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Understanding and improving the 9-coefficient pressure viscosity temperature (PVT) model

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Abstract. Data describing the physical properties of a mixed refrigerant-lubricant blend is necessary for compressor and system design and is measured using a pressure, viscosity, temperature (PVT) instrument setup. Measurements are taken at discrete conditions and refrigerant concentrations and a model is regressed which can describe pressure (refrigerant solubility), working viscosity, and density across the range of interest. Understanding the applicability of the model is crucial in choosing a suitable lubricant, since the tested conditions are unlikely to exactly match all operating conditions of interest.
This paper describes how the PVT model is created, and how choices in input data can affect the resulting model. Emphasis is placed on the range over which PVT models are valid and what can be done to increase model accuracy.

1. Introduction

Efficiency requirements, environmental concerns in the form of global warming potential (GWP) limitations, and other regulatory specifications have caused a shift in refrigerant chemistry as well as compressor and system design and application area [1, 2]. Air conditioning and refrigeration systems today are being tasked with functioning across wider operating condition ranges, including higher temperatures and pressures which create challenging environments for lubrication. These industry changes have brought a renewed focus on the physical properties of the refrigerant-lubricant mixture and specifically the refrigerant solubility and the mixture working viscosity. Understanding the properties of the lubricant-refrigerant blend under realistic operating conditions is critical in choosing the best lubricant for a specific application [3].

Measuring the physical properties of refrigerant-lubricant mixtures is typically done using a pressure, viscosity, temperature (PVT) instrument setup. The PVT setup can be part of a closed loop in which different instruments measure the same fluid or may be a combination of individual measurements on unique samples. The data generated by measurements is regressed to form models which can typically describe pressure (solubility), working viscosity, and density across the range of interest. The commonly used model is based on a statistical fit of the measured data and is therefore influenced by choices in input data and regression methods.

The fluids in a refrigeration cycle undergo large changes in temperature, composition and refrigerant phase but lubrication properties such as viscosity are primarily important in the compressor. PVT tests are conducted under refrigerant vapor pressure and no applied mechanical pressure which mimics the equilibrium compressor oil sump condition. This assumption has been validated by compressor sump

measurements [4]. The composition and physical properties of this fluid represents that which enters the inlet of the compressor bearings. The physical properties of the fluid under bearing pressure can be measured using a high-pressure viscometer [5-7] to complete the picture of refrigerant-lubricant mixture properties in a compressor.

The PVT model for working fluid properties is a critical element in refrigeration system design and there are many choices that influence model behavior. This paper will describe the steps involved in creating a PVT model and elucidate how the inclusion of different data or regression methods changes the model fit.

2. Model description

Compressor operating temperature and pressure vary depending on compressor type, load, application, etc. which makes testing refrigerant-lubricant blends at all necessary conditions unwieldy. Models that interpolate between measurements allow for a relatively small number of tests to describe a large operating map. Just as understanding how an instrument operates is necessary in using the results, understanding how a model is developed is necessary in drawing accurate conclusions. The maxim "All models are wrong but some are useful" [8] holds true for PVT data but understanding the background and choices made in the model can minimize this "wrongness".

2.1. Model equations

The typical equations used to describe PVT data consist of nine adjustable values or coefficients (hereafter called 9C equations) for each of pressure (solubility), viscosity, and density. These equations are shown below and describe the desired property with respect to temperature T in kelvin and composition ω in refrigerant mass fraction.

$$log(P) = a_1 + \frac{a_2}{T} + \frac{a_3}{T^2} + log(\omega)\left(a_4 + \frac{a_5}{T} + \frac{a_6}{T^2}\right) + log^2(\omega)\left(a_7 + \frac{a_8}{T} + \frac{a_9}{T^2}\right) \tag{1}$$

$$\rho = a_1 + a_2 T + a_3 T^2 + \omega(a_4 + a_5 T + a_6 T^2) + \omega^2(a_7 + a_8 T + a_9 T^2) \tag{2}$$

$$\ln\left(\ln\left(v + 0.7 + e^{-v} K_0(v + 1.244068)\right)\right) = a_1 + a_2 \ln(T) + a_3 \ln^2(T)$$
$$+ \omega(a_4 + a_5 \ln(T) + a_6 \ln^2(T))$$
$$+ \omega^2(a_7 + a_8 \ln(T) + a_9 \ln^2(T)) \tag{3}$$

