001)) was applied for Bis(2-ethylhexyl)adipate. Figure 5 shows that this type of estimation is not suitable for POE oils, as they are a mixture of unknown

components. A more accurate approach according to Thome (2011) is described in chapter 3 (results), which is suitable when at least the oil type is known and already quite accurate, when just one measured point is available.

2.3. Estimation of thermodynamic data of refrigerant-refrigeration oil mixtures

For mixtures of refrigerant and oil, the thermodynamic data depend not only on the temperature, but also on the concentration of the refrigerant in the oil. In addition, the refrigerant, i.e. its chemical structure, influences the thermodynamic data of the mixture. However, it has been found, that for a certain type of oil, the dependence of most thermodynamic parameters on temperature and concentration is similar for different pure oils of the same type of oil and the same refrigerant. For example, the density of the mixtures can be calculated using a mean function of the pure correspondig oil type and of the correspondig refrigerant, only by shifting the base function of the oil by one point of the concentration dependencies in the mixtures as described later in chapter 3. The vapour function of refrigerant-oil mixtures can also be estimated using the mean function of the correspondig oil type and refrigerant. To refine the prediction of the whole data set, a single measurement point in the centre of the range of interest can be used.

3. RESULTS

3.1. Density of pure oils and refrigerant-oil mixtures

The first step was to show that similar density-temperature dependencies could be identified between oils of the same type. For this purpose, the available data for MO, PAG and POE were compared using a linear function:

$$\rho = \alpha + \beta \cdot T \qquad \text{Eq. (2)}$$

Figure 6 and Figure 7 show the distribution of the intersection point at $T = 0$ K (α in Eq. (2)) and temperatur slope parameter (β in Eq. (2)) of several oils, measured at ILK Dresden for the three most commonly used oil types in refrigeration applications (PAG, POE and MO).

The axis intercepts of PAGs show a low scatter. In contrast, the MO and POE oils have a greater spread. For POE, this behaviour is due to the fact that polyolesters are a large group of chemicals synthesized with different starting materials. The properties of POE for refrigeration applications can be achieved by specific selection of the alcohol and acid components to be esterified (Fahl 2002), resulting in a wide distribution of the carbon-oxygen ratio. This ratio significantly influences the density of the oil. The temperatur slopes for the PAGs to each other. However, there are also some outliers. The spread of the MOs and POEs is larger. From these data a mean density function can be determined for each oil type (Table 1).

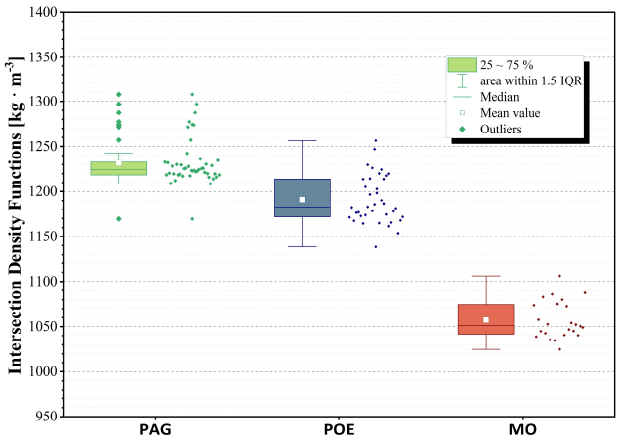

Figure 6: Distribution of the intersection point of different oil types at T = 0 K (α in Eq. (2))

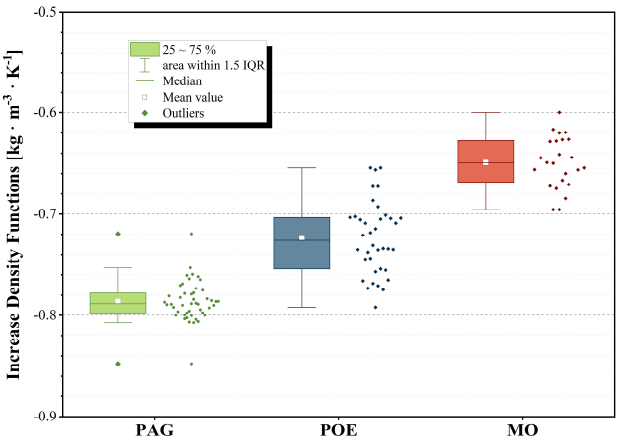

Figure 7: Distribution of the temperature slope parameter of different oil types (β in Eq. (2))

