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Clearing the Cloudiness of Lubricant-Refrigerant Miscibility

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ABSTRACT

The phase interaction of liquid refrigerant with liquid lubricant is commonly described as miscibility. Lubricant and refrigerant combinations can be described as single liquid phase (miscible) or multiple liquid phases (immiscible). In specific system designs, good miscibility between the compressor lubricant and refrigerant play important roles in system functionality. Inadequate miscibility can lead to lubricant accumulation in the evaporator, which can cause degraded heat transfer properties as well as lubricant starvation in the compressor.

Governments are implementing stricter environmental standards in the HVAC&R industry including higher efficiency targets and lower GWP (global warming potential) refrigerants. Equipment design changes are increasingly required in order to meet these regulations. Changes in refrigerant chemistry or operating conditions are causing lubrication challenges due to generally increasing refrigerant dilution and lower working viscosity. Maintaining sufficient miscibility ranges while upholding all other lubricant properties is no longer guaranteed.

The miscibility boundary is generally described as a transition from one single phase to two distinct phases, however that is rarely the case. Within this paper a broader range of miscible and immiscible phase interactions will be discussed. Interesting and unique phenomena that occur during miscibility testing will be looked at with the ultimate goal of understanding how these behaviors translate into evaporator performance and lubricant return.

1. INTRODUCTION

The primary role of a compressor lubricant is to lubricate bearings and moving parts within the compressor or system. Compressor lubricants can also function as a sealant, noise dampener, and when properly additized can help protect against corrosion (Rudnick, 2013). In compressors designed for heating, air conditioning, or refrigeration (HVACR) applications, there are several properties that need to be taken into consideration when selecting or developing a lubricant, and these properties are almost always impacted by the refrigerant(s) that will be used. Examples of these important properties include working viscosity, solubility, chemical stability, and miscibility. In this paper, we will explore the topic of miscibility. Specific miscibility phase behaviors will be looked at in-depth, in order to expand the understanding of what behaviors can be considered acceptable for application use.

In the majority of HVACR systems, the circulating fluid is a mixture of refrigerant and lubricant. Oil circulation rate (OCR) is the concentration of lubricant in the refrigerant that leaves the compressor. Oil circulation rates are impacted by many factors, including working conditions, mass of oil charged into the compressor, and compressor and system design (Wu & Wang, 2013). Oil return refers to the tendency of the circulating lubricant to come back to the compressor. It is important to ensure that adequate lubricant is available for the compressor to perform its primary functions. Proper oil circulation and oil return within an HVACR system are necessary for optimized performance and reliability. For example, excessive oil circulation may negatively impact system

efficiency, but insufficient oil circulation may inhibit the proper function of valves or other moving parts. Likewise, insufficient oil return may lead to decreased heat transfer efficiency as a result of lubricant accumulation in the heat exchangers, or in extreme cases compressor failure due to lubricant starvation (Lootin, Guillemet, & Lebreton, 2003) (Wu, et al., 2020).

Miscibility testing is used to screen a lubricant for its likelihood to return to the compressor. This is done by evaluating the separation tendencies of the refrigerant and lubricant as a function of temperature and lubricant concentration. In the HVACR industry, miscibility can be defined as the mixing of the lubricant and refrigerant in their liquid phases. The chemical compatibility between the refrigerant and lubricant dictates how miscible a combination will be, and the chemistry of the lubricant can be adjusted to achieve a specific miscibility target or range. Miscibility is particularly relevant in the assessment of existing or new lubricants for use with a broader range of refrigerant chemistries, or in expanded operating conditions with incumbent or new refrigerants.

In this paper, we take a closer look at factors that impact the designation of the miscible/immiscible boundary, discuss miscibility considerations for different applications, and propose different methods to make and view miscibility curves. By exploring and challenging the boundaries of acceptable miscibility performance, there is the potential to expand the availability and selection of lubricant options to meet the needs of a particular application, or the broader industry as a whole.