Equations 1-3: PVT model equations for pressure, P (1), density, ρ (2), and viscosity, v (3), as a function of temperature, T, and composition, ω. The coefficients a_1-a_9 are unique for each equation. The K_0 term in the viscosity equation is a zero order Bessel function of the 2nd kind.

These equations are semi-empirical in nature and have been used for decades within the refrigeration industry. The pressure equation has a form similar to the Antoine equation (a simplified Antoine equation is created if a_3-a_9 are all 0) and the viscosity equation is based on the Wright ASTM equation. Further description of the viscosity equation is available elsewhere [9].

2.2. Coefficient regression

The values for the 9C equations are regressed from measured PVT data. The data typically consists of samples of discrete refrigerant concentration measured across a temperature range. Ultimate end use dictates what range of compositions and temperatures are tested, but 3-5 refrigerant concentrations across 100 °C or more is common. The result from this testing is hundreds or thousands of unique temperature and composition data points for each of pressure, viscosity, and density. A model is created using multilinear least squares regression to calculate the coefficients that yield the best fit to the data. A coefficient of determination (R^2) can also be calculated from the regressed model.

The property against which the regression is performed influences the model behaviour. The 9C equation for pressure relates the logarithm of pressure versus the nine coefficients and therefore the regression is against $\log(P)$. A different fit would be optimal if the regression is against the non-logarithmic pressure. This same characteristic is present with viscosity, where the double logarithm is taken. The effect of this distinction is that larger measured values do not have outsize influence on the fit. This is necessary so that the difference between 900 cSt and 902 cSt (a miniscule error) does not have the same effect on the model as the difference between 2 cSt and 4 cSt.

