IDENTIFICATION AND CHARACTERIZATION OF NON-FLAMMABLE AZEOTROPIC MIXTURES FOR PRECISION CLEANING

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by

Jacob David Perry

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IDENTIFICATION AND CHARACTERIZATION OF NON-FLAMMABLE AZEOTROPIC MIXTURES FOR PRECISION CLEANING

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DEDICATION

This thesis is dedicated to all the people who have helped me to get to where I am now. However, I want to give special thanks to two of those people.

First, I want to thank my wife and best friend, Megan, for standing by me and giving me support in trying times. She has helped me remember to do things that need to be done, and try to stay on track when I feel like procrastinating or being unproductive. However, she has helped me to be unproductive enough to maintain my sanity. Most of all, she has loved me through easy times and hard times, and made it easier for me to love myself. I appreciate all the things that you do for me, both big and small.

I also want to thank my research advisor and friend, Dr. Darren L. Williams, for all the knowledge and advice that he has bestowed upon me. Not only knowledge and advice pertaining to research and school, but all the guidance for life in general as well. He has helped to keep me on track in my research and the writing of this thesis, as well as in life. I have learned so much from you in the time that I have known you, and wanted to let you know that it is appreciated.

ABSTRACT

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The goal of this thesis is to provide methods that can be used to search for new azeotropes with specific desired properties, and methods to characterize these new azeotropes. All azeotrope possibilities that were examined in this study were low-boiling azeotropes composed of non-aqueous solvents, and the desired properties were for the azeotropes to be non-flammable and have good solvency against hydrocarbon grease.

In this study, azeotropes were formed for use in cleaning applications, specifically vapor degreasing. For cleaning applications, the most important quality of the azeotrope is solvency. However, in a vapor degreaser flammability is an issue. To obtain the desired solvency in an azeotrope, the Hansen Solubility Parameters (HSPs) were used to decide what solvents were good candidates. However, the solvents that were found from this search were flammable. In an attempt to get the desired properties, the solvents were paired with non-flammable solvents that had similar boiling points to obtain a blend with good solvency and no flammability. Then, these pairs were mixed and distilled to identify whether the pairs formed low-boiling azeotropes.

The resulting azeotropes were characterized by obtaining their boiling point, flash point, thermal expansion coefficient, surface tension, density, viscosity and composition. The boiling points were obtained from the distillation process. The flash points were found using a modified ASTM D56 method. Thermal expansion coefficients were obtained through the dependence of the density on temperature. The surface tension and density were obtained using a DuNouy ring tensiometer. Viscosity was found using a ball drop viscometer. Finally, the composition was found using Raman spectroscopy. All these standard procedures can be found in the appendix.

A solubility parameter-based model for predicting azeotropic behavior in binary mixtures was explored as an extension of the results of this thesis work. The goal of this model is to predict the likelihood that a given pair of solvents will form a low-boiling azeotrope. Such a model would save time in the laboratory, reduce personnel exposure, and reduce waste by steering the researchers away from unpromising mixtures that are unlikely to form azeotropes.

KEY WORDS: Azeotrope, Vapor degreasing, Non-flammable, Hansen Solubility Parameters (HSPs), Flash point, Viscosity, Hydrostatic density, Surface tension, DuNouy tensiometer, Ball drop viscometer.

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PREFACE

This research project was a small piece of a bigger project. Dr. Darren L. Williams, from the Department of Chemistry at SHSU, received a research grant from the Strategic Environmental Research and Development Program (SERDP) to test solvent replacements for vapor degreasing.[1] SERDP was looking for more environmentally-friendly and worker-friendly solvents that could be used to replace trichloroethylene (TCE) and n-propyl bromide (nPB) in vapor degreasing operations. This was a concern, because of the impending ban from the use of these solvents. It was clear that a pure solvent was not an option as a replacement in vapor degreasing, because the many restrictions in place eliminated all of the good possibilities. In general, any solvent that had similar HSPs to the solvents that needed to be replaced, would also be flammable, toxic, or bad for the environment. The restrictions on solvent replacement require that the solvent is non-flammable, is not a hazardous air pollutant (HAP),[2] has a low volatile organic compound (VOC) content,[3] not an ozone depleting substance (ODS),[4] has a low global warming potential (GWP),[5] has good solvency for the particular soil that is being cleaned, and is cost effective.

In the case of nPB and TCE, the Environmental Protection Agency (EPA) categorizes them as HAPs. The causes of the categorization of these molecules as HAPs are the chlorine and bromine atoms in the molecules being deemed as hazardous. While these halogens can make molecules ODSs, these molecules are reactive enough to react in the lower atmosphere before they pose a threat to the ozone layer. However, these chlorine and bromine atoms also make these substances good solvents. The reason being that the chlorine and bromine atoms make the electron cloud of the molecule much more polarizable. So, instead of a hard ball of electrons that do not want to interact with anything, these molecules have a looser hold on those electrons. This increases the dispersion term of the HSPs for these molecules, which makes the solvents much better, because the dispersion term is the most important HSP term for solubility.

So, how could all the requirements for a replacement for nPB and TCE be met with a single replacement? The answer is a low-boiling azeotropic solvent blend. These blends will not separate upon boiling, and allow the blending of solvents with very different properties. This carries the possibility of suppressing unwanted properties and enhancing wanted properties. The obstacles that were faced in the work on the SERDP project led to the methods outlined in this thesis.

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CHAPTER I

Introduction & Theory

The purpose of this research project was to provide methods that could be used to search for azeotropic solvent blends with targeted properties as well as to characterize these blends. This study focused on non-flammable, non-aqueous, binary blends for cleaning applications. However, these methods should be applicable to all solvent blends used in any application where a blend with targeted properties is wanted. Another goal was to explore a way to predict azeotrope formation mathematically, without any vapor-liquid equilibrium (VLE) data.

Azeotropy

An azeotrope is a mixture of two or more components that maintains the same composition in both the liquid and gas phases. An azeotrope has properties that reflect its components' properties. For example, one solvent may have extremely good solvency but an extremely low flash point, while another solvent has a poor solvency but no flash point. If the two solvents form an azeotrope, the component with no flash point may quench the flammability of the other component. The solvency of the mixture will suffer due to the poor solvent, but sometimes the level of solvency required to do the job is actually much lower than that of the good solvent anyway.

There are other important considerations besides physical properties, which can be improved using azeotropes. An example of one such consideration is an occupational exposure limit. An occupational exposure limit is a maximum that an employee can be subjected to a particular chemical substance or other work-related health hazard such as extremely loud noise. Some of these limits are law and are enforced by the Occupational

Safety and Health Administration (OSHA) in the United States. There are several types of exposure limits including permissible exposure limits (PELs), threshold limit values (TLVs), time weighted average PELs (TWA-PELs), and short term exposure limits (STELs). A PEL is a purely legal limit that states that a worker cannot be exposed to more than a certain amount of a health hazard on any given day.[6] A TLV is a more scientific limit that defines a maximum amount that it is believed a worker can be exposed to a health hazard during every day of the person's working lifetime without having adverse effects.[7] A TWA-PEL is applicable to health hazards that are only noticeably harmful after accumulation, and allows workers to be subjected to these health hazards in large amounts for short periods of time without breaking the PEL.[6] STELs are applicable to health hazards that are immediately harmful to the human body, this type of exposure limit does not allow the exposure to be averaged over the entire work day.[6] These exposure limits for chemical substances are measured in parts per million (ppm) by volume. Considering all of these types of limits, some substances have no exposure limit, while others have exposure limits at very low concentrations. If a 1 to 1 mixture between one substance with no exposure limit, and one with a low exposure limit forms an azeotrope, then the exposure to each substance is halved. This means that a worker could be exposed to the azeotrope twice as long as the pure substance (with the low exposure limit) before reaching the limit.

By definition, an azeotrope cannot be separated using distillation, which can be a good or bad quality depending on the point of view. It is a good quality if the goal is to make a flammable solvent non-flammable by adding a flame retardant as was done in this study. This is because a certain amount of the flame retardant is required to quench the flammability, and if the composition were to shift, the mixture may become flammable again later. However, if there is a mixture of miscible liquids that needs to be separated, and they form an azeotrope, the fact that it cannot be separated by distillation can be very troublesome. There are ways to “break” an azeotrope, but these methods are beyond the scope of this thesis.

There are several types of binary azeotropes that have been reported. The categories are as follows: homogeneous azeotropes in completely miscible systems, homogeneous azeotropes in partially miscible systems, heterogeneous azeotropes, low-boiling or pressure maximum azeotropes, high-boiling or pressure minimum azeotropes, and double azeotropes.[8] A completely miscible system means that the mixture will always be one phase when temperature or pressure is changed. However, a partially miscible system will be one phase in a certain range of temperatures or pressures, but multiple phases in other ranges. A low-boiling azeotrope is an azeotrope that has a lower boiling point than the lowest boiling component of the mixture. Analogously, a high-boiling azeotrope is an azeotrope that has a higher boiling point than the highest boiling component of the mixture. A double azeotrope is a mixture that forms two different azeotropes at two different compositions, a low-boiling azeotrope at one composition, and a high-boiling azeotrope at a different composition. A binary azeotropic mixture is always defined as being in two of the categories given above, one of the first three categories and one of the last three categories. For example, a low-boiling azeotrope in a completely miscible system, uses two of the descriptive categories to form an enhanced description of a binary azeotrope. Some mixtures have also been reported as “near-azeotropic”, meaning that they are not actually azeotropic mixtures, but are treated similarly because they are extremely difficult to separate. The different types of binary azeotropic systems are represented by the phase diagrams in Figure 1.

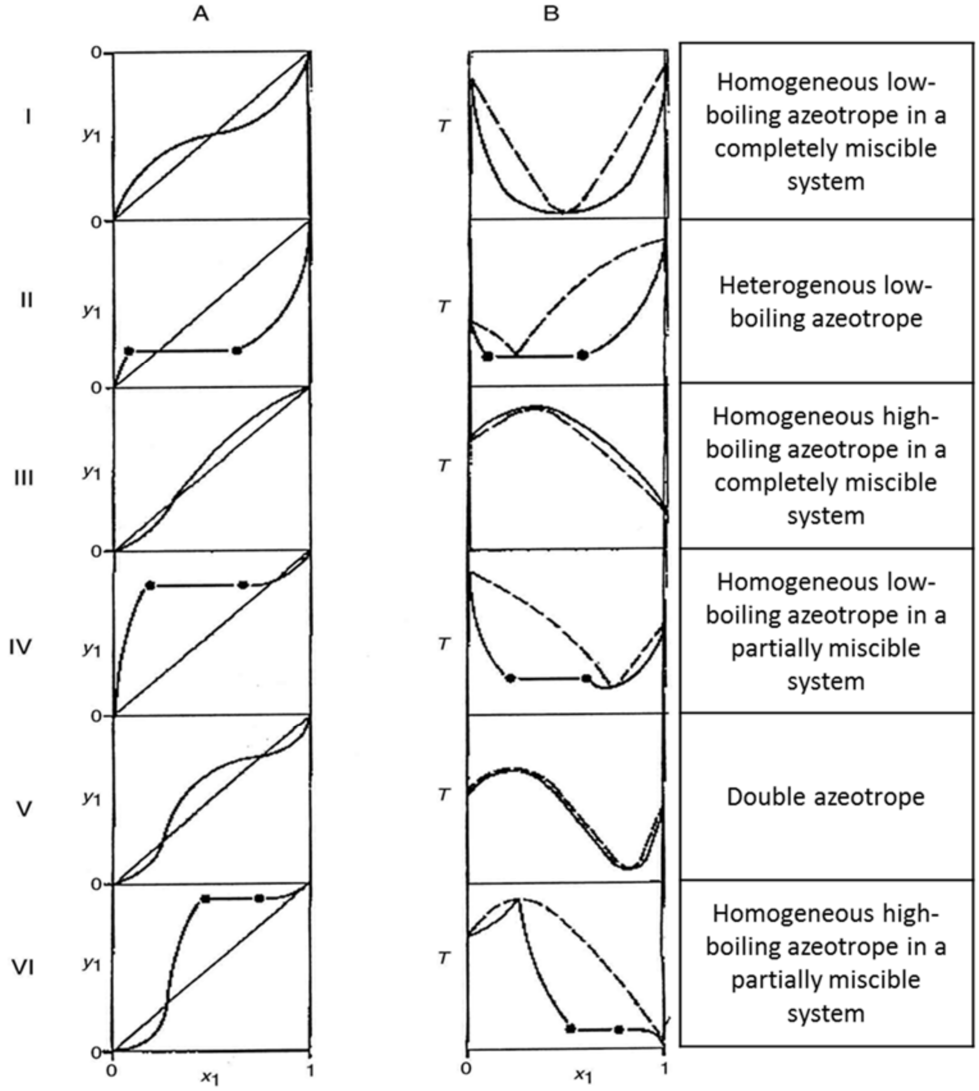


Figure 1. Different types of binary azeotropic systems.[8]

In Figure 1, the variables x_1 and y_1 are the mole fractions of the liquid and gaseous phases respectively in terms of one of the components. It is irrelevant which component is taken to be component one because these phase diagrams are generic examples that do not represent any particular azeotropes, and if the other component was taken as component one, the pattern would be a mirror image of the pattern shown. Column A shows plots of y_1 versus x_1. Column B shows plots of temperature versus x_1, and temperature versus y_1 on the same plot. In column B, continuous lines represent x_1, and dashed lines represent y_1. Row I shows a homogeneous low-boiling azeotrope in a completely miscible system. Row II shows a heterogeneous low-boiling azeotrope. Row III shows a homogeneous high-boiling azeotrope in a completely miscible system. Row IV shows a homogeneous low-boiling azeotrope in a partially miscible system. Row V shows a double azeotrope, which is a mixture that forms a high-boiling azeotrope and a low-boiling azeotrope at different compositions. Row VI shows a homogeneous high-boiling azeotrope in a partially miscible system.