Table 1. Parameters of the mean density functions

Oil type (*)	α [kg · m^{-3}]	$\Delta\alpha$ [kg · m^{-3}]	β [kg · m^{-3} · K^{-1}]	$\Delta\beta$ [kg · m^{-3} · K^{-1}]
PAG (47)	1231.8	25.2	-0.7862	0.0189
POE (38)	1190.9	26.4	-0.7236	0.0352
MO (24)	1057.2	20.3	-0.6493	0.0250
PAO (12)	1020.4	3.8	-0.6278	0.0139
all HC (47)	1045.8	23.7	-0.6444	0.0240

*) number of data records

Oil manufacturers usually specify a measured value for the density on their data sheets, usually at 15 °C. Using this point, the general density functions can be derived by placing the function through the point using parallel displacement. As can be seen in Figure 8, the first estimation using the mean PAG coefficients for a certain PAG 68 oil fits the measured curve (black line - among the others) almost exactly. Corrections with one (P1) or two measured points (P1, P2) shift the line to the correct course.

$$V_{ideal,mixture} = V_{oil} + V_{refrigerant} \quad \text{Eq. (3)}$$

$$\rho_{real,mixture} = \rho_{ideal,\ mixture} - \rho_{excess} \quad \text{Eq. (4)}$$

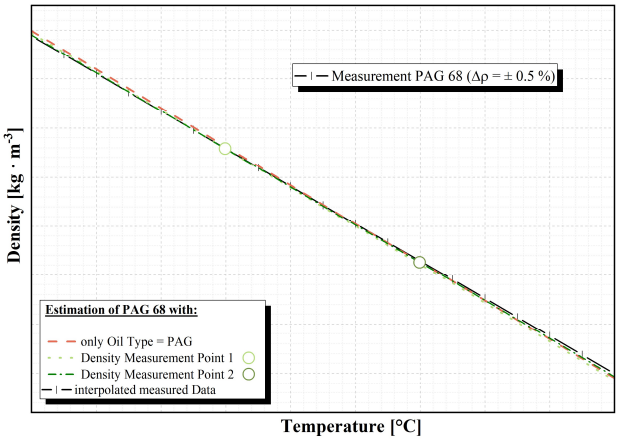

Figure 8: Estimation of density-temperature dependence with manufacturer and measured data

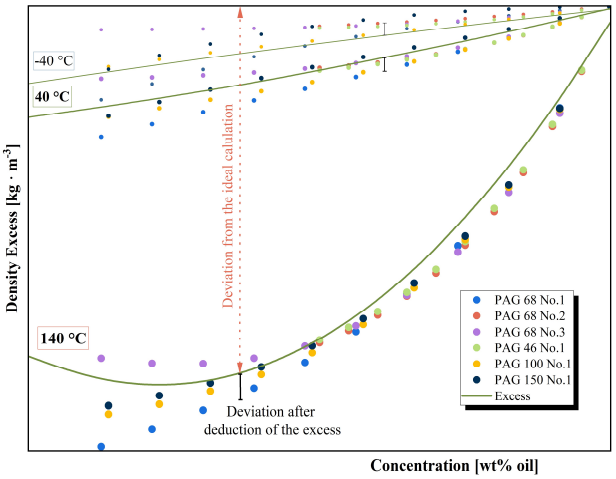

Figure 9: Excess density calculation and generalising

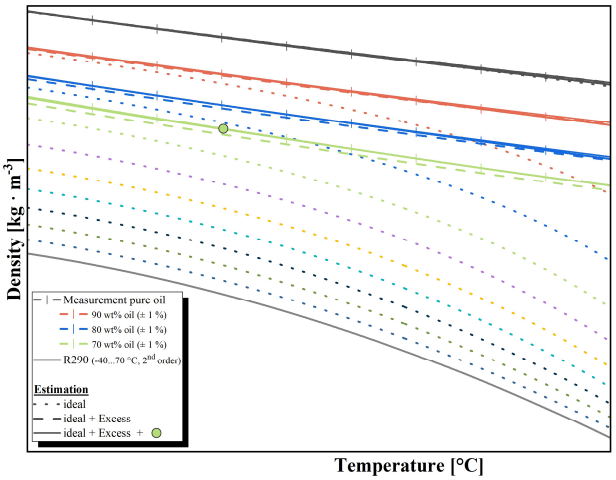

Figure 10: Estimation density of R290-PAG 68 system

As a next step we calculated the ideal density of R290-oil mixtures with eq. (3), to compare it with measured data. This calculation requires knowledge of the temperature dependence of the density of the pure refrigerant, also for temperatures in the near of and above the critical point of the refrigerant. Several fitting approchase were tested, and best results were achieved with a second order polynomial fit with the data from -40 to 70 °C to extrapolate the data of the density above the critical temperature of propane up to 140 °C. Afterwards, we calculated the excess density ($\rho_{excess,}$ eq.(4)) of several R290-oil mixtures and generalize the function (Figure 9). With this generalized function, the density of the mixture in the working range of a compressor can be estimated using only one known density value of the pure oil (at 15 °C from a correct data sheet), knowing the type of oil and the refrigerant. The

uncertainty is less than 1 %. By adding one measurement point to the formula (Figure 10) the estimation becomes much better.