A perfect model would exactly reproduce all measured points. Since the number of data points greatly exceeds the number of coefficients, a perfect fit is not possible and an indicator of goodness of fit is required. The coefficient of determination (R^2) describes the proportion of variance in the dependent variable that is predicted by the independent variable and a value close to 1 is desirable. However, the nature and quantity of data in PVT tests can obscure model error in seemingly high R^2 values. Figure 1 shows two different fits to the same dataset. Graphically, it is clear that the model in Figure 1a does a better job fitting the data, however both models exhibit R^2 values above 0.99. In the absence of a graphical comparison, it would be difficult to determine practical model accuracy from R^2 values alone.
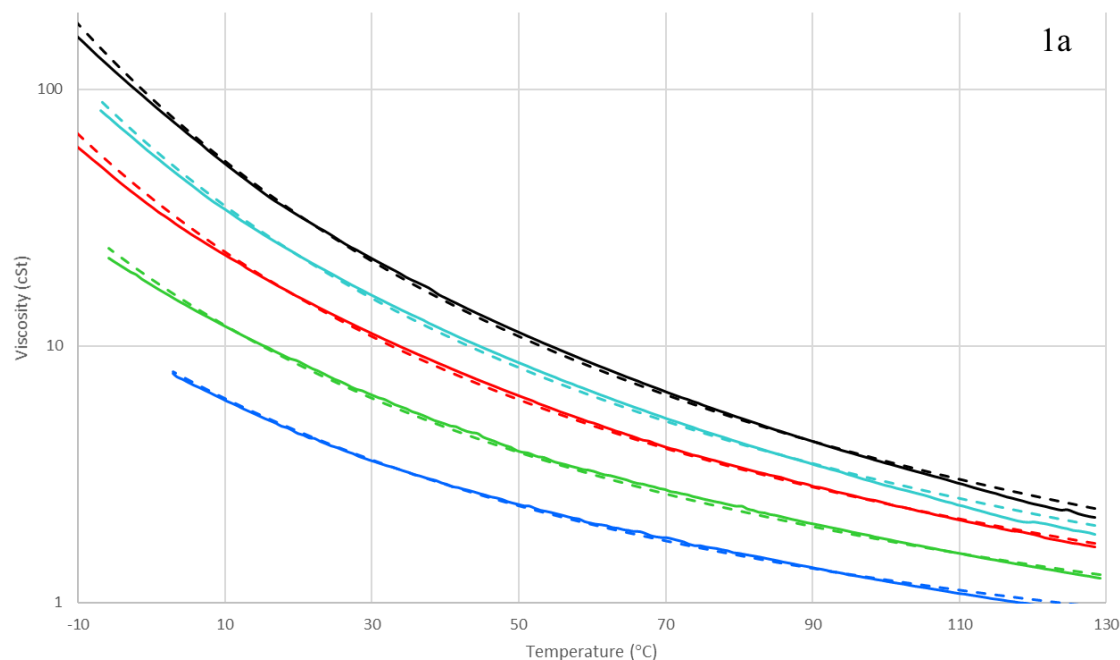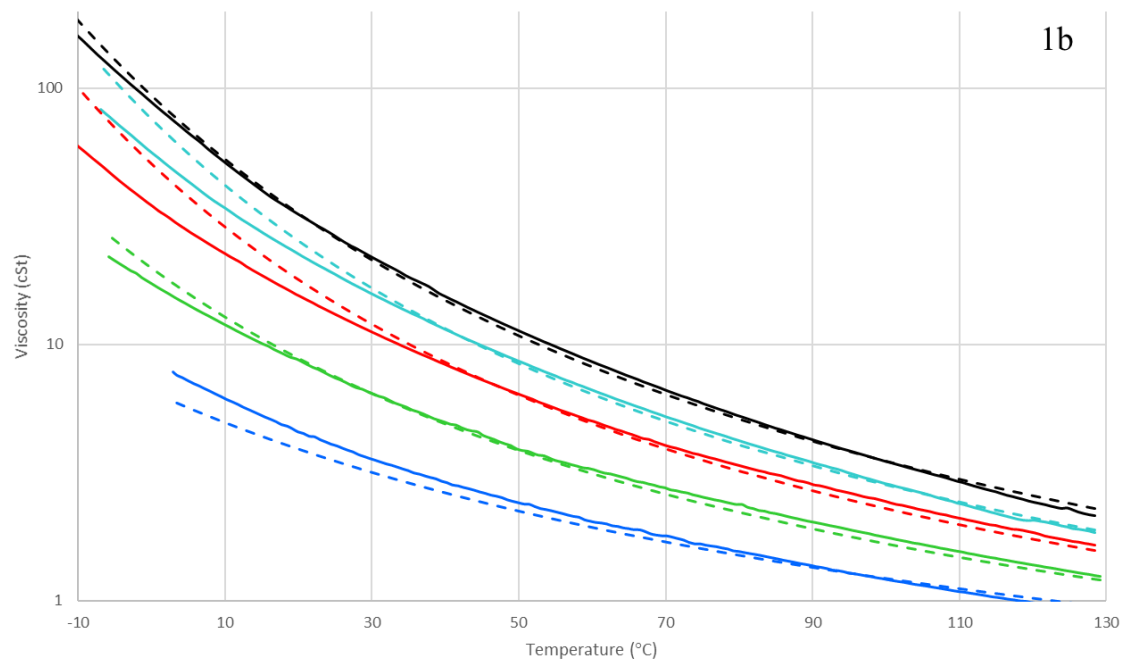
Figure 1. Comparison of viscosity data (solid) and model (dashed) for a refrigerant-lubricant combination. Different colors represent different mass dilution runs: neat lubricant (**black**), 5% refrigerant (**cyan**), 10% refrigerant (**red**), 20% refrigerant (**green**), 30% refrigerant (**blue**). The model fit in Figure 1a has an R2 value of 0.995 and the model fit in Figure 1b has an R2 value of 0.991.