Mixture Thermodynamics

When preparing mixtures of solvents for dissolving a substance, the mixture needs to be one continuous phase so that the properties are the same throughout the mixture. So, the components need to like each other enough to spontaneously mix. Spontaneous mixing is not to be confused with azeotropy. Azeotropes do not have to be homogeneous. This spontaneous mixing can be predicted using the Gibbs free energy of mixing (ΔG_{mix}). A negative value for ΔG_{mix} means that the substances will spontaneously mix, and a positive value predicts that they will not spontaneously mix. ΔG_{mix} can be expressed in terms of enthalpy (ΔH_{mix}), entropy (ΔS_{mix}), and temperature (T) as seen in eq 1. Equations 1, 2, and 3 were found in several different texts.[9–13]

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} \tag{1}$$

This equation shows that higher temperatures increase the likelihood of spontaneous mixing if ΔS_{mix} is positive. Luckily, entropy always favors mixing due to the universe's tendency toward disorder. This can be seen in eq 2.

$$\Delta S_{mix} = -n_T R(x_1 ln x_1 + x_2 ln x_2) \tag{2}$$

In eq 2, n_T is the number of moles of molecules, R is the gas constant and is equal to 8.3145 J mol^{-1} K^{-1}, x_1 and x_2 are the mole fractions of components 1 and 2 respectively. Because the mole fractions are always less than one, the natural logarithms are always negative which causes ΔS_{mix} to always be positive. This makes ΔS_{mix} always favor mixing. From this, it can be deduced that ΔH_{mix} is the sole reason for two substances to not spontaneously mix. ΔH_{mix} can be calculated using eq 3.

$$\Delta H_{mix} = \phi_1 \phi_2 V_T (\delta_{T1} - \delta_{T2})^2 \tag{3}$$

Equation 3 uses the volume fractions (ϕ) in terms of the total volume (V_T), and the Hildebrand parameter (δ_T), which is described in the HSP section of this chapter. The 1's and 2's represent component 1 and 2 of the mixture respectively.

Hansen Solubility Parameters (HSPs)

Hansen solubility parameters are a quantitative way of predicting if one substance will dissolve in, or interact with, another. Hansen solubility parameters were produced by Charles M. Hansen in 1967 as part of his Ph.D. thesis. They were developed through the idea that if a molecule interacts with its own kind in a similar way that another molecule interacts with its own kind, then the two different molecules are energetically alike, and like dissolves like. This thinking was started by Joel H. Hildebrand with the Hildebrand solubility parameter.[12] Equations 4, 5, 6, and 9 in this section were taken from the HSP user handbook.[11] The Hildebrand solubility parameter is defined as the square root of the cohesive energy density as shown in eq 4.

$$\delta_T = \sqrt{\frac{E}{V_M}} \tag{4}$$

In eq 4, δ_T represents the total solubility parameter or Hildebrand solubility parameter. The cohesive energy, E, is the sum of all the cohesive bonds in the substance. Thus, E can be measured by breaking the cohesive bonds, or simply evaporating the liquid substance. So, E is equal to the change in enthalpy for vaporization (ΔH_{vap}). V_M represents the molar volume of the substance in mL / mol, and can be calculated by dividing the molar mass by the density of the substance. Hansen reasoned that the total cohesive energy could be split into three parts as seen in eq 5.

$$E = E_D + E_P + E_H \tag{5}$$

In eq 5, E_D is the dispersion cohesive energy, E_P is the polar cohesive energy, and E_H is the hydrogen bonding cohesive energy (also called electron exchange cohesive energy). These cohesive energy terms can each be divided by the molar volume, and using the relationship in eq 4, eq 6 can be obtained.

$$\delta_T^2 = \delta_D^2 + \delta_P^2 + \delta_H^2 \tag{6}$$

Solubility relies on the square root of these three different terms when using the HSP model. These three HSPs are the square root of the cohesive energy density in (J/mL)$^{1/2}$ from dispersion forces (δ_D or D), dipolar intermolecular forces (δ_P or P), and hydrogen bonding forces (δ_H or H). Large differences in the D, P, and H values can cause the ΔH_{mix} to become large enough to make ΔG_{mix} positive, so that the substances will not spontaneously mix.

The HSPs can be estimated for any substance whose refractive index and dipole moment are known. According to the Hansen Solubility Parameters in Practice (HSPiP) e-book, the dispersion term can be estimated by eq 7 using the refractive index (R).[10]

$$\delta_D = \frac{R - 0.784}{0.0395} \tag{7}$$

This equation represents a correlation and is by no means perfect. An equation was also given to estimate the polar term from the dipole moment (μ) of the molecule in units of Debyes. This equation can be seen here as eq 8.[10]

$$\delta_P = \frac{37.4\mu}{V_M^{1/2}} \tag{8}$$

The hydrogen bonding term can be calculated by subtracting the polar and dispersion cohesive energies from the total cohesive energy, then dividing by the molar volume and taking the square root as in eq 4.

The three parameters can be calculated in other ways such as using group contributions, but these methods are beyond the scope of this thesis. The HSPiP software has an extensive database of HSP values and other properties for many compounds. The HSPiP software also includes a tool that will estimate the HSPs of a molecule whose structure is submitted to the program.

The usefulness of the HSPs is easily seen when the parameters are plotted in a 3-dimensional plot known as the Hansen space. Each set of HSP values are a set of coordinates in three dimensions. However, this 3-dimensional space has been deemed the Hansen space instead of Cartesian space, because the D parameter is multiplied by two in order to make interaction zone spherical with radius R_0. The R_0 defines a sphere for the solute and any solvent inside of the sphere is predicted to interact strongly with the solute. R_0 is an experimentally determined value. This value is determined by testing the solubility of the solute in many different solvents and finding the distance in Hansen space that is larger than the distance to the solvents that will dissolve the solute, but smaller than the distance of those that will not. The Hansen space can be seen in Figure 2.[14]

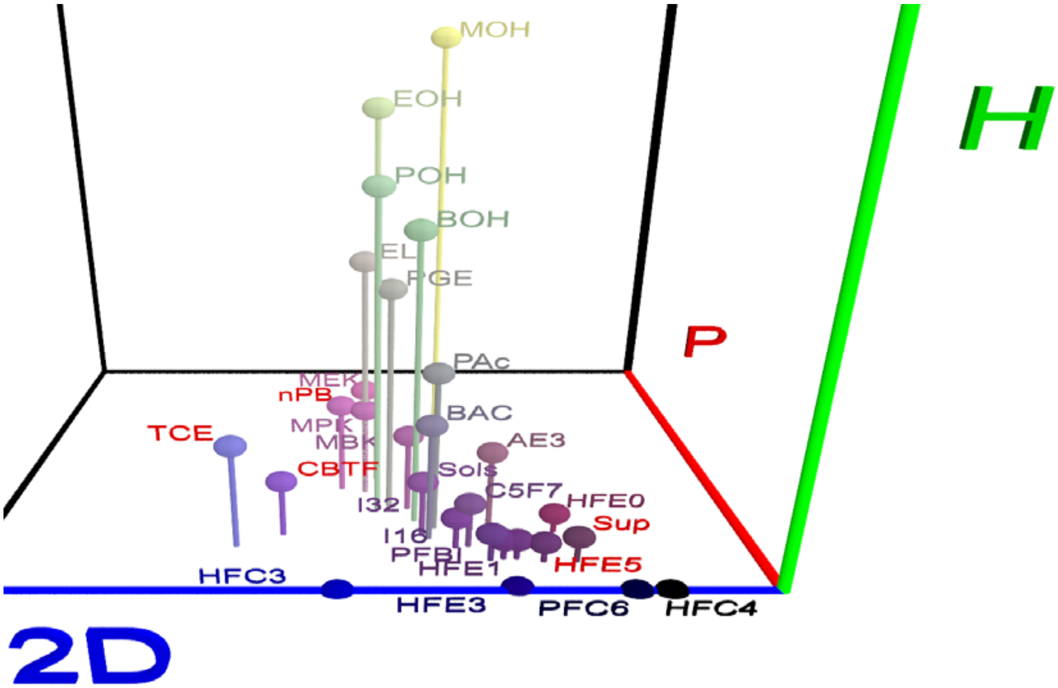


Figure 2. The Hansen space showing the solvents used in this study.[14]

In Figure 2, the substances are abbreviated according to Table 1, which is located in Chapter II. The colors are weighted combinations of the three colored axes. The closer two substances are in Hansen space, the stronger their interaction is predicted to be. Therefore, the points in Figure 2 with similar colors are predicted to interact strongly. The distance between two points in Hansen space is termed the Hansen distance (R_a). The Hansen distance can be calculated using eq 9.

$$R_a = \sqrt{4(\delta_{D2} - \delta_{D1})^2 + (\delta_{P2} - \delta_{P1})^2 + (\delta_{H2} - \delta_{H1})^2} \tag{9}$$

In eq 9, the 1’s and 2’s signify that these are the values that correspond to either substance 1 or substance 2.

The Hansen space is very useful for finding suitable solvents for a particular solute or for finding a replacement for a commonly used solvent. Solvent blends are also very useful, and easily made with this tool. For example, if the solvents that are available have HSPs that are outside the interaction sphere of a particular solute, then two solvents that are on opposite sides of the solute in Hansen space could be blended to bring the blend inside the interaction sphere. The HSPs of the blend are just the volume-fraction weighted average of the HSPs of the components. This idea was used in this study to predict possible solvent blends to use for dissolving hydrocarbon grease, however, this method cannot predict if the blend will form an azeotrope.

Using the Hansen space, the HSPs of a solid or semi-solid substance can also be easily determined experimentally. Using many different solvents whose HSPs are known and thoroughly cover Hansen space, one could attempt to dissolve the substance. If each solvent is scored, the HSPs of the solute would be somewhere in the middle of the cluster of good solvents in Hansen space. This is not an exact measure, but it is a good estimate. The HSPiP software can help with this endeavor as well, because the program allows the user to select the solvents that were used in the experiment and input the scores that were given to those solvents. Then, the program will pinpoint the likely position of the solute in Hansen space based on the scores that were provided for each solvent, and it will give the R_0 of the interaction sphere that contains the good solvents and excludes the bad solvents.

Structural & Operational Information about Vapor Degreasers

The purpose of this project was to find a solvent replacement for use in vapor degreasers, so it is important to provide some information about what a vapor degreaser is and how it works. A vapor degreaser is a piece of machinery used in industrial settings for precision cleaning. A diagram of a top-down view of the inside of a vapor degreaser is seen in Figure 3 to help describe the parts of a vapor degreaser.

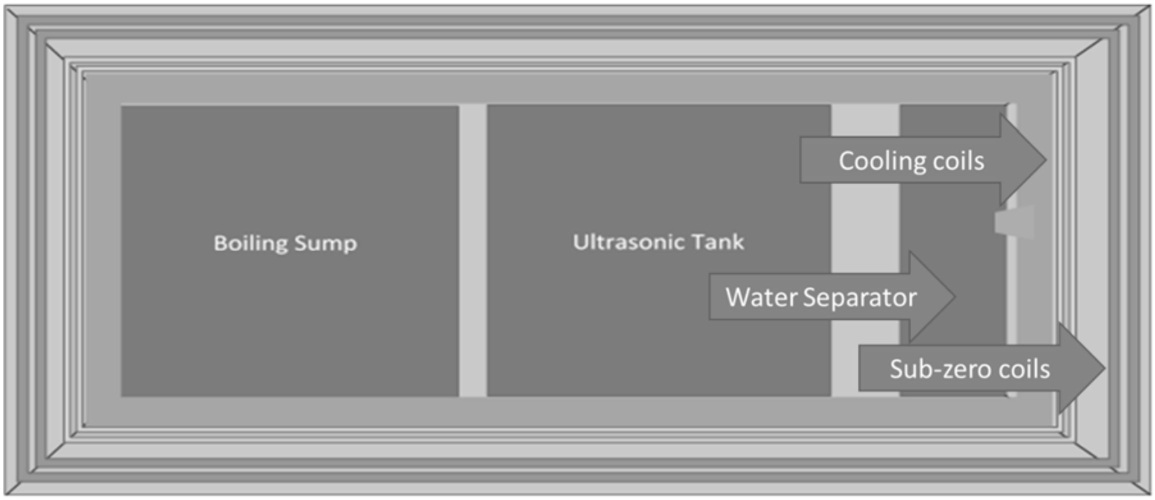


Figure 3. Diagram of the inside of a vapor degreaser (top view).

In Figure 3, it can be seen that there are two major tanks in the bottom of a vapor degreaser. These two tanks are the boiling sump and the ultrasonic tank. The other important parts are the coils along the walls of the degreaser. When a degreaser is operating, solvent is boiled in the boiling sump. This creates vaporized solvent. The bottom set of cooling coils cool the vaporized solvent, allowing it to condense and drip down into the water separator tank. The top set of cooling coils are referred to as the sub-zero coils, because they are super-cooled in an attempt to condense all of the vaporized solvent reaching that height in the degreaser. This helps to contain the solvent and prevent it from boiling away. This is very important for many reasons. Any solvent could be harmful if enough of it is inhaled, the solvent could be harmful to the environment, and boiling away all of the solvent is wasteful and defeats the purpose of the machine.