3.2. Heat Capacity of pure oils and refrigerant-oil mixtures

The mean density function of the individual oil types calculated in the previous section 3.1 can be used to estimate the heat capacity with the formula of Thome (2011) (Eq. 1). Figure 5 shows the specific heat capacity of POE oils (ILK data collection) in comparison with the specific heat capacity calculated using the formula of Thome (2011). The application of this formula shows an acceptable estimation of the slope, but the heat capacity is consistently too low. With the available data sets for the heat capacity of pure oils, the coefficients could be calculated for each oil type and a generalized heat capacity can be calculated using Eq. (1). The differences between calculated and measured data depend on polarity of the oil and also on additives. For example, for both PAG 68 (Figure 11) and PAO 68 the mean value of the relative deviation between calculated to measured heat capacity was less than 3 %.

Table 2. Parameters of the mean heat capacity functions (Eq. (1))

Oil type (*)	a [kg · m^{-3}]	Δa [kg · m^{-3}· K^{-1}]	b [kg · m^{-3}]	Δb [kg · m^{-3}· K^{-1}]
PAG (4)	1.13	0.02	$2.52 \cdot 10^{-3}$	$2 \cdot 10^{-5}$
POE (9)	1.02	0.06	$2.69 \cdot 10^{-3}$	$1.5 \cdot 10^{-4}$
MO (7)	0.747	0.027	$3.66 \cdot 10^{-3}$	$5 \cdot 10^{-5}$
PAO (4)	1.02	0.03	$3.11 \cdot 10^{-3}$	$7 \cdot 10^{-5}$

*) number of data records

With the new coefficients derived from our approach for Eq. (1) (Table 2) better results are achieved than by using a MO-based formula for polyolester or glycols, as done for example by Ossorio et al. (2022). First measurements of R290-oil systems with DSC in pressure proof vessels show a non-ideal behavior of the concentration dependence of the heat capacity. There is also a problem with the approximation of the heat capacity of propane, as we showed in chapter 3.1 with the considerations on density and a large difference between the measured data for propane and the literature data. If we succeed in solving these problems, we could probably go into a deeper analysis to estimate heat capacity behaviour of the mixtures.

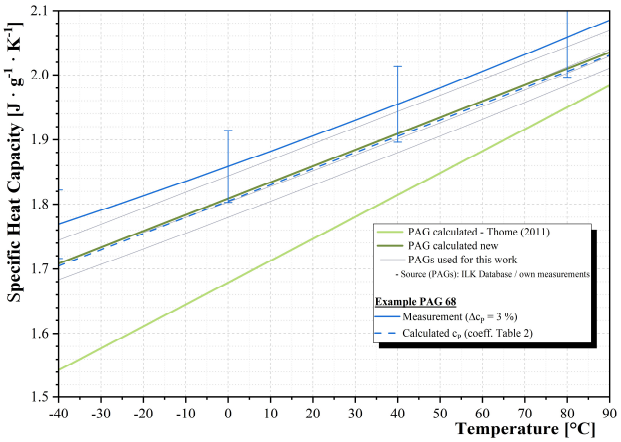

Figure 11: Specific heat capacity c_P of pure PAGs measured versus calculated (with coefficients Table 2)

3.3. Vapor Pressure of refrigerant-oil mixtures

Vapor pressure is the key property to get information about the performance of refrigeration and heat pump cycles. It is also the thermodynamic property that gives an idea of the solubility and miscibility of the refrigerant in the oil. With the data sets available to us, it has been found that again the dependencies of the vapour pressure on concentration and temperature are very similar for a given oil type and refrigerant. It is therefore very likely that the vapour pressure behaviour can be estimated if the type of oil and the refrigerant are known, as can be read in many publications, for example in Ossorio et al. (2022).