Model complexity is a challenging topic and the debate between parsimony and robustness is persistent in statistics [8,10]. The risk of too simple a model is that important trends in the data will be unrepresented while too much model complexity can risk exhibiting unintended trends or overparameterization. The correct model will depend on the intended use and available resources. Figure 2 gives an example of a viscosity model based on six coefficients (where a_3, a_6 and $a_9 = 0$) and one with nine coefficients. Both models fit the data well over the middle temperature region, but the 9C fit triumphs at the temperature extremes.
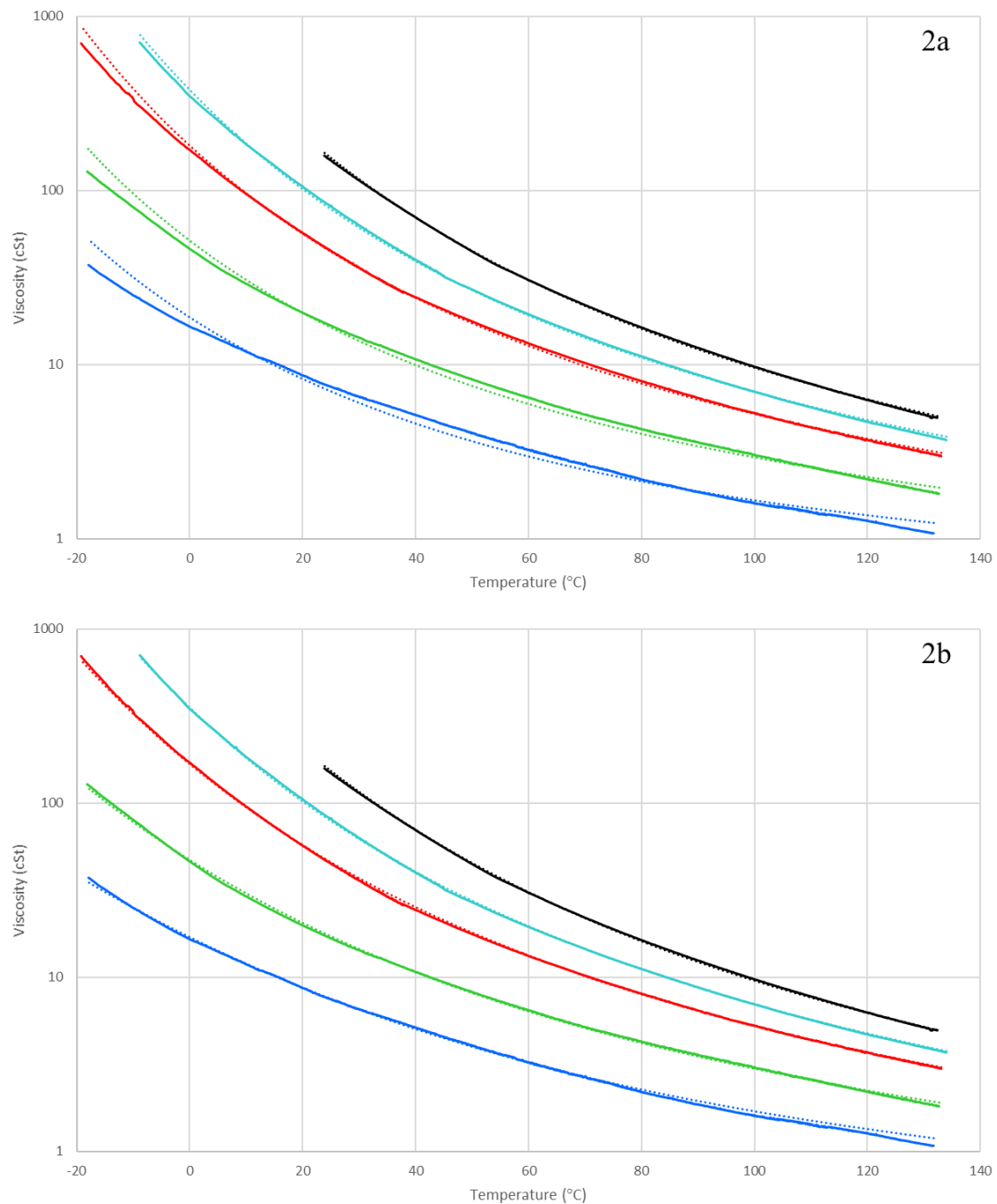
Figure 2. Comparison between a 6-coefficient viscosity model fit (a) and a 9-coefficient viscosity model fit (b) for a 68 cSt POE with R-1234yf. Data as solid lines, models as dotted lines. Colors represent the refrigerant concentrations described in Figure 1.