These sub-zero coils also trap moisture to keep the solvent dry by condensing and freezing water vapor in the air that gets close to the coils.

The part of the vapor degreaser that makes the machine work, is also the part that causes concern. When the vapor degreaser is operating, the heater of the boiling sump is creating as much vaporized solvent as possible and the cooling coils are condensing the solvent when it reaches a certain height. This creates a concentrated vapor zone between the surface of the solvent in the boiling sump, and the first set of cooling coils as seen in Figure 4. The first set of cooling coils cannot contain 100 percent of the vapor, and this creates a vapor concentration gradient.

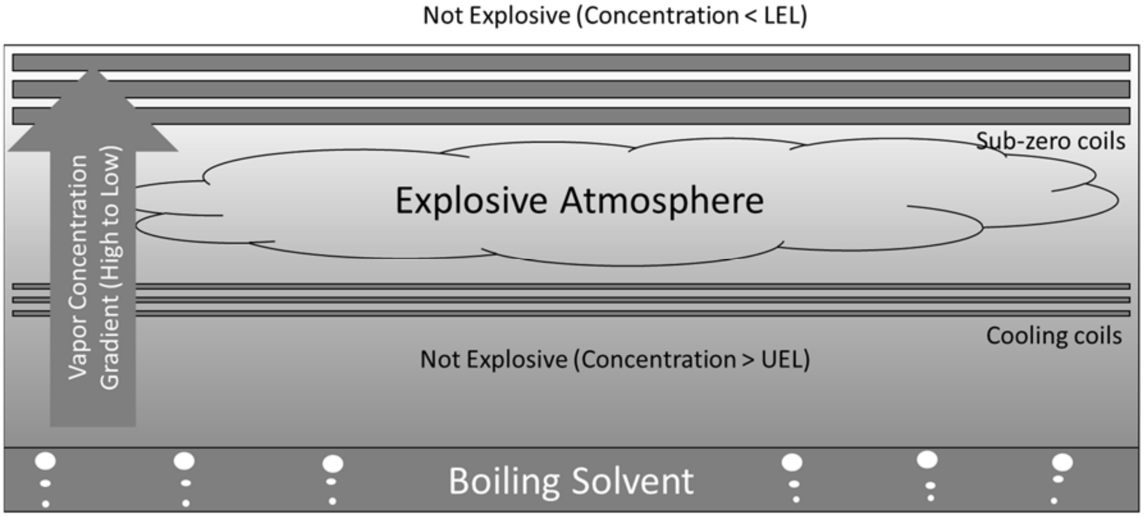


Figure 4.The vapor concentration gradient and explosive environment in a vapor degreaser.

The cleaning takes place in the concentrated vapor zone between the boiling solvent and the first set of cooling coils by allowing the solvent vapor to condense on a colder object and drag off any grease. The continuous vaporization and condensation is analogous to distillation because the cooling coils are not perfect at containing the solvent, and the solvent is condensing and running into a water separator before reentering the ultrasonic and boiling tanks. This provides the reasoning for needing a low-boiling azeotrope if a mixture is used. An azeotropic mixture keeps the vapor and liquid the same composition. More cleaning takes place in the ultrasonic tank when the greasy object is submerged in solvent and ultrasonic waves collapse solvent cavities. The collapse of solvent cavities accelerates the solvent molecules, some of which impact the surface of the object and help to remove grease and other particulates.

The vapor concentration gradient, seen in Figure 4, from the surface of the liquid to the outside of the degreaser will create an explosive atmosphere if flammable solvent is used. This occurs, because every flammable substance has an Upper and Lower Explosive Limit (UEL & LEL) when vaporized in air. These limits define the concentrations of flammable vapor in air at which there is either too much vapor in too little air to combust (UEL), or there is too little vapor in too much air to combust (LEL). The concentrations in the gradient that are between these two limits will combust if an ignition source is applied. The ignition source could be anything from a small spark caused by plugging something into an electrical outlet to an ignited Bunsen burner across the room, because the cooling coils are not perfect at containing the vapor and the amount of vapor that escapes depends on the sub-zero coils ability to condense the vapor. This is why solvents used in a vapor degreaser should be non-flammable, and this also justifies the need for flash point measurements in this study to determine if a solvent is safe for use in a vapor degreaser.

Flash Point

A flash point is a minimum temperature at which a flammable substance's vapor will ignite in the presence of an ignition source, and rapidly lead the flame back to the source of the vapor. The process of rapidly leading the flame back to the source of the vapor is referred to as "flashing", hence the name "flash point". At this temperature, the vapor pressure of the substance is high enough to create a ratio of flammable molecules to oxygen in the air that overcomes the LEL of the substance. To make the flash point measurement as objective as possible, the ASTM D56 method is very clear about what constitutes a flash, because the operator must see the flash event (which occurs very quickly) and judge if it was a flash or not. Also, some substances participate in burning by making the test flame larger, changing its color, or producing a halo around it, while not actually exhibiting a flash. Flash point is not the only tool for determining flammability. The fact that a substance does not flash, does not mean that the substance will not burn. However, flash point is a good method for determining if a substance is safe for use in a vapor degreaser.

There are different methods of flash point testing for different types of materials. There is open-cup flash point, which is used for substances with low volatility, and closed-cup flash point, which is used for substances with high volatility. Within these categories, there are tests that deal with large volumes (such as liters or more), small volumes (such as microliters or less), different types of ignition sources, different methods of heating the sample, with stirring, without stirring and many more variations. In this study, a closed-cup flash point tester with an electric bath heater and a natural gas ignition flame was used. More information about the flash point tester, procedure, and reasoning for choices made for this test can be found in other Chapter II and Chapter IV of this thesis.

Distillation Theory

A simple distillation of a mixture of two liquids will yield a distillate that is enriched in the component of the mixture that has the lower boiling point. A fractional distillation is a little more complex. A fractional distillation will yield the pure component with the lower boiling point in most cases, because of the long fractionating column that is used. This fractionating column works as if many simple distillations are occurring as the distillate makes its way up the column. The hotter-to-cooler temperature gradient in the column allows the sample to vaporize and move up the column then condense on a cooler part of the column to run down into a hotter part which vaporizes the sample again. In most cases, more than enough of these simple distillation steps occur to purify the lowest boiling component as the distillate in a fractional distillation.

The cases where the distillate is still composed of more than one substance after fractional distillation are deemed low-boiling azeotropic mixtures or near-azeotropic mixtures. When looking at a temperature versus composition phase diagram, which can be seen in Figure 5, a distillation will always yield a distillate that is down-hill on the curve from the starting point.

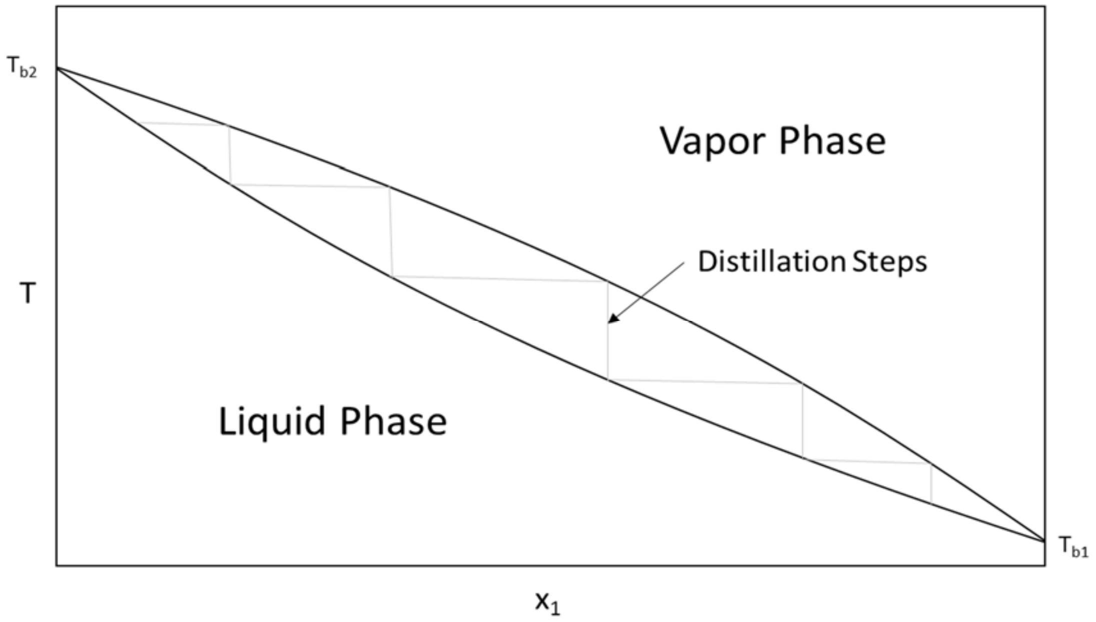


Figure 5. Temperature versus composition phase diagram of a non-azeotropic mixture.

In Figure 5, T_{b1} and T_{b2} represent the boiling points of components one and two respectively. One distillation step shows what happens to the composition if a simple distillation is performed. For vaporization of the mixture one follows the horizontal line, and for condensation the vertical line. In a temperature versus composition phase diagram of a low-boiling azeotrope, the azeotropic point is down-hill from everything. So, the azeotrope will be collected as the distillate. If a mixture is collected as the distillate, and it is not an azeotrope, the mixture would be near-azeotropic.

Hydrostatic Density

Density determination using a DuNouy Tensiometer is quite simplistic. The mass of a Pyrex standard density sinker is taken. This is referred to as the dry mass (m_d), and the density of the sinker is represented by ρ_1. The sinker is submerged in the liquid whose density (ρ_2) is to be determined, and the sinkers apparent mass is taken. This is referred to as the wet mass (m_w). These measurements are discussed in more detail in Chapter II and the Appendix. The density of the air (ρ_3) is also used, but is relatively constant in a temperature controlled room. The setup of this experiment is shown in Figure 6.

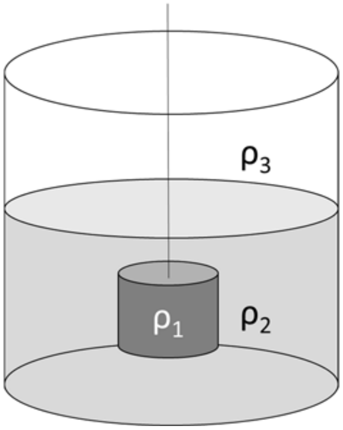


Figure 6. Diagram of a hydrostatic density measurement.

Once all of this information is gathered, the density of the liquid can be calculated using eq 10.[15]

$$\rho_2 = \left(\frac{m_d - m_w}{m_d}\right)\rho_1 + \left(\frac{m_w}{m_d}\right)\rho_3 \tag{10}$$

Because density changes with temperature, and surface tension and viscosity depend on the density, the density measurement will need to be interpolated or extrapolated to the temperatures of those measurements. The interpolation or extrapolation can be performed using the thermal expansion coefficient (β). This coefficient can be calculated for a small temperature range as seen in eq 11, and its derivation and the derivation of its relation to density is discussed elsewhere.[13,16]

$$\beta = \frac{\left(\frac{\rho_0}{\rho_1}\right)-1}{(T_1-T_0)} \tag{11}$$

In equation 11, ρ_0 and T_0 are the density and temperature at the lower temperature, and ρ_1 and T_1 are the density and temperature at the higher temperature.

Surface Tension

The experimental steps taken during a surface tension measurement with a DuNouy ring tensiometer are simple, however, the calculations needed to get to the final surface tension are quite long compared to the density calculations. A diagram of the tensiometer can be seen in Figure 11 in Chapter II. In the measurement, a platinum-iridium ring is submerged in the liquid sample, and the liquid sample is slowly lowered until the ring begins to rise out of the surface. When the ring rises out of the surface of the liquid, it lifts the meniscus. The basic concept of the measurement is that the maximum amount of liquid lifted by the ring is proportional to the surface tension of the liquid. This lifting of the meniscus can be seen in Figure 7. The figure was used with permission from reference 14.

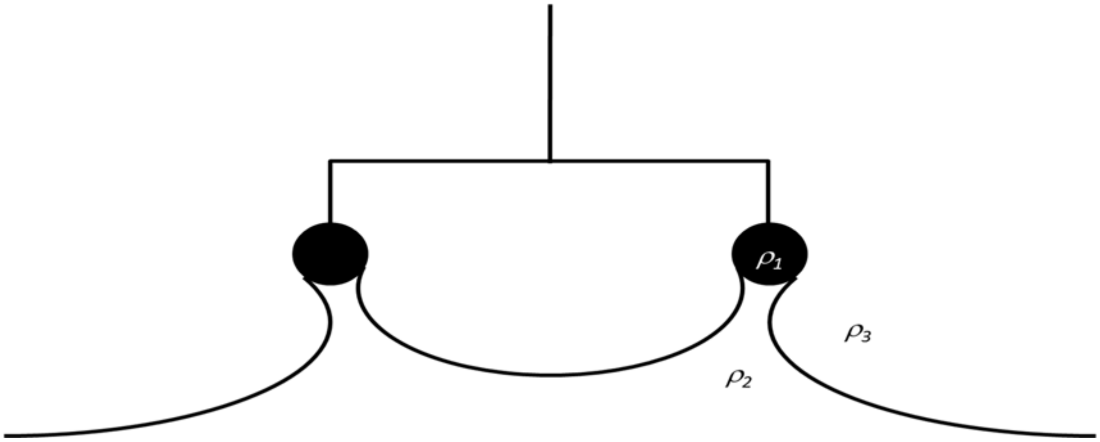


Figure 7. Tensiometer ring lifting the meniscus of the sample.[15]

This measurement produces a force curve such as the one shown below in Figure 8.