2. BACKGROUND

The phase behavior in liquid-liquid mixing is governed by the Gibbs free energy of mixing (ΔG_m), which relates the enthalpy (ΔH_m), temperature (T), and entropy (ΔS_m) of the mixed constituents:

$$\Delta G_m = \Delta H_m - T\Delta S_m$$

A single-phase solution is produced when $\Delta G_m \leq 0$. Mixture properties such as intermolecular attraction or repulsion between both like and unlike molecules, and relative size difference between molecules, influence ΔG_m. Thermodynamic behavior is often described in equilibrium terms, but metastable behavior can also be observed. The spinodal is defined as the limit of metastability where the second derivative of Gibbs free energy with respect to concentration is zero (Cowie, 1991). This metastable region can exist as a single phase and withstand small perturbations but will undergo phase separation under larger fluctuations. Due to the difficulty in explicitly measuring these properties, parameters to describe mixing have been developed and used in some applications (Hansen, 2004). While it may be tempting to try and ascribe theoretical explanations to observed behavior, this study is focused on practical observations and their effects on real world applications. Further theoretical discussion of Gibbs free energy of mixing is outside the scope of this work and can be found elsewhere (Cowie, 1991) (Elliot & Lira, 1999).

In consideration of the practical methods used for miscibility testing of refrigerants and lubricants, industry standard methods such as ANSI/ASHRAE Standard 218 (Method of Test for Lubricant and Refrigerant Miscibility Determination), and others exist (Matsumoto, Kaneko, & Kawaguchi, 2014) (Smith, 2014) (Pate, Zoz, & Berkenbosch, 1993). The purpose of ANSI/ASHRAE Standard 218 is to "establish a test procedure to determine the critical solution locus of miscible properties of a lubricant and refrigerant mixture" and applies to pure-component and multicomponent refrigerant and lubricant mixtures (ASHRAE, 2019). This method covers the preparation and assessment of refrigerant/lubricant samples and provides categorical descriptions for different phase behaviors. However, the standard does not clarify which phase behaviors should be considered miscible or immiscible, or which phase behaviors are acceptable for an application. Phase behaviors that are considered as acceptable or unacceptable are dictated by the application and the method users. This leaves a cloud of ambiguity in how to designate certain phase behaviors that are immiscible by thermodynamic definitions but could potentially be usable in some application scenarios.

Figure 1 represents an example miscibility chart for a lubricant-refrigerant mixture. The chart shows temperature on the y-axis and lubricant concentration on the x-axis. Designated regions on the graph indicate the areas in which the refrigerant and lubricant mixtures are identified as miscible or immiscible, and the points on the graph represent the actual measured concentrations. The lines drawn between these points are interpolated, and as the curve approaches 0% lubricant, the line is extrapolated to indicate single-phase behavior of the liquid refrigerant. In

this chart, both an upper and lower critical solution temperature are identified. The upper and lower critical solution temperatures indicate the lowest and highest temperatures, respectively, at which the mixture remains miscible throughout the concentration range. It should be noted that critical solution temperatures are not always observed. In some cases, only an upper or lower immiscible region is observed and in other cases, the mixture is miscible or immiscible throughout the entire temperature and concentration range.
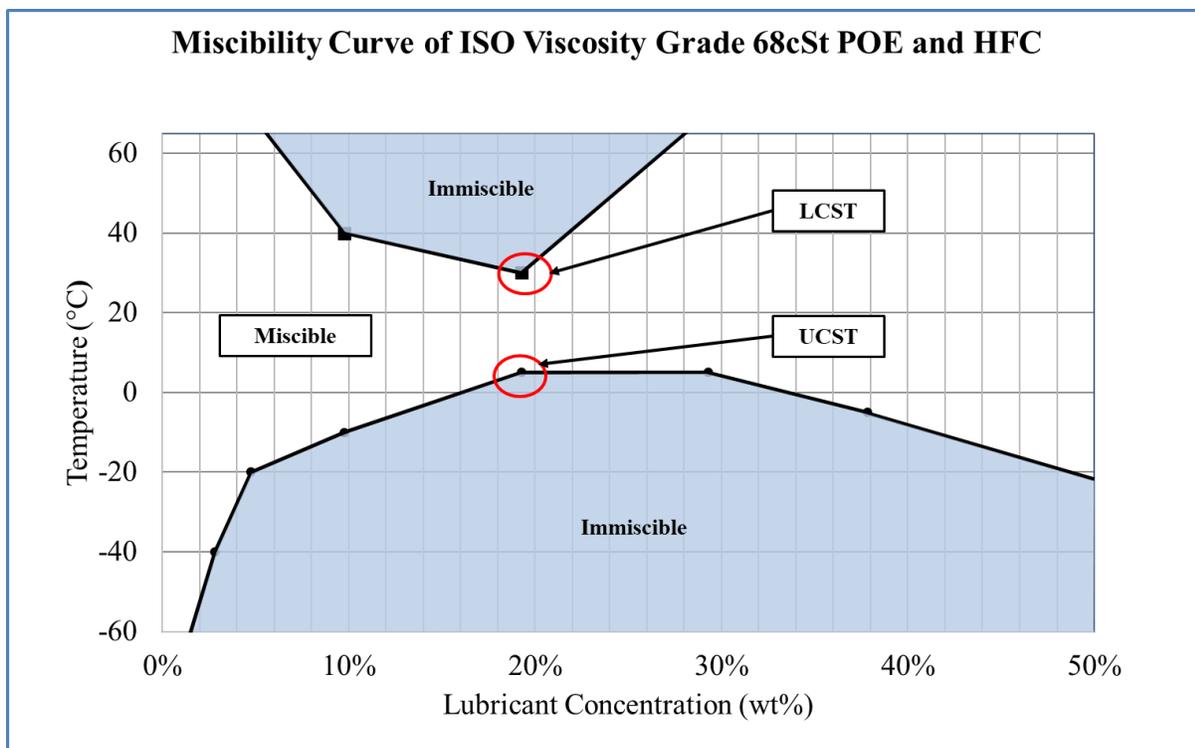