3. Model and real data

A model is only as good as the data input, so it is important to understand the behaviours and limitations of PVT measurement systems. The wide temperature range of interest in PVT data leads to an even larger range of measured properties like pressure and viscosity. Pressure for refrigerants like R-1233zd(E) or R-514A is often below 1 bar while tests with R-32 can approach 100 bar and R-744 will be well over 150 bar. Measurement accuracy at these extremes will vary and one instrument may not

be able to accommodate such different property ranges. Viscosity ranges can be even more extreme. An ISO 68 lubricant can experience viscosities above 1000 cSt at neat, cold conditions but can also approach 1 cSt at hot, highly diluted conditions.

It is also important to realize that the PVT equations are empirical and may have difficulty describing real behaviour, especially pertaining to extrapolation beyond measured values. Figure 3 shows theoretical pressure behaviour from pure lubricant to pure refrigerant at constant temperature. The 0% value is the lubricant vapor pressure and the 100% value is the refrigerant vapor pressure. A smooth curve will connect the two values unless there is immiscibility between the refrigerant and lubricant chemistries, and the model should never exceed the 100% value.
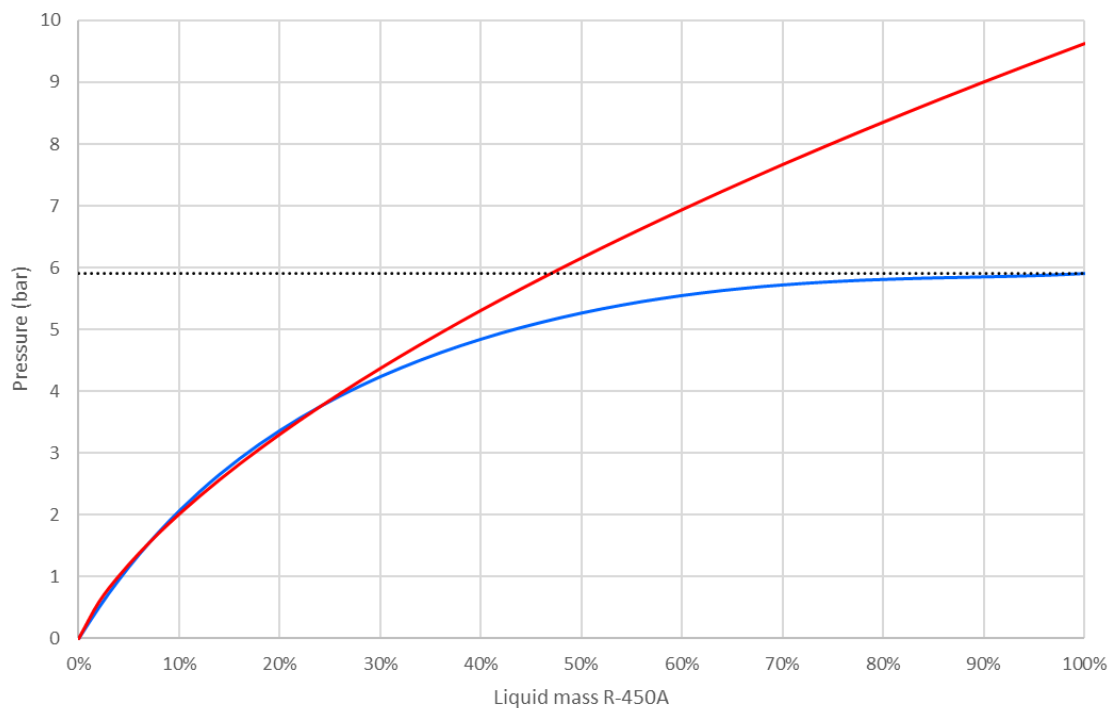
Figure 3. Example of solubility for a 100 cSt POE with R-450A at 25 °C. Theoretical behavior in blue, PVT equation in red, refrigerant saturation pressure as black dotted line. The PVT equation was constructed with data from 0-30% mass R-450A.