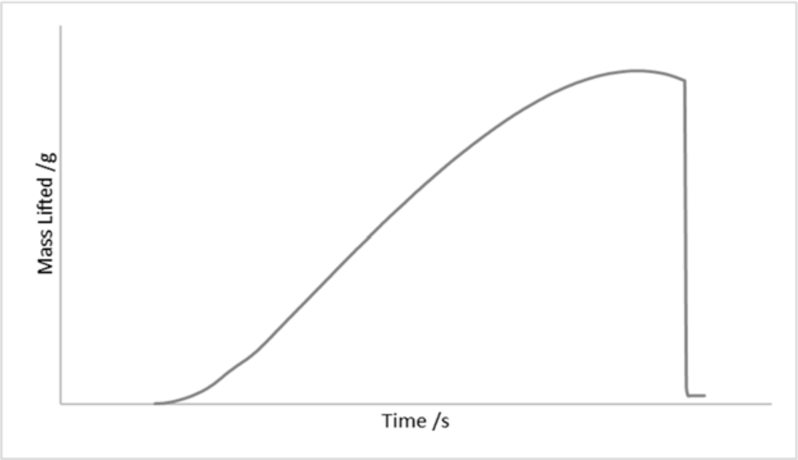


Figure 8. Force curve example.

The mass lifted reaches a maximum value, then the mass starts to decline as the meniscus thins before it breaks free from the ring. The maximum mass lifted (m) is used to calculate the maximum liquid volume lifted (V) in eq 12. Equations 12-20 were taken from reference 14.[15]

$$V = \frac{m}{\rho_2 - \rho_3} \tag{12}$$

The maximum mass lifted can also be used to calculate the maximum equilibrium force of detachment (F) as seen in eq 13.

$$F = mg \tag{13}$$

In eq 13, g is the gravitational acceleration ($g = 980.665$ cm/s^2). This force and the radius of the ring (R) can be used to calculate a first approximation of the surface tension (γ) as seen in eq 14.

$$\gamma = \frac{F}{4\pi R} \tag{14}$$

Two consecutive corrections are applied to this approximation. The sources of these corrections are discussed further elsewhere.[15] The first correction term is for the interface between phase 2 and phase 3, the liquid and the air. This correction (f_{23}) is a function of R^3/V and R/a where a is the wire radius of the ring. This correction term is applied as seen in eq 15.

$$\gamma_{23} = \frac{F}{4\pi R} f_{23} \tag{15}$$

The second correction term is calculated using the shape of the interface between phases 2 and 3. The corrected surface tension from eq 15 is used to calculate a scaling factor (C_{23}), seen in eq 16, for *R* and *V*.

$$C_{23} = \frac{(\rho_2 - \rho_3)g}{\gamma_{23}} \tag{16}$$

This scaling factor is applied to the radius of the ring as seen in eq 17.

$$R' = R\sqrt{C_{23}} \tag{17}$$

The scaling factor is applied to the volume lifted as seen in eq 18.

$$V' = VC_{23}^{3/2} \tag{18}$$

R' and *V'* are used to calculate the second correction to the surface tension (*f '*) as seen in eq 19.

$$f' = \frac{4\pi R'}{V'} \tag{19}$$

The final surface tension value is calculated using eq 20.

$$\gamma' = \left(\frac{F}{4\pi R}\right) f' \tag{20}$$

It is recommended to the reader to do these calculations in a spreadsheet, especially if the calculations need to be done more than once.

Viscosity

Viscosity can be defined as a measure of a substance's resistance to flow. This property can be measured in a few different ways. However, the ball-drop method was used in this study. The experimental steps for this method are discussed in Chapter II. The main concept of the experiment is that a ball of known density is allowed to fall through a tube whose dimensions are well defined and is filled with the sample whose density is also known. When the ball is falling to the bottom of the tube, it forces the liquid sample to flow around it. This flow rate is measured by the amount of time that the ball takes to fall through a predetermined timing zone. Equations 21 and 22 are taken from ASTM D1343.[17] Equation 21 is normally used to calculate a term known as the viscometer constant (*K*), which contains all of the information about the dimensions of the viscometer tube and ball.

$$K = 2gr^2 \frac{\left(1-2.104\left(\frac{d}{D}\right)+2.09\left(\frac{d}{D}\right)^3\right)}{9L} \tag{21}$$

In eq 21, g is the acceleration of gravity in cgs units, r is the ball radius in cm, *d* is the ball diameter in cm, *D* is the tube diameter in cm, and L is the distance of the ball-drop in cm. Equation 22 is used to calculate the viscosity (η).

$$\eta = K(\rho_b - \rho_s)t \tag{22}$$

In eq 22, ρ_b is the ball density in g/mL, ρ_s is the sample density in g/mL, and *t* is the time of the ball-drop in seconds.

Wetting Index

The wetting index (*W*) is a measure of how well a solvent will physically be able to wet a surface and flow under particulates on the surface. This wetting index is focused on the properties of the solvent, and not the interactions that the solvent has with any particular surface. In precision cleaning, it is good for the solvent to have a good solvency for the solute of interest, but it is better for the solvent to also be able to wet the entire surface of the item that is being cleaned. The entire surface of the item includes grooves, holes, threads, and any other areas that may be soiled. A higher wetting index indicates that the solvent will wet the surface better, while a lower wetting index indicates the opposite. The wetting index relies on density in g/mL, surface tension in mN/m, and viscosity in cP. This was the main reason for measuring these properties in this study. The equation for calculating the wetting index was deduced from the data in the Kanegsberg book, and is shown here in eq 23.[18]

$$W = \frac{1000\,\rho}{\gamma\eta} \tag{23}$$

A low surface tension and viscosity allows the solvent to access grooves, small holes, and threads. A large density allows the solvent to impact the surface with more force when a spray or ultrasonic bath of the solvent is used for cleaning.

CHAPTER II

Materials and Methods

All the developmental solvents and flame retardant solvents used in this study were procured from the following companies and manufacturers: 3M, ChemLogic, Chemours, Daikin, DuPont, Honeywell, Houghton, Kyzen, MicroCare, Nugentec, Reliance, Sherwin-Williams, Sigma Aldrich, Solvay, SolvChem, and Specialty Materials Corporation. Some of the solvents were obtained as research samples, and were provided free of charge. The solvents examined in this study are shown in Table 1with Chemical Abstracts Service (CAS) registry numbers and abbreviations used in this study. Some trade names and more common abbreviations are also shown. Ethylene glycol antifreeze was also used in this study as a bath solution in flash point testing.

Table 1. List of chemical compounds examined in this study.

ACE	acetone, CAS:67-64-1
AE3	1,1,2,2-tetrafluoroethyl-2,2,2-trifluoroethyl ether (AE3000), CAS:406-78-0
BAC	*tert*-butyl acetate (tBAc), CAS:540-88-5
BOH	*tert*-butanol (tBOH), CAS:75-65-0
C5F7	1,1,2,2,3,3,4-heptafluorocyclopentane, CAS:15290-77-4
CBTF	*para*-chlorobenzotrifluoride (PCBTF), CAS:98-56-6
DCE	*trans*-1,2-dichloroethene, CAS:156-60-5
EL	ethyl lactate, CAS:97-64-3
EOH	ethanol (EtOH), CAS:64-17-5

Table continued

HEX	*n*-hexane, CAS:110-54-3
HFC3	1,1,1,3,3-pentafluorobutane (HFC365 or Solkane 365), CAS:406-58-6
HFC4	1,1,1,2,2,3,4,5,5,5-decafluoropentane (HFC-4310mee), CAS:138495-42-8
HFE0	methoxyperfluoropropane (Novec-7000), CAS:375-03-1
HFE1	methoxyperfluorobutane (Novec-7100), CAS:163702-07-6
HFE3	methoxyperfluorohexane (Novec-7300), CAS: not found
HFE5	4-ethoxyperfluoro-5-methylhexane (Novec-7500), CAS:297730-93-9
I16	iodoperfluorohexane* (I-1600), CAS:355-43-1
I32	iodoperfluoropropane* (I-3200), CAS:677-69-0
MBK	methyl isobutyl ketone (MIBK), CAS:108-10-1
MEK	methyl ethyl ketone (MEK), CAS:78-93-3
MOH	methanol (MeOH), CAS:67-56-1
MPK	methyl propyl ketone, CAS:107-87-9
nPB or 1-BP	*n*-propyl bromide or 1-bromopropane, CAS:106-94-5
PAc	isopropyl acetate (IPAc), CAS:108-21-4
PFBI	iodoperfluorobutane*, CAS: 375-51-9
PFC6	perfluorohexane, CAS: 355-42-0
PGE	propylene glycol monomethyl ether (PGME), CAS:107-98-2
POH	isopropanol (IPA), CAS:67-63-0
Sols	*trans*-1-chloro-3,3,3-trifluoroprop-1-ene & *trans*-1,3,3,3-tetrafluoroprop-1-ene (Solstice PF), CAS:102687-65-0 & 29118-24-9

Table continued

Sup	1,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoro-1-methoxy-1-heptene (*cis* and *trans* isomers) (Suprion UP), CAS:69296-04-4
TCE	trichloroethylene (TRI), CAS:79-01-6

Note: Some of these abbreviations are the widely accepted abbreviations for these compounds, while others have been shortened for the purpose of figures in this project. The compounds with an "*", are unknown isomers of the name given.

The boiling points and chemical structures of the substances in Table 1 are shown in Table 2.

Table 2. Boiling points and chemical structures of the compounds used in the study.

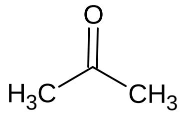
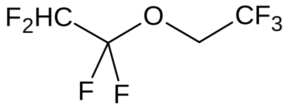
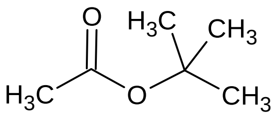
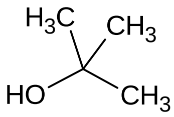
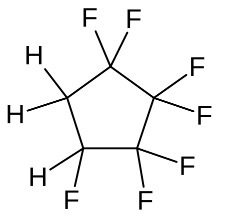
Substance	Boiling Point (T_b) / °C	Chemical Structure
ACE	56	
AE3	50	
BAC	96	
BOH	82	
C5F7	63	

Table continued

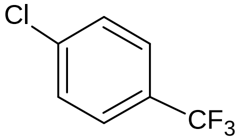
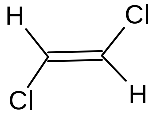
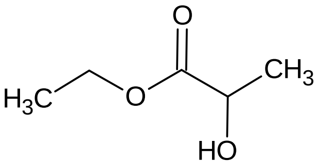
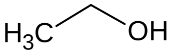
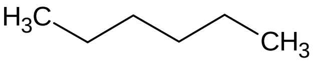
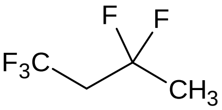
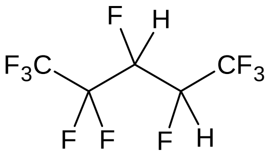
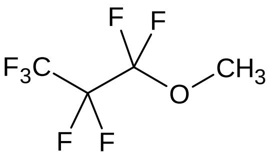
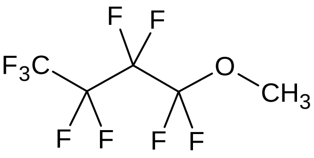
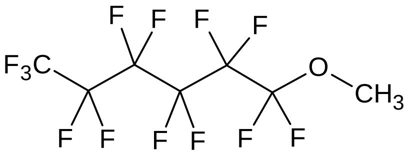
CBTF	145	
DCE	48	
EL	155	
EOH	78	
HEX	69	
HFC3	41	
HFC4	54	
HFE0	34	
HFE1	60	
HFE3	99	

Table continued

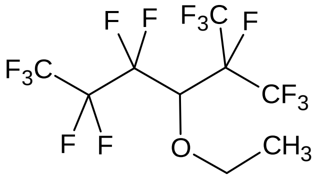
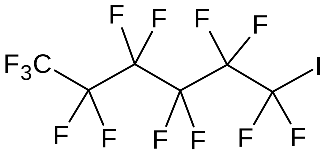
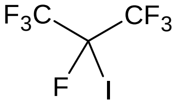
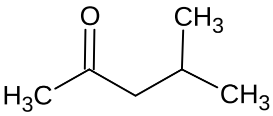
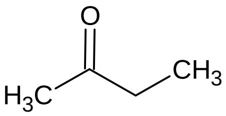
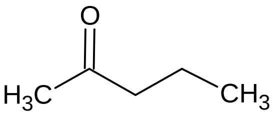
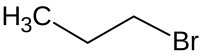
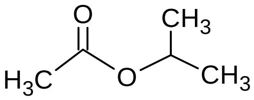
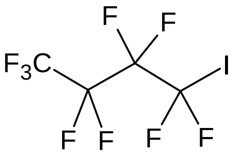
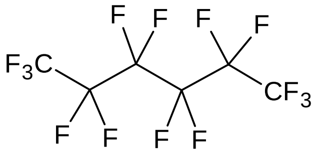
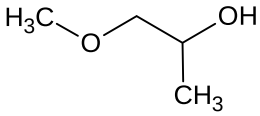
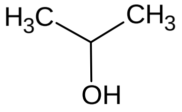
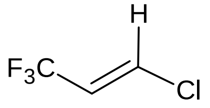
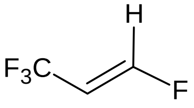
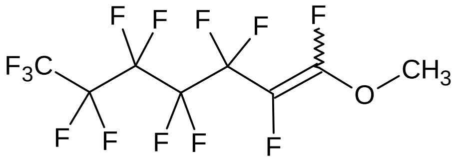
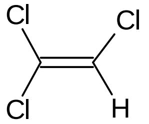
HFE5	130	
I16	113	
I32	40	
MBK	116	
MEK	80	
MOH	65	$H_3C{-}OH$
MPK	102	
nPB or 1-BP	71	
PAc	89	
PFBI	65	

Table continued

PFC6	57	
PGE	120	
POH	82	
Sols	19	 and 
Sup	111	
TCE	87	

Note: Some of the chemical structures shown are only one isomer in a mixture of the isomers that make up the bulk solvent.