Figure 1: Example miscibility chart displaying Upper Critical Solution Temperature (UCST), Lower Critical Solution Temperature (LCST), measured miscibility points, miscible and immiscible regions.

Two phase miscibility behavior is demonstrated by distinct refrigerant-rich and lubricant-rich volumes separated by a meniscus. The relative density of each volume dictates their position, with the denser fluid on the bottom and the less-dense fluid on top. The liquid density of synthetic halogenated refrigerants is often significantly above 1 g/mL and will generally form the bottom layer when immiscible with a lubricant, whereas the liquid density of natural refrigerants (hydrocarbons, ammonia, carbon dioxide) is often well below 1 g/mL and forms the top layer when immiscible with lubricants. It is important to note that liquid density is strongly dependent on temperature, and phase inversion could occur depending on temperature.

When interpreting a miscibility chart, one might think that the miscible region on the chart describes a mixture that is clear and colorless single phase, and that the region designated as immiscible describes a mixture that consists of two distinct phases separated by a meniscus. However, as shown in **Figure 2**, there are other phase behaviors that may be encountered that fit neither of these descriptions, such as haziness or cloudiness. Separating what is considered hazy phase behavior from what is considered cloudy phase behavior is a matter of how opaque a solution is and varies depending on the method of analysis. For example, when using borosilicate glass tubes, whether the lines from notebook paper can be seen through the mixture can distinguish hazy from cloudy phase behavior. From a theoretical standpoint, any suspended droplet formation, no matter how small or how stable, would be considered immiscible. However, in an HVACR application the goal is for the lubricant to return to the compressor, so a stable but turbid solution may be acceptable and would be deemed usable. When miscibility tests are conducted decisions need to be made about which behaviors should be designated as acceptable and therefore would fall within the miscible region of the graph, and which should be designated as unacceptable, falling within the immiscible region of the graph.

To further investigate compressor lubricants for various applications, borosilicate miscibility tubes containing lubricant-refrigerant mixtures at multiple lubricant concentrations ranging from 1% to 50% (weight %) lubricant were created. The sealed tubes were equilibrated in hot and cold baths and observed at specific temperature intervals in order to document their phase behavior, potential phase changes, and to identify their critical solution temperatures. Throughout the testing process multiple miscibility behaviors that do not correlate with behaviors that ANSI/ASHRAE Standard 218-2019 acknowledges were observed. Phase behaviors such as refrigerant-lubricant time-based mixture stability, varying degrees and locations of cloudiness, droplets, and phase inversion were observed.
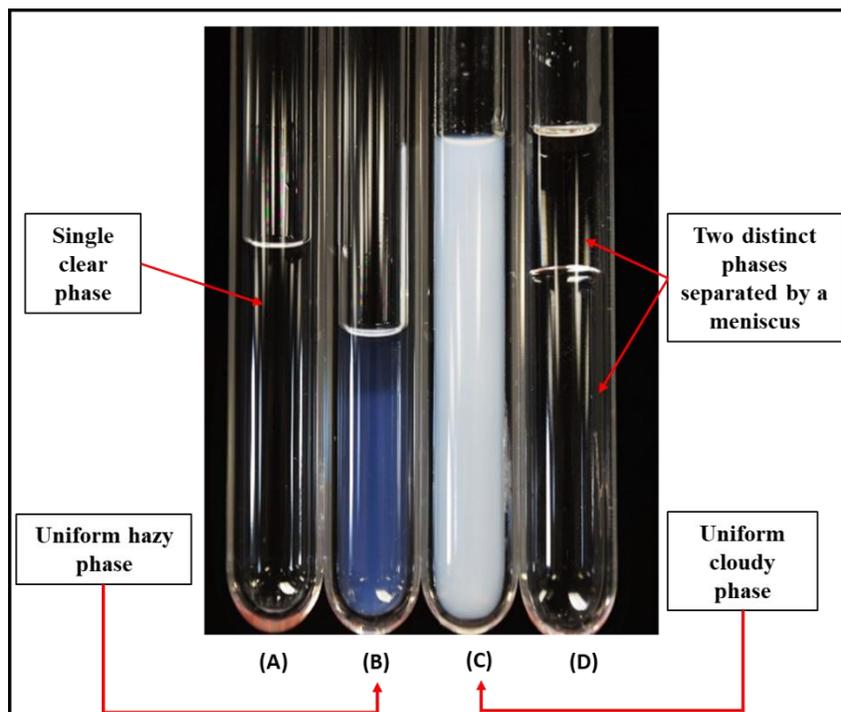