Compressor sump conditions are lubricant-rich and typically do not extend beyond 30% refrigerant. A model between 0% and 30% refrigerant does an excellent job of representing the data. However, if this model is extended to predict the pressure of a 50% refrigerant mixture, a nonsensical value is obtained. Real behaviour is constrained by the refrigerant vapor pressure and asymptotically approaches this value whereas the statistical 9C pressure model has no such constraint. If data is measured out to 50% refrigerant, then a model utilizing that data will be accurate up to that composition. For this reason, the standard PVT model may not be appropriate to apply to specific scenarios, such as flooded refrigerant starting conditions.

3.1. Practical use

Understanding potential sources of error is important for using PVT models. Some of these have to do with measuring real samples and others focus on how data choices affect the model accuracy.

Virtually all commercial compressor lubricants are mixtures of different molecules. This often manifests as a distribution of molecular weight or a mixture of known chemistries. The exact composition will depend on many different variables such as reaction time and temperature for synthetic lubricants or feedstock for mineral oils. To accommodate these variables, a specification will be agreed

upon by all parties that lists the acceptable ranges for various physical properties such as density and viscosity. This property range will propagate to the PVT data and model. If an ISO 68 lubricant has a specification that allows ± 4 cSt then it is reasonable to assume that the viscosity model for in spec lubricants could have ± 6% or larger error bars. Good engineering judgement must be used when choosing a lubricant for an application such that there is an ample safety margin to accommodate for expected manufacturing variances.

Calibration of test instruments should be done by standard methods, but PVT tests have added complexity due to the presence of refrigerant which will undergo phase change with changing temperature. Any instrument used for this purpose must have vapor head space to account for the vapor-liquid equilibrium of the refrigerant. This phase change requires accurate knowledge of the system volume for calculation of liquid phase composition. Table 1 shows examples of composition calculations for various volume or mass charge errors. Row 1 indicates the correct values while rows 2-7 demonstrate the magnitude of error for different incorrect values. In this scenario the measured temperature, pressure, and liquid density are accurate and the values for composition calculation (system volume or mass charges) may be incorrect. The correct volume is 400 mL and the correct mass charges for lubricant and refrigerant are 200 g and 100 g, respectively. The magnitude of errors shown in Table 1 are far greater than would be expected during typical operation, and the difference in liquid refrigerant composition is at most roughly ±1%.

Table 1: Example of the effect of mass charge and system volume calculation errors on the calculated liquid refrigerant composition (solubility) for PVT data. The values in the table are based off an ISO 68 POE with R-134a.