Other materials used in this study include: a fractional distillation apparatus, a tag closed-cup flash point tester (Koehler Model K14600), a DuNouy ring tensiometer made in-house, a ball drop viscometer (RGI V-2200 size no. 2), and a Raman spectrometer (Ocean Optics Raman Systems R-3000).

Choosing Components to Tune Properties

In this study the components of each mixture were carefully chosen. The goal was not to find as many azeotropic mixtures as possible, but to find azeotropic mixtures that were non-flammable and had good solvency against hydrocarbon grease. First, the list of available components was narrowed down from the 22,406 compounds in the Hansen Solubility Parameters in Practice (HSPiP) software database to 28 compounds using the restrictions mentioned in the preface of this document, boiling point restrictions for energy conservation, and market availability. From these 28 compounds, the HSPs helped to predict which compounds would provide good solvency. Generally, solvents that have good solvency against hydrocarbon grease are flammable. These compounds were paired with non-flammable compounds with similar boiling points, because compounds with similar boiling points were believed to have a higher chance to form a low-boiling azeotrope. This would produce mixtures that had the potential to be non-flammable solvents with high solvency against hydrocarbon grease. However, the mixtures need to be azeotropes in order to maintain these properties while boiling.

The solvents that made up these pairs were mixed and distilled in order to identify the pairs of solvents that produced low-boiling azeotropic mixtures. The pairs that formed low-boiling azeotropic mixtures were tested to ensure that they were non-flammable using flash point determination, because the percentage of flame retardant in the azeotrope is determined by the intermolecular attractions between the components, and a certain amount is required to quench the flammability of the flammable component. The azeotropes that were found to be non-flammable were tested against hydrocarbon grease in a vial-based solvency study and those with extremely poor solvency were studied no further. The remaining azeotropes were characterized using standard operating procedures (SOPs) that were produced in this study. The SOPs for identifying and characterizing the azeotropes are summarized in the following sections of this chapter and the full SOPs are included in the appendix section of this thesis. The equations used for data analysis are provided in Chapter I.

Distillation

For the identification of low-boiling azeotropic mixtures, a fractional distillation is the easiest laboratory technique. The distillation process used an ordinary fractional distillation apparatus. The setup of the apparatus is discussed in detail in the appendix section. Either a fractionating column that contains a stainless-steel chain or a Vigreux column with built in deep pointed indentations in the glass was used to maintain the temperature gradient and prevent convective currents in the column. In addition to this, a Teflon sleeve was used on each of the ground glass joints instead of stopcock grease. This ensured that the joints were sealed, and that the distillate was uncontaminated. The fractional distillation was used for two purposes in this study: to identify whether an azeotrope would form, or to purify contaminated solvents so that they may be recycled.

When attempting to form a low-boiling azeotropic mixture, the two pure solvents were combined in a 1:1 (v/v) ratio in the round bottom boiling flask. The mixture was brought to boiling and heated until the first drop of distillate reached the receiving flask. At this point, the temperature was recorded. If the temperature reading was below the boiling points of the two components of the mixture, then the distillate was an azeotropic composition of the two components. If this occurred, the distillation was stopped when the temperature began to increase. If the temperature reading after the first drop of distillate was received was at or close to the boiling temperature of one of the components, the distillation was continued until the temperature reading began to increase. This was done for a few different reasons. Sometimes a low-boiling azeotrope has a boiling point that is very close to the boiling point of the lowest boiling component. Near azeotropes may also form between components that are difficult to separate. Also, if the mixture has no azeotropic point, then it is advantageous to continue the distillation so that the pure solvents can be reclaimed. In the case where the temperature is at or close to the boiling point of the lowest boiling component, the next step in determining if the mixture is an azeotrope or near azeotrope was to perform a Raman chemometric analysis on the mixture. This method is outlined later in this chapter. Figure 9 is an example of the distillation setup.

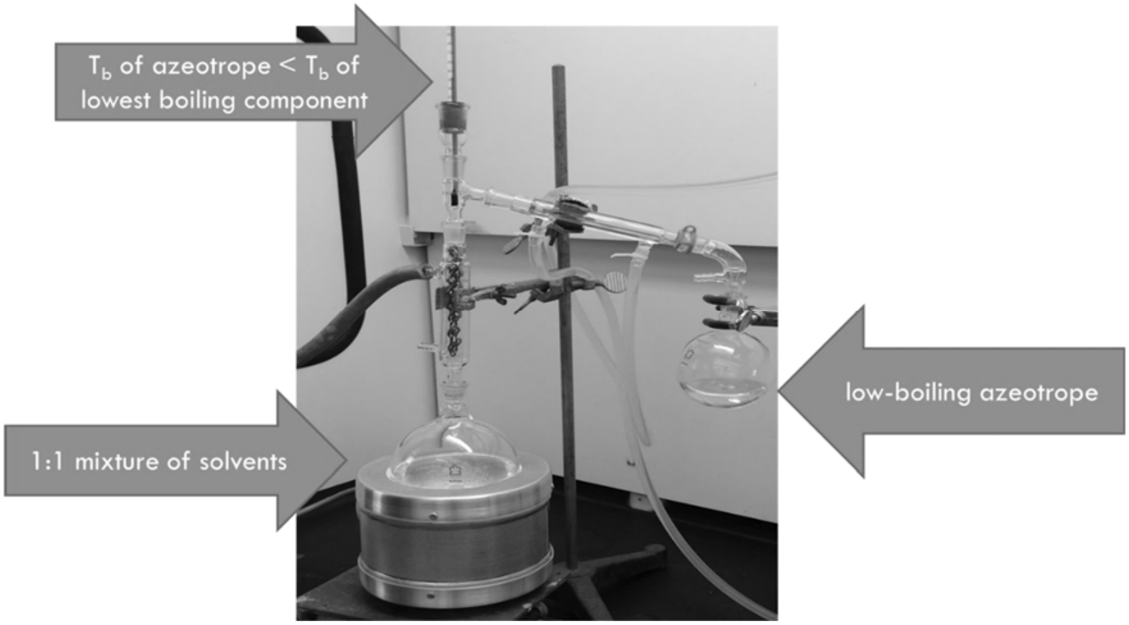


Figure 9. Example of a distillation setup.

When attempting to separate a soil from a solvent or multiple solvents from each other using fractional distillation, the process started in the same manner as the previous scenario. The solvent was the lowest boiling substance in every case when attempting to clean a solvent, so the distillation could be continued until the boiling temperature of the distillate began to increase or the solvent in the boiling flask was almost exhausted. When separating multiple solvents, the distillate was collected in fractions. The first fraction was collected until the boiling temperature increased, then the next fraction was collected. This process was repeated until the boiling flask had only a small amount of liquid remaining.

Raman Chemometric Technique

A chemometric technique is a technique that allows the calculation of the amount of certain substances that make up an unknown sample. Unknown, in this context, means that the identities of the sample's components are known, but the amount of each component is not known. A Raman chemometric technique is used in this study to find the composition of azeotropic mixtures. This technique takes very little work and very little time.

In the chemometric analysis, the Raman spectrum of each component was taken and the photon counts versus pixel number data was recorded. Next, the Raman spectrum of the mixture was taken. The diode array of the Raman Spectrometer was calibrated with the IR and Raman spectra of acetonitrile by using the peaks with the following Herzberg designations[19]: $2\nu_8$, ν_4, ν_7, ν_3, ν_6, and ν_2. These peaks were chosen because they were in the range of both the IR and the Raman instrument. This calibration allowed the x-axis of the spectrum to be expressed in wavenumbers Raman shift (cm^{-1}). In Microsoft Excel, a weighted average of the spectra of the components was made and the residuals between the combined spectrum and the experimental mixture spectrum were calculated between 200 and 2715 cm^{-1}. This range was chosen to avoid fitting the Rayleigh line. These residuals were used to calculate the sum of the squares of the residuals. Finally, the solver tool was used to minimize the sum of the squares of the residuals by changing the weighting of the different components in the combined spectrum.

Two mixtures were made by mixing known amounts of HFE5 and CBTF. The first mixture was made up of 50 % (v/v) of each of the two substances, and the second was 60 % (v/v) HFE5 and 40 % (v/v) CBTF. The Raman chemometric analysis technique was applied to these two mixtures. The results of these analyses were compared to the volume percentages as prepared, the calculated mole percentages, and the calculated mass percentages. Through these comparisons, it was shown that this analysis yielded the volume ratio of the components in the mixture. These results can be seen in Chapter III.

Flash Point

Flash point determinations in this study were made with a Koehler Model K14600 tag closed-cup flash point apparatus, which can be seen in Figure 10, and a modified ASTM D56[20] method. The tag closed-cup apparatus seemed exceptionally appropriate to determine the flash point of these azeotropic mixtures, because the azeotropes were meant for use in a vapor degreaser and this tester mimics the situation that occurs in a vapor degreaser by creating a concentrated vapor zone within the sample cup. The modifications to the method were that the test flame was applied to the sample after every one degree Celsius of temperature rise from the start of the test, and the heating bath was pure ethylene glycol antifreeze. These modifications had to be made because the ASTM D56 method is written to verify flash points of substances whose flash points are known. In this study, the flash points of substances whose flash points were not known were being determined. This means that it is impossible to start applying the flame to the sample after the temperature reaches five degrees Celsius below the expected flash point, because there is no expected flash point. This also means that the bath could not be changed according to the expected flash point. The modified method was used to verify the flash points of decane and methanol. This helped to ensure that the flash point apparatus and the modified method were capable of accurately determining the flash points of substances with known flash points. The flash point tests performed in this study were recorded on video to provide visual evidence.

Figure 10. Koehler Model K14600 tag closed-cup flash point apparatus.

The detailed setup information for the flash point tester is included in the appendix. When performing a flash point test, the test was performed with fresh sample, under dim lighting, and with a draft shield. To begin the test, the sample was added to the test cup and the test flame was lit. The apparatus was powered on and the control knob was used to adjust the heating rate to approximately one degree Celsius per minute. The test flame was applied to the sample for one second after every one degree Celsius of temperature rise. If the sample exhibited a flash when the test flame was applied, the temperature was recorded as the flash point. If no flash occurred after the sample reached boiling, the sample was said to have no flash point. If the sample flashed within ten degrees Celsius of the starting temperature, the test was performed again with a lower starting temperature. The definition of a flash, as well as other important information, will be provided in the discussion section.

Vial-Based Solvency Testing

A solvency screening test was developed during this project to compare the solvency of many solvents against hydrocarbon grease. This test also helped decide which solvents should be used in blends as cleaning agents, and which blends had potential as vapor degreasing solvent replacements. The blends that failed this screening were not tested or characterized any further.

This test used a gravimetric analysis with a 5-place laboratory balance (Kern model ABT 120-5DM) equipped with an automated data printer. A 4-mL glass vial and lid were weighed, and approximately 0.1 g of marine grade hydrocarbon grease was placed in the bottom of the vial using a large bore syringe. The grease was applied with similar glass contact in all cases. The mass of the vial with grease and the lid was measured to obtain the mass of grease applied to the vial (m_o), and approximately 3 mL of the test solvent was added to the vial. The vial was shaken on a laboratory shaker for 1 hour, and then poured into a pre-weighed aluminum pan. Any of the grease that fell out of the vial when it was turned up-side-down was taken as being removed from the vial by the solvent. After emptying the vial, the aluminum pan was placed in a clean laboratory oven to evaporate the solvent. When all of the solvent was evaporated, the pan was weighed again to obtain the mass of grease that was transferred to the pan (m_t). The percentage of the mass of grease transferred from the vial by the solvent ($P_{transferred}$) was calculated by taking the ratio of m_t and m_o (m_t / m_o) and multiplying by 100.