Figure 2: Borosilicate glass miscibility tubes demonstrating single, hazy, cloudy, and two-phase miscibility behavior (from left to right).

3. DISCUSSION

Categorizing behaviors as acceptable or unacceptable for an application can be challenging. Many observed phase interactions are not standard, and the applicable use of these behaviors are poorly defined. ANSI/ASHRAE standard 218-2019 does not acknowledge many types of miscibility behaviors observed in a laboratory setting, nor does the standard designate what phase behaviors are acceptable for use. Phase interaction such as the ones described above are considered fringe because it is not clear if these types of behaviors would be usable within HVACR. **Figure 3** depicts examples of these fringe phase behaviors.
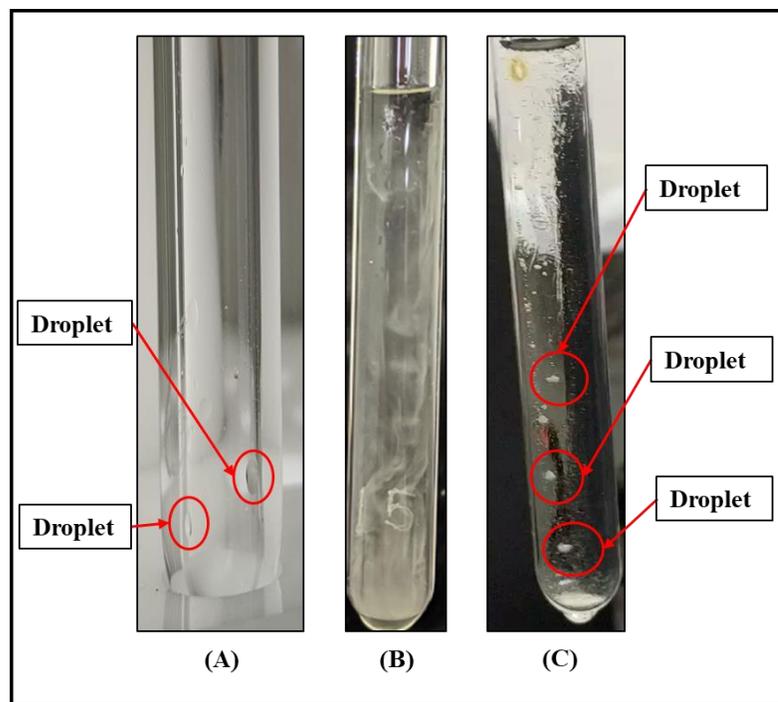
Figure 3: Droplets adhered to miscibility tube walls, nonuniform cloudiness, and droplets falling from top of tube.

Cloudy and hazy phase behavior occur due to a separation between the refrigerant and lubricant. The turbidity arises specifically due to light scattering between the two phases, and depends on droplet size, refractive index of the phases, and light wavelength (Song, Cho, Kim, & Kim, 2002). The phase separation arises when component-rich droplets (typically oil) form without coalescence or settling, creating what appears to be a uniform mixture without the presence of a meniscus. What appears to be one uniform phase is the separate lubricant rich and refrigerant rich layers suspended in a turbid state within one another. The presence of turbid fluid can be uniformly distributed throughout the entire solution or may be localized. **Figure 2** displays uniform hazy and uniform cloudy phase behavior. The stability of turbid refrigerant-lubricant mixtures can determine if the mixture is usable for a given application.