Row	Temp. (°C)	Pressure (bar)	System volume (mL)	Lubricant charge (g)	Refrigerant charge (g)	Liquid density (g/mL)	Vapor density (g/mL)	Liquid refrigerant composition
1	50	9	400	200	100	1.01	0.040307	32.4%
2	50	9	400	**210**	100	1.01	0.040307	31.4%
3	50	9	400	**190**	100	1.01	0.040307	33.4%
4	50	9	400	200	**105**	1.01	0.040307	33.5%
5	50	9	400	200	**95**	1.01	0.040307	31.1%
6	50	9	**420**	200	100	1.01	0.040307	32.2%
7	50	9	**380**	200	100	1.01	0.040307	32.6%

All sources of variance can be quantified to generate a plot that encompasses test repeatability, reproducibility, and model variation. Figure 4 displays relative standard deviation overlaid on a Daniel plot for five separate series of tests for a 68 cSt POE with R-134a. These tests were run with different commercial batches of lubricant over the course of several years and each series of tests consisted of a neat lubricant run and four refrigerant dilution (5%, 10%, 20%, 30% mass refrigerant) runs. The vast majority of operating range is below 5% relative standard deviation, with greatest deviation at very cold, low pressure, high viscosity conditions. Note that this depiction is for one instrument system and model construction method; all systems will have a unique variance map.
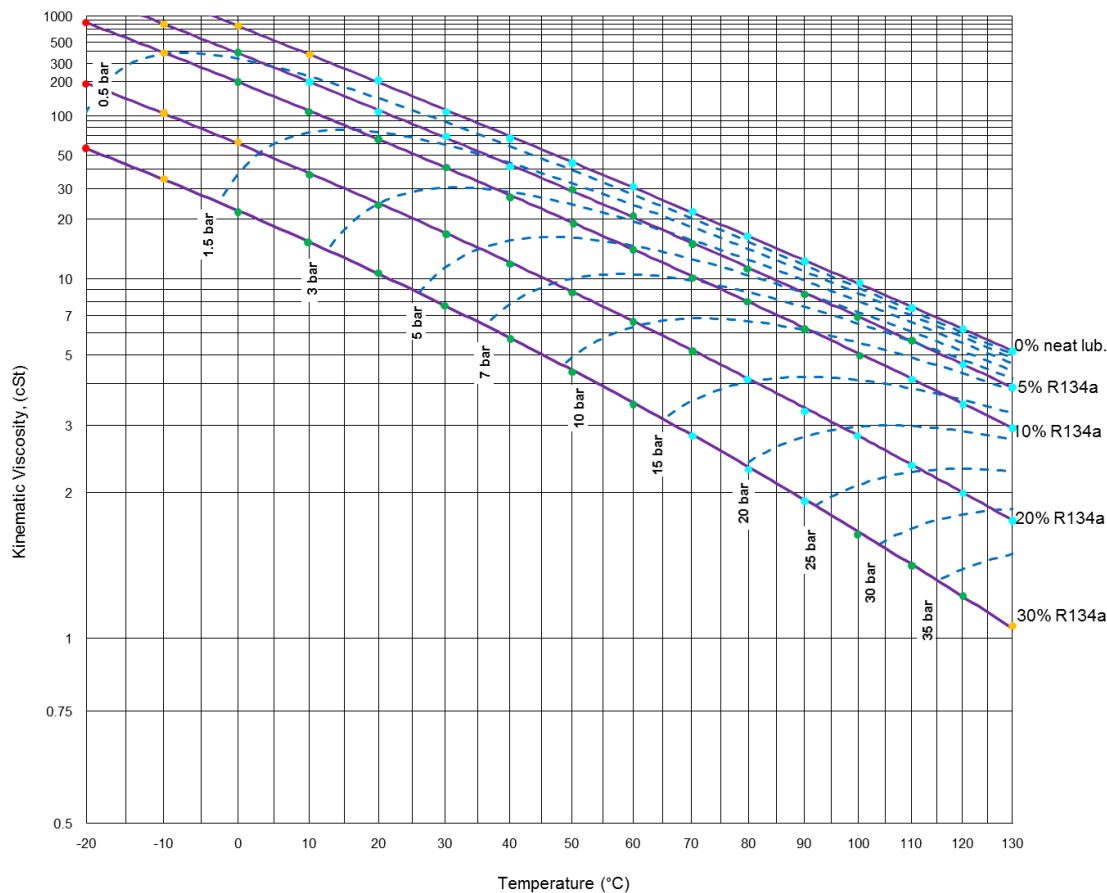
Figure 4. Variance map overlaid on a Daniel plot for a 68 cSt POE with R-134a. Calculations are based on a series of five runs. Cyan represents below 3% variance, green 3-5%, yellow 5-10%, and red 10+%.