Density and Surface Tension

The density and surface tension measurements in this study were performed with a DuNouy ring tensiometer. A diagram of this tensiometer can be seen in Figure 11, and its construction is described elsewhere.[15]

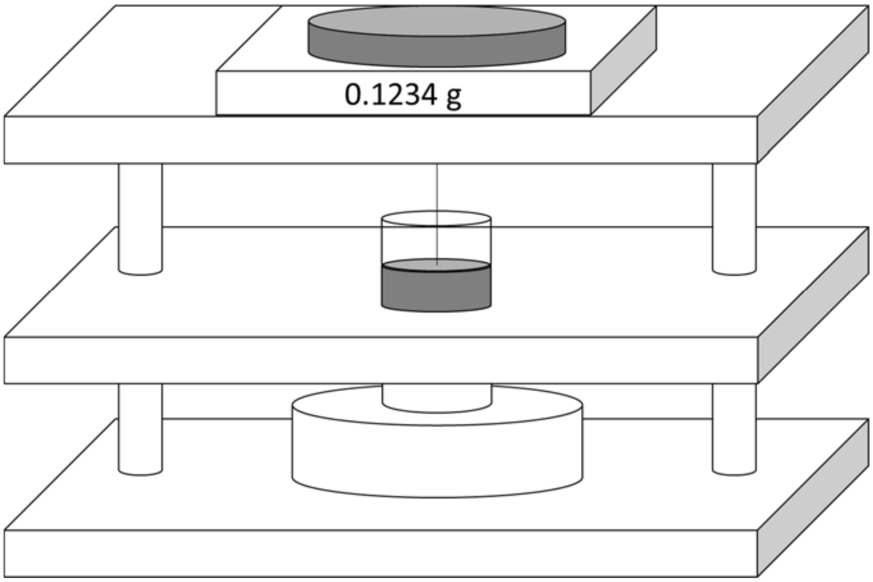


Figure 11. Diagram of a digital DuNouy tensiometer.[15]

The tensiometer in Figure 11, consists of a 4-place digital lab balance mounted above a hydraulic platform where the sample was placed. A chain with a hook connector on the end was hung from the under-hook of the balance. Instructions for preparing the tensiometer for measurements are included in the Appendix. A DuNouy ring tensiometer is a very inexpensive, easy, and accurate way to measure hydrostatic density and surface tension. The data collection is outlined in this section, but the theory and analysis equations are described in Chapter I.

To perform a hydrostatic density measurement with this tensiometer,[15] the data collection software (Hyperterminal) was started and the lab balance was tared. Data collection software was not required for the density measurements, but it was convenient due to the height of the lab balance. A 10.000 mL Pyrex density standard was weighed by placing it on the hook connector. This mass is the dry mass. The wet mass was taken by submerging the sinker in the sample. The temperature of the sample was taken using a thermocouple. This was all of the data needed to calculate the density. This process was repeated at ambient temperature, higher temperature, and lower temperature within a 10 to 20-degree Celsius temperature range. After the calculation of these densities, they could be used to calculate the thermal expansion coefficient for the substance through a regression analysis. The thermal expansion coefficient and its relationship with density are described in Chapter I. The thermal expansion coefficient was used to interpolate the density value so that it may be reported at 25 °C, because this is the temperature at which the density is most commonly reported. This also allowed the density to be calculated at any other temperature within the range for use in any other measurements that required density. The information in the regression analysis allowed a measure of uncertainty in the density to be calculated.

The surface tension measurements were performed according to ASTM D1331[21]. For this method, the data collection software was crucial. A platinum iridium tensiometer ring (with a radius of 0.9537 cm from the center of the wire to the center of the ring and a wire radius of 0.01779 cm) was hung from the hook connector and submerged just below the surface of the sample. The sample was in a container whose diameter was large enough for the meniscus to not affect the surface of the liquid in the center of the container. At this point, the data collection software was started and the balance was tared. The hydraulic platform was lowered slowly, allowing the ring to rise out of the surface of the liquid. The ring lifted the meniscus of the liquid and the mass of liquid lifted was measured every second until the ring lost contact with the surface of the sample. Then, the temperature was measured with a thermocouple. Like in the density interpolation, the process is repeated at ambient, higher, and lower temperatures. Using interpolated densities, the surface tension value for each measurement was calculated. A regression analysis revealed a strong inverse linear relationship between temperature and surface tension. This relationship was used to interpolate the surface tension to a new temperature, and calculate the uncertainty if the slope and intercept of the line were found to be statistically significant. This allowed the surface tension to be reported at 25 °C.

Viscosity

The viscosity measurements were made with a ball drop viscometer also called a falling ball viscometer, which can be seen in Figure 12. The ball drop viscometer is very inexpensive compared to other methods of measuring viscosity, and it is extremely simple to use for data collection. For precision, a more sophisticated modified ASTM D1343[17] method was used for these measurements.

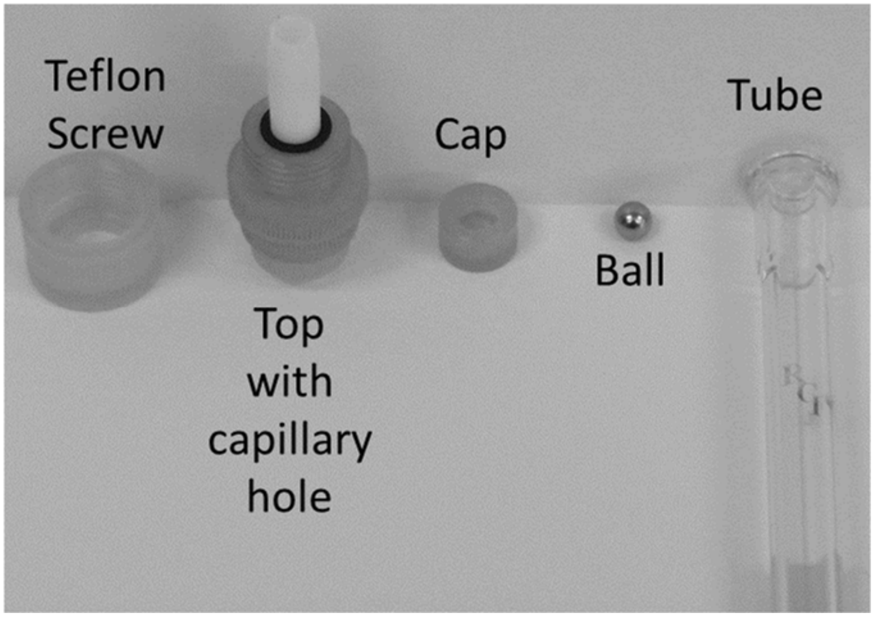


Figure 12. Parts of a ball-drop viscometer.

The first modification was to build an apparatus that allowed for video assisted timing of the ball drop, which can be seen in Figure 13. This was done using a laser table and laser table attachments. This apparatus consisted of three stands, a viscometer stand, an optics stand, and a video camera stand. Since this was done on a laser table, all three stands were locked into place. The viscometer stand consisted of a rotating viscometer holder at the top of the stand, a colored piece of paper behind the top set of timing lines to keep the camera in focus, and a catcher at the middle of the stand to ensure that the viscometer is completely vertical. The optics stand consisted of a microscope slide at a 45-degree angle in front of the top set of timing lines on the viscometer, and a front-silvered mirror at a 45-degree angle in front of the bottom set of timing lines. The video camera stand was only a rod that held the camera so that it was recording the top set of timing lines through the microscope slide on the optics stand. This modification allowed the timing data to be recorded digitally for reviewing later. This also made the timing more accurate, because the camera recorded at 30 frames per second, which gave the timing an uncertainty of ±1 frame or ±0.03 seconds.

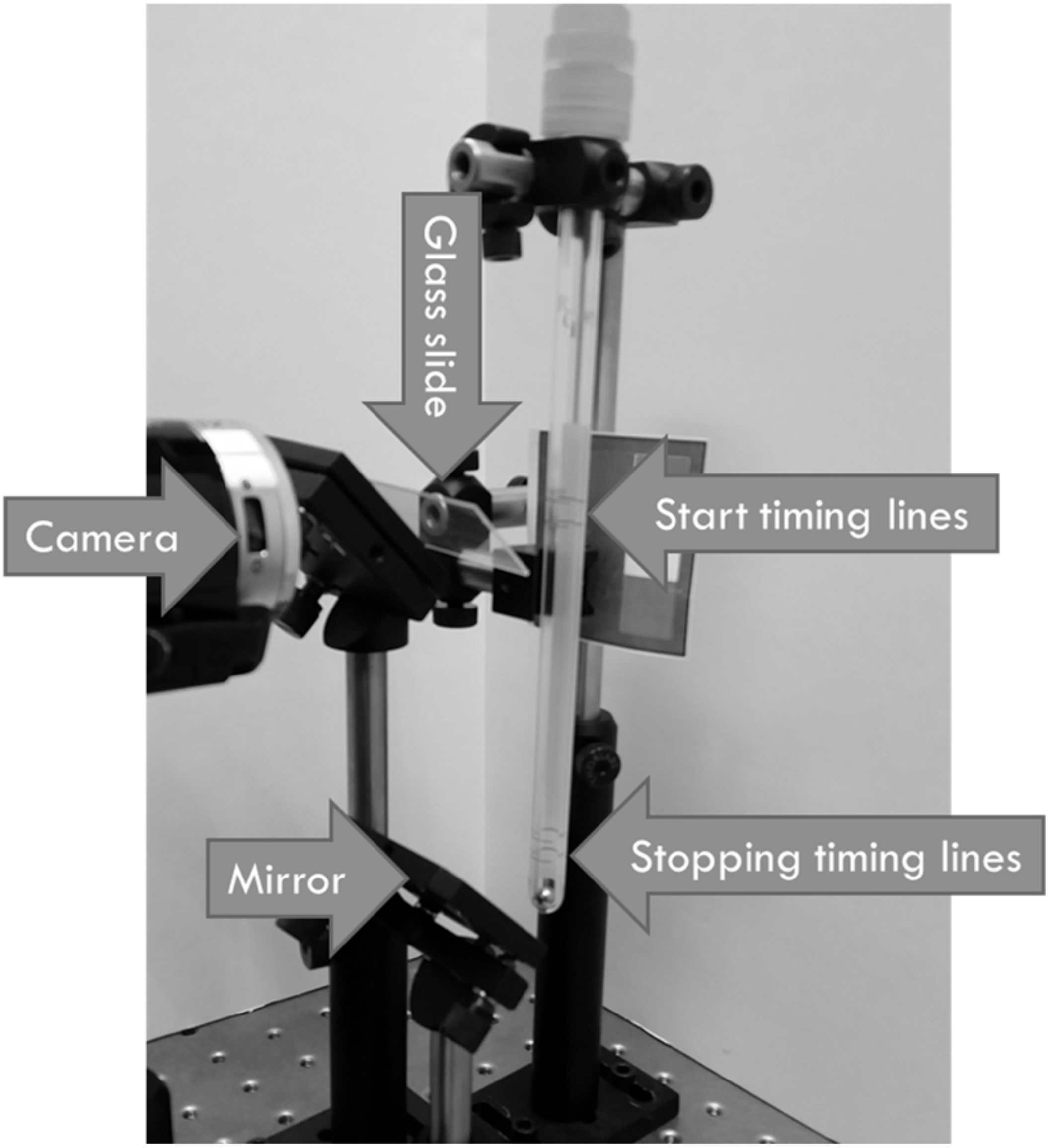


Figure 13. Viscosity apparatus for video assisted timing.

The other modification was to use Type I deionized water and the NIST database of densities and viscosities to calculate a temperature dependent viscometer constant. This was achieved by performing regression analyses on the density versus temperature and viscosity versus temperature data for water. These regression equations for density (ρ) and viscosity (η) in terms of temperature (T) can be seen here as eq 24 and eq 25 respectively.

$$\rho_{water} = -5.00(2)x10^{-6}\, T^2 - 5.6(7)x10^{-6}\, T + 1.000271(9) \tag{24}$$

$$\eta_{water} = 4.30(2)x10^{-4}\, T^2 - 4.2(1)x10^{-2}\, T\ + 1.668(1) \tag{25}$$

After measuring the time of the ball drop for water, the regression equations were used to calculate the density and viscosity of water at the temperatures of each of the ball drops. This allowed the calculation of the viscometer constant for each measurement of water based on the time of the ball drop and the temperature. The temperature was usually slightly higher for each successive measurement, and the calculated viscometer constant was slightly different for measurements with different temperatures. Because of this, the temperature versus viscometer constant data for water allowed a temperature dependent viscometer constant to be calculated based on a regression. This was used to calculate the viscometer constant for the specific temperature of every subsequent viscosity measurement.

While the data analysis for the ball drop method was a bit intricate, the operation of the viscometer was very simple. Once the viscometer was filled with the sample and a ball of known density, the viscometer could be placed into the rotating viscometer holder on the homemade apparatus. The temperature was measured by placing the end of a thermocouple into the capillary hole under the cap. The lights in the room were turned off and the viscometer was rotated upside down until the ball was resting at the top of the tube. Then, the video camera was powered on and the recording was started. The name of the sample, the trial number, and the temperature were said aloud for the recording. The tube was rotated right side up, and the ball began to fall through the liquid. Once the ball had passed the first set of timing lines, the bottom set of timing lines were illuminated with a light. The bright reflection in the microscope slide made the camera focus on the bottom set of timing lines. Once the ball passed the bottom timing lines the test was over. This process was repeated until five measurements were made on each sample.

The fact that each consecutive measurement had a slightly higher temperature, could be used to extrapolate the viscosity to 25-degrees Celsius. A regression analysis revealed a negative correlation between temperature and viscosity within a small temperature range. This was useful for reporting the viscosity at a temperature of 25 °C, which is the temperature normally used to report viscosity. This was also useful for comparing the measurements of pure substances to the literature values, since the measurements were not temperature controlled.

Azeotrope Prediction

A method for predicting the formation of binary azeotropic mixtures was produced as an addition to this thesis work. The method is described in this section.