Hazy and cloudy phase interactions will separate into their respective lubricant rich and refrigerant rich layers when held at constant temperature, with hazy behaviors taking longer to separate verses cloudy. The difference in settling time between these two behaviors can be attributed to a difference in droplet size. Hazy refrigerant-lubricant mixtures have smaller refrigerant droplets than cloudy mixtures, which create a more stable suspension. Mixture stability can determine if lubricant-refrigerant mixtures are viable options even though they may be defined as immiscible from a theoretical standpoint. For example, consider a lubricant- refrigerant mixture that exhibits single phase cloudy behavior as shown in **Figure 2 (C)**. If the cloudy mixture is unstable and separates into a refrigerant rich layer and lubricant rich layer within 30 seconds, then this combination may be unacceptable within an application. However, if that same mixture has better stability and held a cloudy state for five minutes before separating, that mixture may be considered acceptable. Agitation can also play a role in whether certain lubricant-refrigerant combinations will be acceptable for use. Mixtures that require a great deal of agitation to become hazy may be less desirable than mixtures that require very little agitation to become cloudy even though cloudy mixtures are considered to have a greater degree of immiscibility.

Nonuniformity is another way hazy and cloudy phase behavior can be expressed. Unlike uniform hazy and cloudy phase behavior, when observing a nonuniform hazy/cloudy miscibility tube there is a distinguishable difference between the refrigerant rich region and the lubricant rich region. One possible cause of non-uniformity could be that a very rich lubricant layer and very rich refrigerant layer have formed. Due to the large difference in densities, these two layers are not able to properly mix from the level of agitation required by the method. **Figure 4 (A)** depicts uniform regions as a function of density within a nonuniform miscibility tube.

Droplets within a miscibility tube are another example of fringe miscibility behavior and were observed in two different forms: droplets forming after inversion or droplets adhered to the sides of the tube as depicted in **Figure 3 (A)** and **(C)**. Droplets adhered to the side of a miscibility tube have the potential to be refrigerant or lubricant. This could present efficiency problems in a system if the lubricant does not flow through the system properly and instead accumulates in heat exchangers or elsewhere. Droplets falling in a miscibility tube are assumed to be refrigerant due to the relative densities and is generally rarer. This form of droplet phase behavior could potentially cause problems in a system if these droplets all coalesce at once causing a large second layer but could be considered acceptable if the droplets formed were very small even though this behavior is theoretically immiscible.

In addition to these fringe behaviors, immiscible behaviors with unique attributes were also observed. Phase behaviors such as multiphase interactions, partially frozen and fully frozen mixtures have been observed during miscibility testing and would be considered unacceptable.

Multiphase behavior has been observed when multicomponent refrigerants are combined with multicomponent lubricants. Multiphase phase behavior is caused by a separation of the blended components whether it be the multicomponent refrigerant or lubricant into their discrete components. This separation is caused by preferential miscibility between the multicomponent refrigerant and lubricant. The behavior that is shown in **Figure 4 (A)** shows multiphase behavior of a blended refrigerant and an ester. The separation of the blended refrigerant and/or the multicomponent lubricant causes there to be a one clear phase and two distinct cloudy phases.
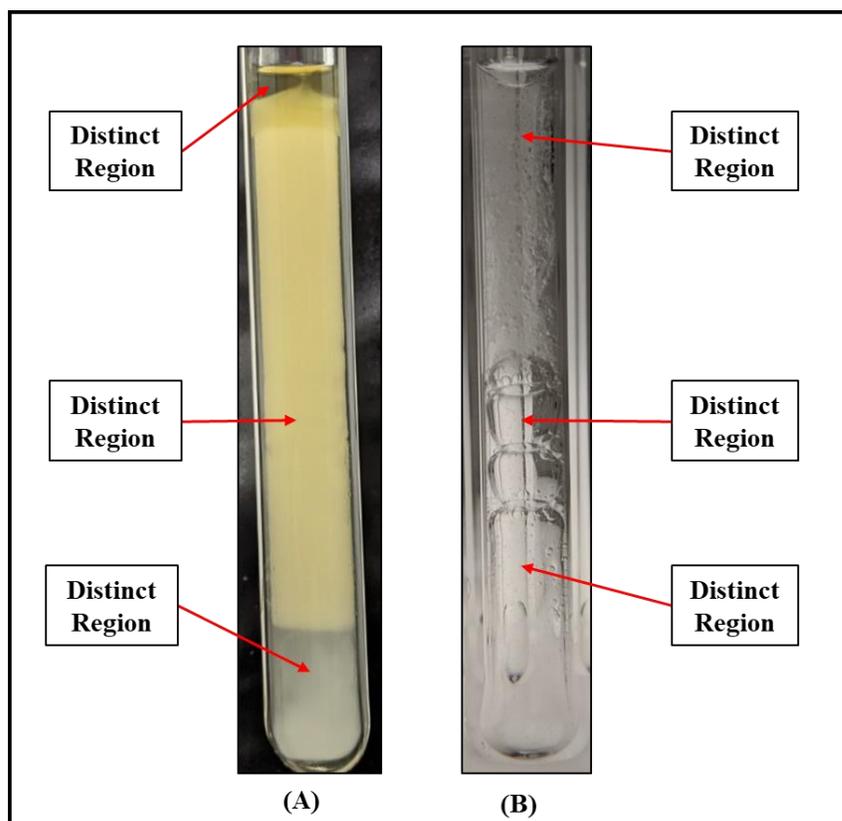