Choices in what test data to include in model regression can have an impact on model accuracy. The multilinear regression will optimize the fit based on all included points, so points extraneous to the region of interest will hinder the model. A narrow model based around a subset of conditions will necessarily represent that area better than a broader model.

The model is also influenced by the spread of data analysed. Assigning more weight to a run, or a subset of data, will cause the model to regress more closely to that data. This can be done unintentionally if data collection quantity varies between tests. Measuring fewer points for a neat run compared to diluted runs will skew the model fit away from low dilutions. Similarly, measuring refrigerant dilutions every 5% between 0% and 30% and then skipping to 50% will give a different model compared to an analysis that used equal spacing between 0% and 50%. None of these scenarios makes the model invalid, but care should be taken to understand how different choices affect model outcome.

4. Conclusion

The multitude of conditions at which a compressor may operate preclude testing a refrigerant-lubricant mixture for every possible scenario. Models generated from PVT data are essential in determining physical properties of working fluids in compressors, which is a key part of designing an efficient, robust refrigeration system. Many choices are made in constructing a PVT model which will influence the range of applicability as well as accuracy of the result. These choices include factors such as how the model is regressed, the data spacing and range included, and practical considerations like sample,

instrument, and calibration variation. Fully understanding the ramifications of PVT model creation ensures that proper design decisions for refrigeration compressor systems will be made.

5. Future considerations
The current state of PVT models has served the refrigeration industry well for over three decades but new challenges stemming from refrigerant transition, as well as continuing improvement of theoretical and computational methods, indicate that improved model understanding is in order. The universal recognition of Equations 1-3 makes them useful for quickly calculating and displaying data, and when used properly can give a superb fit to data (Figure 2b). These equations lack a strong theoretical underpinning and more rigorous techniques may bring additional insight when extrapolated properties or chemistry-level information is desired. As complexity in the industry increases, descriptive and predictive models based in molecular dynamics [11], thermodynamic equations of state [12], and quantitative structure-property relationship [13] may become necessary to quickly and accurately model the important physical properties of refrigerant-lubricant blends.

References

[1]   Calm, J 2008 *Int. J. Ref.* **31** 1123-1133
[2]   Bhutta M, Khan Z, Garland N, and Ghafoor A 2018 *Tribol. Ind.* **40** 19-51
[3]   Karnaz J 2014 *Int. Compres. Eng. Conf.* 2331
[4]   Ginies P, Even Y and Guesnay Q 2018 *Int. Compres. Eng. Conf.* 1246
[5]   Gunsel S and Pozebanchuk M 1999 Elastohydrodynamic lubrication with polyolester lubricants
         and HFC refrigerants, final report **1**
[6]   Jonsson U and Lilje K 1998 *Int. Compres. Eng. Conf.* 1227
[7]   Bair S, Baker M and Pallister D 2017 *Lub. Sci.* **29** 377-394
[8]   Box G 1979 *Robust. Stat.* 201-236
[9]   Seeton C 2006 *Tribo. Lett.* **22** 67-79
[10] Box G 1976 *J. Am. Stat. Assoc.* **71** 791-799
[11] Sun H 1998 *J. Phys. Chem. B* **102** 7338-64
[12] Wahlstrom A and Vamling L 1997 *Can. J. Chem. Eng.* **75** 544-550
[13] Afantitis A, Melagraki G, Sarimveis H, Koutentis P, Markopoulos J and Igglessi-Markopoulos O
         2006 *Polymer* **47** 3240-48