Data for each proposed azeotrope component was extracted from the HSPiP database. This data included the molar volume (V_m), the Antoine coefficients (A, B, and C), and the HSPs (D, P, and H). This data was used in an Excel spreadsheet to perform the following calculations. Equation 26, the Antoine equation, was used to calculate the saturated vapor pressure (P^{SAT}) in units of mm Hg at 25 °C using the Antoine coefficients (A, B, and C) in units of mm Hg, mm Hg * °C, and °C respectively.

$$log_{10}P^{SAT} = A - \frac{B}{C+T} \tag{26}$$

In eq 26, T is the temperature in °C. The Hansen distance (R_a) was calculated using the HSPs and eq 9. A random number between zero and one was used as an initial value for the mole fraction of component A (x_A). The mole fraction of component B (x_B) was taken as one minus x_A, because of the relationship in eq 27.

$$x_A + x_B = 1 \tag{27}$$

Using an assumption that the volumes of the components are additive when mixed, the volume fractions of component A and B (ϕ_A, and ϕ_B) could be calculated using eq 28 and eq 29.

$$\phi_A = \frac{V_M^A x_A}{V_M^A x_A + V_M^B x_B} \tag{28}$$

$$\phi_B = \frac{V_M^B x_B}{V_M^A x_A + V_M^B x_B} = 1 - \phi_A \tag{29}$$

In eq 28 and eq 29, the A's and B's correspond to component A and component B. Equations to calculate the activity coefficients of component A and B (γ_A, and γ_B) were taken from the HSPiP e-book.[10] These equations are shown here as eq 30 and eq 31.

$$ln\gamma_A = \ln\left(\frac{\phi_A}{x_A}\right) + R_a^2\phi_B^2\frac{0.6V_M^A}{RT} \tag{30}$$

$$ln\gamma_B = \ln\left(\frac{\phi_B}{x_B}\right) + R_a^2\phi_A^2\frac{0.6V_M^B}{RT} \tag{31}$$

In eq 30 and eq 31, R is the gas constant (8.31445 $\mathrm{Jmol^{-1}K^{-1}}$), and T is the temperature (298.15 K). With the above information, the separation factor (α_{AB}) could be calculated. The separation factor was calculated using eq 32.[8]

$$\alpha_{AB} = \frac{\gamma_A P_A^{SAT}}{\gamma_B P_B^{SAT}} \tag{32}$$

The separation factor is a measure of how difficult it is to separate two substances using distillation. When the values of the numerator and denominator are far apart, the substances are easily separated using distillation. However, when the values of the numerator and denominator are closer to each other, it will be harder to separate the two substances. When the numerator and denominator are equal, α_{AB} equals one, and the two substances have formed an azeotrope and cannot be separated with a normal distillation. This fact was exploited in order to calculate the composition at which an azeotrope forms. This was easily done in an Excel workbook using the Solver tool. Solver was used to make α_{AB} equal a value of one by changing x_A. If solver is unable to find a solution, then no azeotrope is predicted to form between the two substances. If solver is able to find a solution, then the composition that solver used to make the separation factor equal one is the predicted composition of the azeotrope.

CHAPTER III

Results

This chapter contains data that was collected using the methods outlined in the Materials and Methods chapter. This data is discussed in Chapter IV. All uncertainties shown arise from regression analyses, and represent one standard deviation. Table 3 shows the composition, boiling points, and flash points of all the azeotropic mixtures discovered in this study.

Table 3. Compositions, boiling points (T_b), and flash points (T_f) of new azeotropic or near azeotropic mixtures.

Label	Component 1 %(v/v)	Component 2 %(v/v)	T_b / °C	T_f / °C
AZ1	85% HFE1	15% MOH	46.6	45.5
AZ2	85% AE3	15% MOH	48.7	48
AZ3	53% HFE3	47% BAC	84	≤ 21
AZ4	50% AE3	50% HFC3	N/R	None
AZ5	83% HFE5	17% EL	112	≤ 50
AZ6	80% Sup	20% CBTF	110	None
AZ7	65% HFE5	35% CBTF	125	None

Note: “None” under the flash point column means that the substance was brought to boiling and still did not undergo a flash. “N/R” means not recorded.

In Table 3, the measured boiling points were obtained by recording the temperature reading on the thermometer of the distillation apparatus after the first drop of distillate was collected and the temperature stabilized. The measured flash points were determined using a closed-cup flash point tester and a modified ASTM D56 method. The volume percentages were obtained using a Raman chemometric technique. The HFE-7500 / ethyl lactate azeotrope was a two-phase liquid where the light fraction (LF) made up 14% of the total volume and consisted of 5% HFE-7500 and 95% ethyl lactate. The heavy fraction (HF) of this mixture made up 86% of the total volume and consisted of 96% HFE-7500 and 4% ethyl lactate. For details about the methods used to obtain this data, refer to chapter II. A deviation from the method was made for the two-phase azeotrope, and this is discussed later in this chapter. The spectral analyses for all the azeotropes are shown in the following figures (Figure 14-Figure 21). The spectra in these figures are vertically offset from each other to allow each spectrum to be seen clearly.

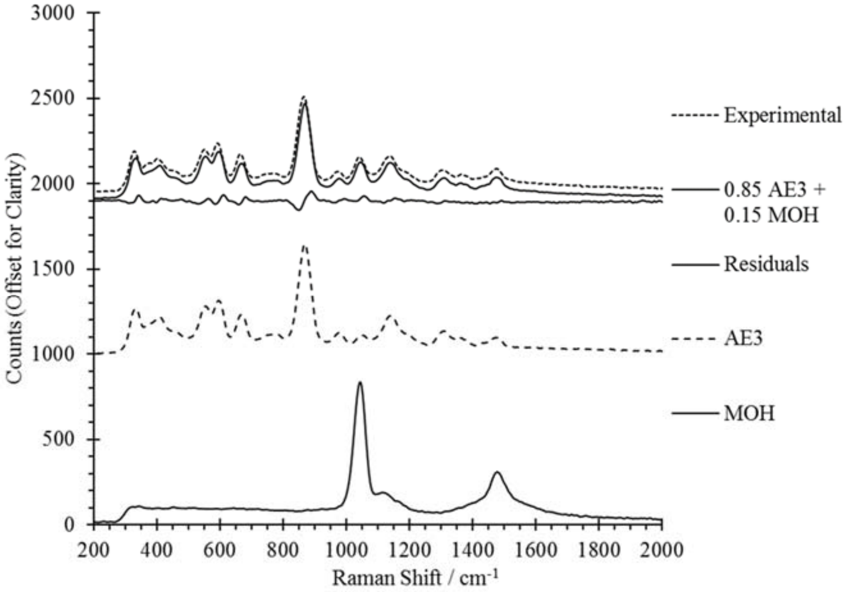


Figure 14. The Raman chemometric analysis of the azeotrope between AE3000 and methanol.

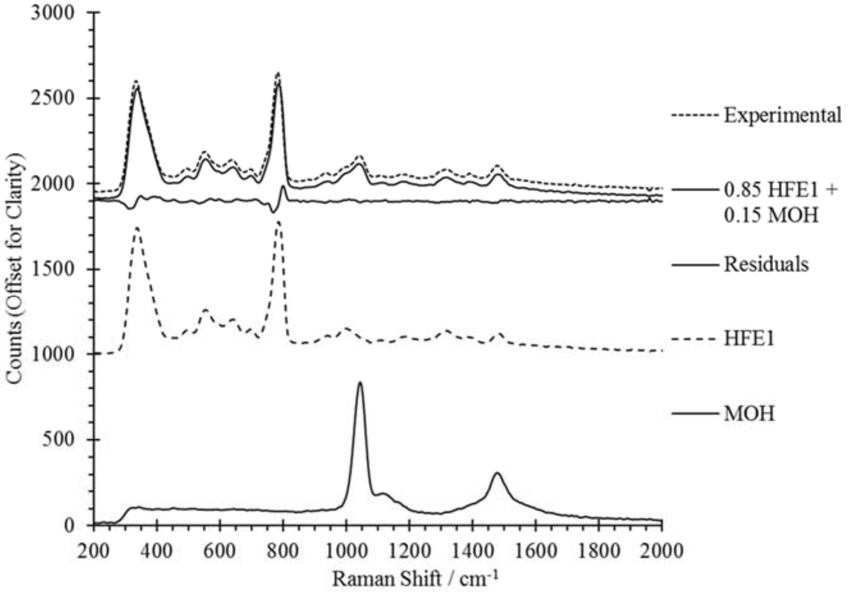


Figure 15. The Raman chemometric analysis of the azeotrope between HFE-7100 and methanol.

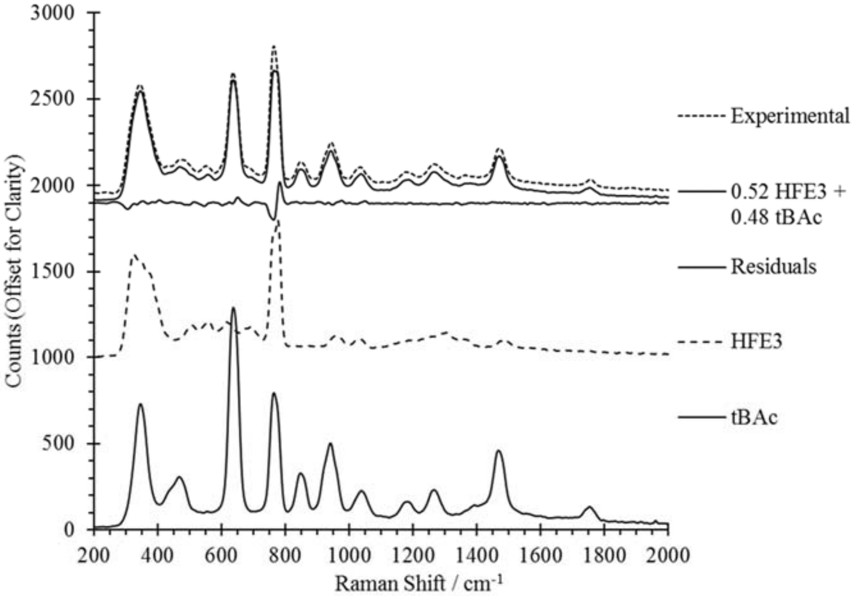


Figure 16. The Raman chemometric analysis of the azeotrope between HFE-7300 and tert-butyl acetate.

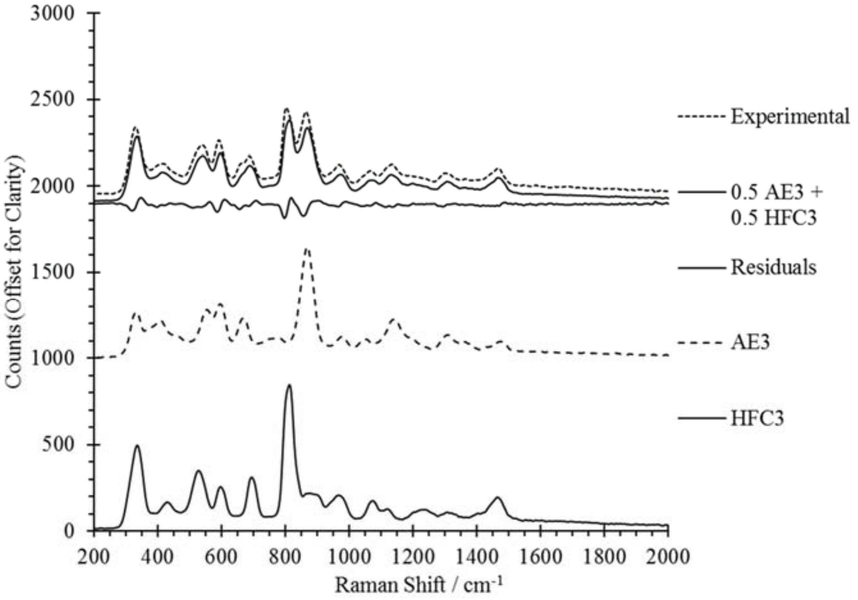


Figure 17. The Raman chemometric analysis of the azeotrope between AE3000 and Solkane 365.

AZ5 consisted of two immiscible layers that were each a mixture of the two components. This led to an interesting way of calculating the total volume composition. The azeotrope was placed in a graduated cylinder, covered with parafilm, and left to settle for a few days. At this point, the fraction of the total volume that each layer made up was calculated, and a sample of each layer was removed from the graduated cylinder with a pipette and analyzed via Raman spectroscopy. The results of these analyses are shown in Figure 18 and Figure 19. Knowing the composition of each layer and the fraction of the total volume that each layer made up enabled the calculation of the overall volume composition.

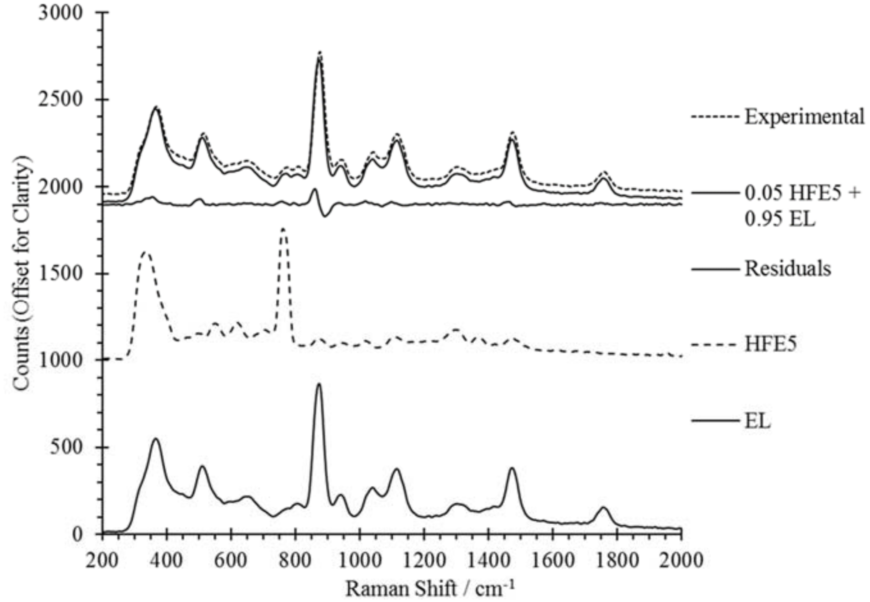


Figure 18. The Raman chemometric analysis of the top layer of the azeotrope between HFE-7500 and ethyl lactate.