Figure 4: Multiphase behavior in borosilicate miscibility tubes

Pour point is an important lubricant property and can be defined as the temperature below which the lubricant loses its flow characteristics. When a lubricant-refrigerant combination reaches this temperature all, or part of the mixture may no longer flow. Immiscible tubes that are separated by a meniscus typically demonstrate partially frozen behavior while fully frozen behavior is observed in tubes that demonstrate single phase or uniform phase behavior.

Compressor lubricants freeze at higher temperatures than the refrigerants they are paired with. Due to this, miscibility tubes that contain a higher concentration of lubricant tend to exhibit frozen behavior.

4. Interpretation

Defining what miscibility behaviors can be considered acceptable is important and varies by application. Some applications require the mixture to be completely miscible or even completely immiscible, meaning the mixture has two distinct liquid phases separated by a meniscus. Where the line is drawn between what is considered acceptable miscibility behavior and what is considered unacceptable miscibility behavior can have dramatic effects on the applicable miscibility temperature range for a refrigerant-lubricant combination. What is truly acceptable behavior should be investigated to build a better understanding of what miscibility behaviors could be acceptable for an application.

Figure 1 demonstrates what the miscibility curve of a POE and HCF looks like when the acceptable miscibility behavior line is drawn between hazy and cloudy phase interactions. This yields a miscibility curve with an UCST of 5°C at 20% lubricant concentration and a LCST of 30°C at 20% lubricant concentration. If we assume the line between what is acceptable and unacceptable miscibility behavior is instead between cloudy and two-phase behavior the outcome would look significantly different. **Figure 5** demonstrates the same miscibility curve as **Figure 1,** but cloudy phase behavior has been considered acceptable for the application. The UCST is now (-5°C) at 30% lubricant concentration and LCST is 35°C at 20% lubricant concentration. This greatly opens the acceptable window of this refrigerant-lubricant combination and could potentially be usable compared to before.
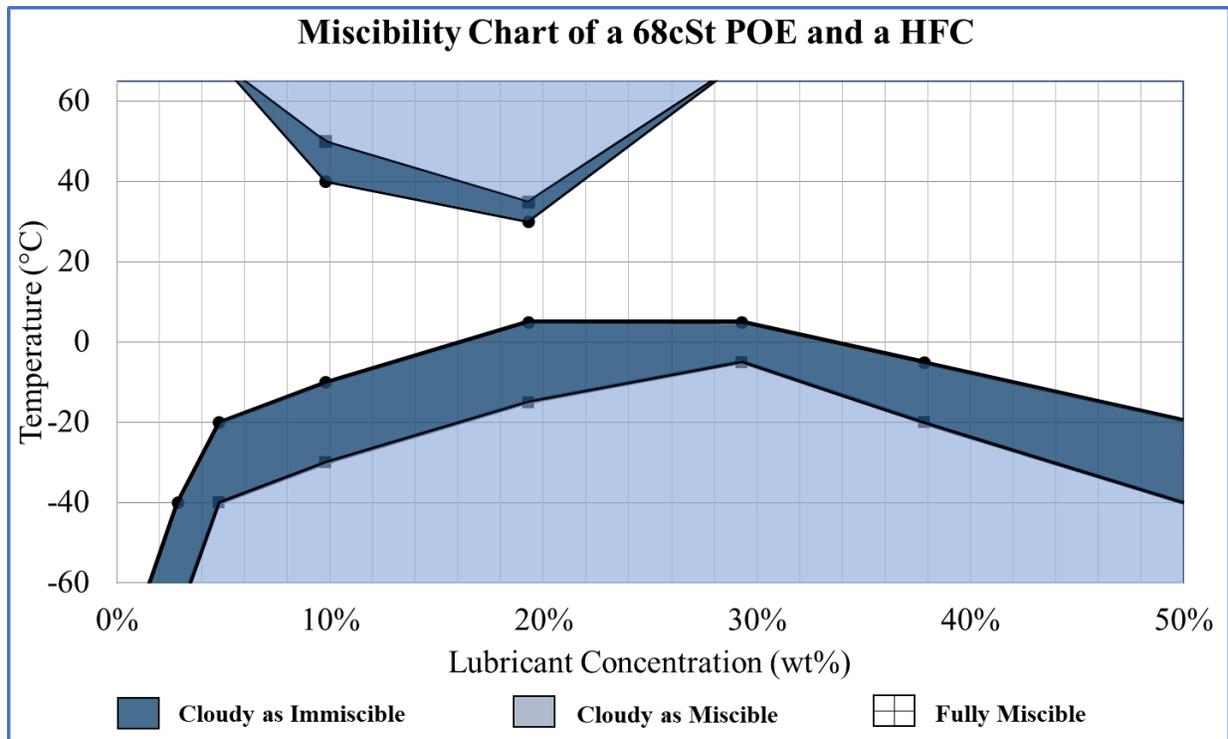