There are a number of different approaches to describe the vapour pressure curves of incongruent mixtures. A common method is according to Weibull (Eq. (5)[*)] without f or f = 1) (Ossorio et al. (2022)).

$$\frac{p}{p_{sat.,R290}} / f^{*)} = (1 - e^{-k \cdot x_{R290}} + e^{-k}) \qquad \text{Eq. (5) (f = 1)}$$

$$log_{10}\mathrm{p} = \sum_{i,j=0}^{2} a_{ij} \cdot T^{-i} \cdot (log_{10} x_{R290})^{j} \qquad \text{Eq. (6)}$$

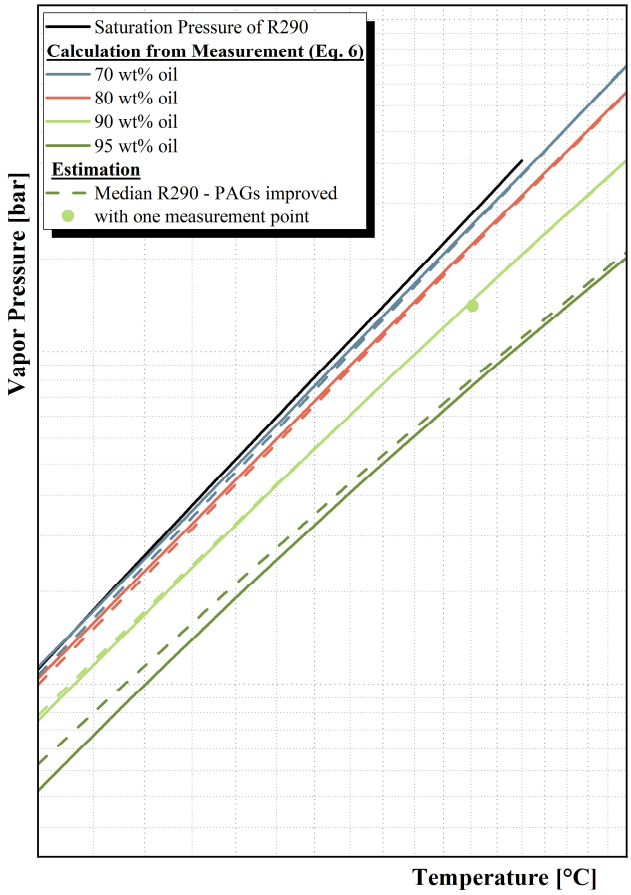

Figure 12: Estimated and measured pressure of a R290-PAG 68 mixture

When we tried to adjust the coefficient *k* for the many propane-oil systems we measured, several problems arose. Firstly, at low temperatures, the vapour pressure at high refrigerant concentrations is calculated to be greater than the saturation vapour pressure of pure propane. This problem could be circumvented by introducing a factor (*f*) which normalises the pressure quotient to 1. Nevertheless, the formula is better suited to high temperatures and high pressures than to lower ones, so that the coefficient of determination R^2 with data from seven R290-PAG systems did not exceed 0.720. A further approach using a tanhyp function on the right-hand side of Eq. (5) did not result in any significant improvement. R^2 remained less than 0.75. Using the formula used by Seeton and Hrnjak (2006, Eq. (6)) and ourselves to calculate the vapour pressure of mixtures, it was possible to successfully adjust the nine parameters with seven data sets with a coefficient of determination R^2 of 0.996. The estimation of the vapour pressure in an R290-PAG68 system with this mean value function led to a very good agreement with the measured values without knowing any of the measured values. By changing a coefficient a_{ij} of the equation, preferably not a second order coefficient, using a measured value in the centre of the measurement range of interest, the estimation is improved even more (Figure 12).

4. CONCLUSIONS AND OUTLOOK

With the help of the new modelling approach presented here, the Daniel Plot can be generated with a few measurements to a sufficiently high accuracy (sufficient for technical considerations) for mixtures of propane and refrigeration oils up to 140 °C and possibly beyond. It is therefore an important aid in the construction and design of refrigeration cycles and heat pumps, up to HTHP working with propane. There is currently a lack of experimental data for estimating the data at the higher compressor end temperatures (> 140 °C) and the refrigerants used (e.g. R600, R601) for high-temperature heat pumps in the same way. The estimation at these high temperatures could only be made with the experimental data up to 140 °C at the expense of accuracy. It is therefore urgently necessary to extend the measurements of the thermodynamic data to the range of > 140 °C (up to 190 °C) in order to enable the estimation of the thermodynamic data in a second step. This will allow the best oil to be selected for each application, in addition to other properties to be considered (e.g. stability, compatibility, foaming behaviour).

ACKNOWLEDGEMENTS

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NOMENCLATURE

p	pressure (kPa)
T	temperature (K)
ν	kinematic viscosity (mPa · s
c_P	heat capacity (J · g^{-1} · K^{-1}
a, b	coefficients to calculate heat capacity
ρ	density (kg · m^{-3})
α, β	coefficients to calculate density
V	Volume
a_{ij}	coefficients for vapor pressure calculation

R290	refrigerant propane
PAG	poly alkylene glycole
HTHP	high temperature heat pumps
vHTHP	very high temperature heat pumps
PEG	polyethylene glycol
PPG	polypropylene glycol
PAG	polyalkylene glycol
POE	polyolester
MO	mineral oil
PAO	poly-α-olefine
HC	hydrocarbon

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