Figure 5: Comparison of miscibility curves between hazy phase behavior being considered acceptable and cloudy phase behavior being considered acceptable.

4.1 Chemistry Influence

The viscosity of a lubricant has dramatic effects on the applicable miscible range. When going from a lower viscosity to a higher viscosity within the same chemical family, the applicable miscible range typically decreases. **Figure 6** demonstrates this behavior. Within the same POE family, the 32cSt, 68cSt and the 220cSt lubricants have

UCST of (-35°C) at 20% lubricant concentration, (-20°C) at 20% lubricant concentration, and 0°C at 20% lubricant concentration respectively. Viscosity increase can be attributed to multiple factors that can affect miscibility temperature ranges including increasing molecule chain length, increasing branching or a combination of both.
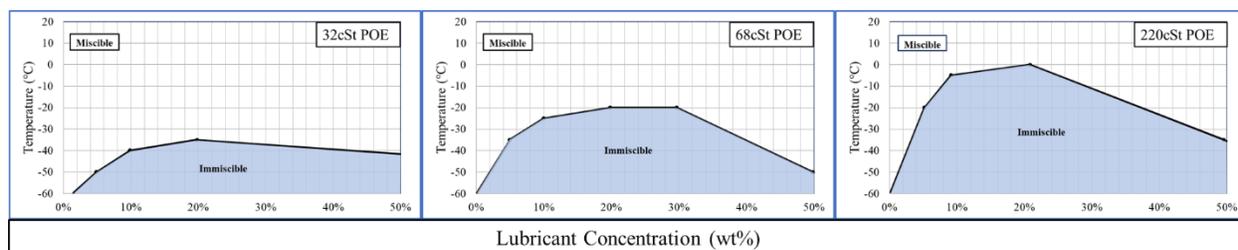

Figure 6: POE lubricant (similar family) miscibility with the same HFC as a function of viscosity grade.

In addition to the miscibility effect of increasing viscosity within a chemistry family, miscibility is influenced by varying chemistries at equal lubricant viscosity. **Figure 7** shows miscibility curves between varying POE chemistry lubricants at equal viscosities and the same HFC refrigerant. Image (A) in **Figure 7** has an UCST of 5°C at 15% lubricant, image (B) has a UCST of (-15°C) at 20% lubricant concentration and image (C) has an UCST of (-20°C) at 20% lubricant. Although these lubricants are all paired with the same refrigerant it can be observed that the varying chemistries between these lubricants have a direct impact on that lubricant-refrigerant applicable miscible range. The varying applicable miscible ranges between the three graphs that **Figure 7** shows a good example of the issue with assuming that any given 68cSt POE will be the same.
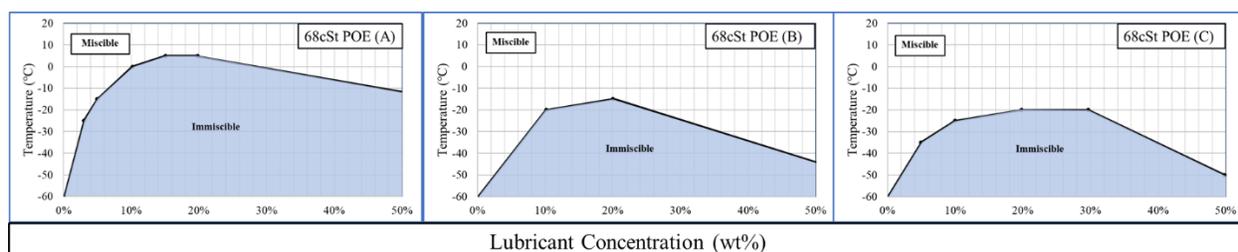

Figure 7: Miscibility curves of an HFC refrigerant with different POE lubricant chemistries of the same viscosity grade.

5. Conclusion

Changes in refrigerant chemistry and operating conditions are causing lubrication challenges due to generally increasing refrigerant dilution and lower working viscosity. Maintaining sufficient miscibility ranges while upholding all other lubricant properties is becoming increasingly difficult.

Real experimental refrigerant-lubricant miscibility behavior is more complicated than a miscible-immiscible dichotomy. Mixtures that include turbidity, transient stability, and small second-phase droplets are technically immiscible but may be acceptable in a specific HVACR application. A more nuanced view of lubricant chemistry is also important in understanding miscibility trends, as small changes in the design of a lubricant molecule can have an appreciable effect on miscibility.

By more clearly explaining miscibility behavior, system designers are better informed in what miscibility looks like in a practical setting. This understanding could lead to a wider range of acceptable lubricant chemistries for next generation refrigerants.

References

ASHRAE. (2019). *Method of Test for Lubricant and Refrigerant Miscibility Determination.* Atlanta: ASHRAE.

Cowie, J. M. (1991). *Polymers: chemistry & physics of modern materials.* New York: Chapman & Hall.

Elliot, J. R., & Lira, C. T. (1999). *Introductory Chemical Engineering Thermodynamics.* Upper Saddle River, NJ: Prentice Hall.

Hansen, C. M. (2004). 50 Years with solubility parameters - past and future. *Progress in Organic Coatings*, 77-84.

Lootin, O., Guillemet, P., & Lebreton, J.-M. (2003). Effects of synthetic oil in a compression refrigeration system using R410A. Part II: quality of heat transfer and pressure losses within the heat exchangers. *International Journal of Refrigeration*, 783-794.

Matsumoto, T., Kaneko, M., & Kawaguchi, Y. (2014, January 21). *Performances of New PVE Lubricants.* Retrieved from ASHRAE Technical Committee 3.4: https://tc0304.ashraetcs.org/documents/programs/ASHRAE%20NYC%202014_Idemitsu%20.pdf

Pate, M. B., Zoz, S. C., & Berkenbosch, L. J. (1993). MISCIBILITY OF LUBRICANTS WITH REFRIGERANTS. *AHRI*.

Rudnick, L. R. (2013). *Synthetics, Mineral Oils, and Bio-Based Lubricants.* Boca Raton, FL: Taylor & Francis Group.

Smith, G. L. (2014). *ASHRAE Technical Committee 3.1.* Retrieved from ASHRAE: https://tc0301.ashraetcs.org/documents/presentations/TC0301%20Seattle%20201406%20Seminar%2035%20Refrigerant%20Lubricant%20Properties%20-%20GSmith.pdf

Song, M.-G., Cho, S.-H., Kim, J.-Y., & Kim, J.-D. (2002). Novel Evaluation Method for the Water-in-Oil (W/O) Emulsion Stability by Turbidity Ratio Measurements. *Korean Journal of Chemical Engineering*, 425-430.

Wu, J., & Wang, G. (2013). Numerical study on oil supply system of a rotary compressor. *Applied Thermal Engineering*, 425-432.

Wu, J., Chen, Z., Chen, R., Du, Y., Duan, J., & Li, X. (2020). Oil retention and its mass distribution within a R290 room air conditioner using miscible or partially miscible oils. *International Journal of Refrigeration*, 20-28.