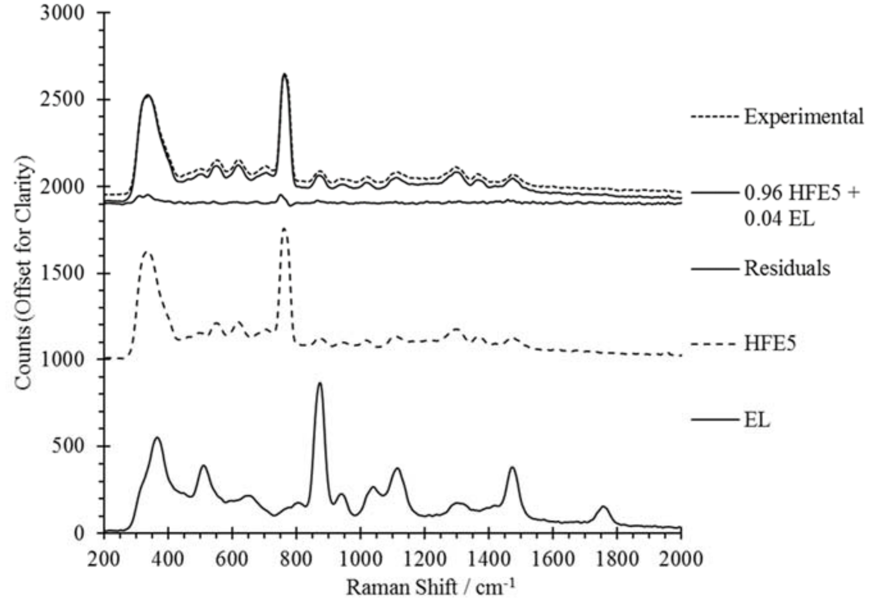


Figure 19. The Raman chemometric analysis of the bottom layer of the azeotrope between HFE-7500 and ethyl lactate.

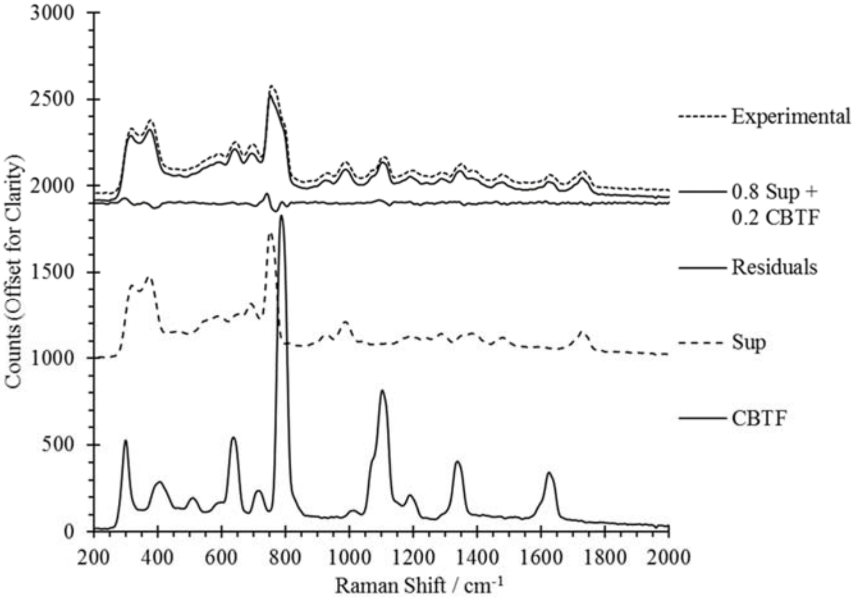


Figure 20. The Raman chemometric analysis of the azeotrope between Suprion and p-chlorobenzotrifluoride.

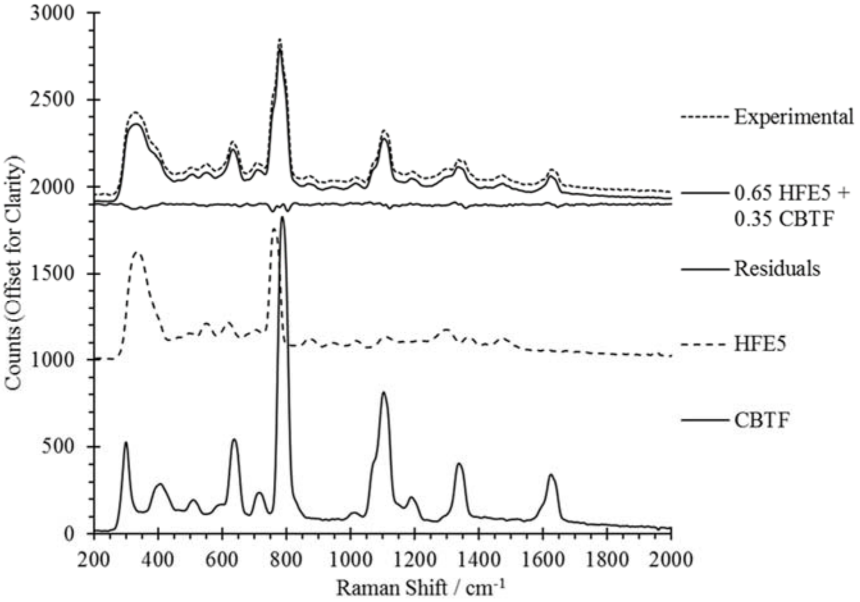


Figure 21. The Raman chemometric analysis of the azeotrope between HFE-7500 and p-chlorobenzotrifluoride.

The volume percent verification data for this chemometric analysis is shown in Table 4.

Table 4. Volume percent composition verification data.

			Chemometric % Composition	
Composition type	CBTF	HFE5	CBTF	HFE5
Prepared Volume %	50	50	50	50
Computed Mole %	61	39		
Computed Mass %	41	59		
Prepared Volume %	40	60	39	61
Computed Mole %	51	49		
Computed Mass %	32	68		

Note: The numbers on the left are the compositions that were mixed, and the numbers on the right are the chemometric analysis results.

The solvency screening test results can be seen in Figure 22.

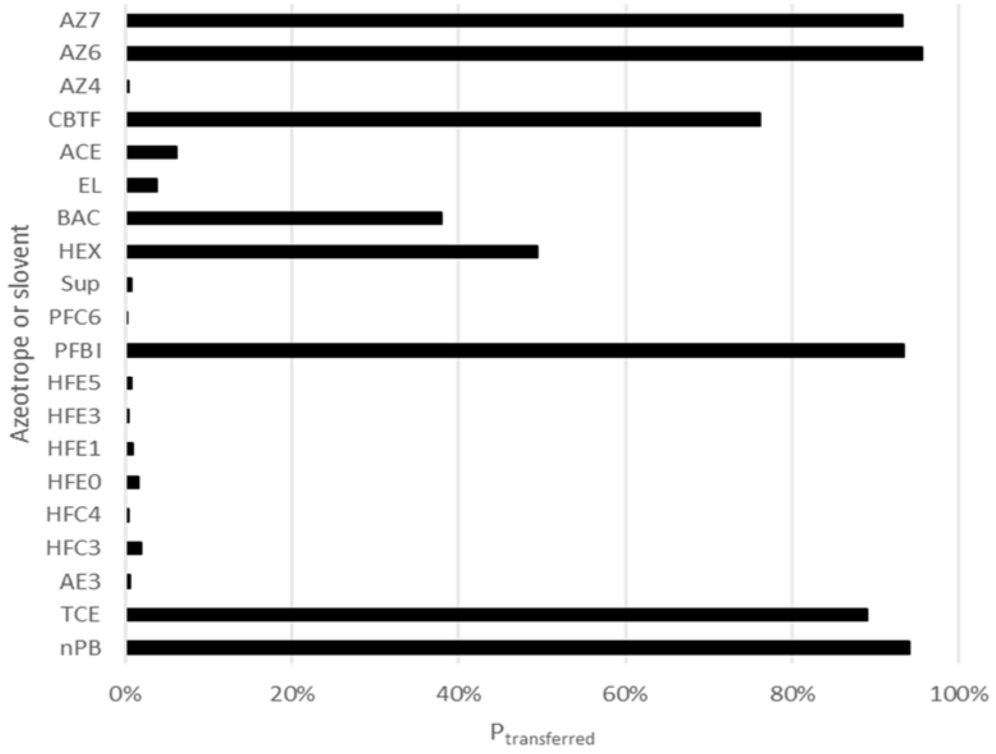


Figure 22. Solvency screening test results.

These results were used to decide which azeotropes to characterize further. The azeotropes that passed the flash point and solvency screening, and the pure components of those azeotropes were characterized in terms of the thermal expansion coefficient (β), density (ρ), surface tension (γ), and viscosity (η). The pure substances were characterized solely for the purpose of testing the accuracy of the methods, and literature values from the SDSs are provided for comparison. These SDSs can be found in the SERDP report.[14] The physical properties for the azeotropes and pure substances can be seen in Table 5.

Table 5. Physical properties of select substances compared to literature at 25 °C.

Substance	β/ 10^{-3} °C^{-1}	Exp. ρ/ g/mL	Lit. ρ/ g/mL	Exp. γ/ mN/m	Lit. γ/ mN/m	Exp. η/ cP	Lit. η/ cP
HFE5	1.55(2)	1.62(2)	1.614	-	16.2	1.08(3)	1.24
sup	1.4(1.1)	1.57(6)	1.59	-	18	1.06(18)	1.12
CBTF	1.03(4)	1.333(3)	1.34	-	25	0.84(7)	0.79
AZ6	1.47(2)	1.521(2)	None	18.8(1)	None	0.97(4)	None
AZ7	1.58(5)	1.516(6)	None	19.3(2)	None	0.94(5)	None

Note: The numbers in parentheses are the calculated uncertainties for the experimentally determined values.

The thermal expansion coefficients (β) were found using the dependence of density on temperature. The determined HSPs and wetting index for AZ6, AZ7, and their components are shown in

Table 6.

Table 6. Hansen Solubility Parameters and wetting indices of select substances at 25 °C.

Substance	D/ (J/mL$^{1/2}$)	P/ (J/mL$^{1/2}$)	H/ (J/mL$^{1/2}$)	W
HFE5	13.3	2.0	1.0	92.6(2)
sup	12.8	2.0	1.3	82.2(8)
CBTF	17.3	4.0	2.9	63.6(1)
AZ6	13.7	2.4	1.6	83.9(1)
AZ7	14.7	2.7	1.7	83.6(1)

Note: The numbers in parentheses are the calculated uncertainties.

In

Table 6, the HSPs for the three pure substances are literature values used to calculate the HSPs of the two azeotropes. The wetting index values were calculated from the experimental values of density, surface tension, and viscosity. However, the literature surface tension values were used for the pure components. The results of the azeotrope prediction model are shown in Table 7.

Table 7. Comparison of predicted azeotrope compositions to experimental compositions.

Label	Components (1/2)	Component 1 Exp (v/v)	Component 2 Exp (v/v)	Component 1 Pred (v/v)	Component 2 Pred (v/v)	Error (v/v)
AZ1	HFE1/MOH	0.85	0.15	0.76	0.24	-0.09
AZ2	AE3/MOH	0.85	0.15	0.80	0.20	-0.05
AZ3	HFE3/tBAc	0.53	0.47	0.68	0.32	0.15
AZ4	AE3/HFC3	0.50	0.50	0.35	0.65	-0.15
AZ5	HFE5/EL	0.83	0.17	0.75	0.25	-0.08
AZ6	Sup/CBTF	0.80	0.20	0.77	0.23	-0.03

AZ7	HFE5/CBTF	0.65	0.35	0.75	0.25	0.10

Note: The error is calculated for component A.

Negative error in Table 7 indicates that the predicted composition of component A is lower than the experimental composition. Positive error indicates the opposite. Since the compositions that are shown in Table 7 are the volume fractions where every number is less than one and greater than zero, error is more appropriate than percent error.

CHAPTER IV

Discussion

This chapter contains a discussion of the methods provided in Chapter II, and the results provided in Chapter III. This discussion includes reasoning for the decisions that were made in this project, as well as data interpretation, and method evaluation.

Solvent Selection

The selection of the solvents used to make the azeotropes reported in Table 3 was far from random. All of the HFEs (hydrofluoroethers), Suprion, AE 3000, and Solkane 365 were chosen, because of their known flame-retardant abilities, which will be discussed in more detail later in this chapter. AE-3000s higher polarity and hydrogen bonding terms, and Solkane 365s higher dispersion term were promising. However, these substances tended to have solvency issues with hydrocarbon grease. CBTF was chosen, because of its VOC-exempt status, and tremendous dispersion term placing it close to TCE in Hansen space. This substance is flammable though, and had to be paired with a flame-retardant substance for safe use in a vapor degreaser. EL and tBAc seemed to be good possibilities as azeotrope components, because of their higher polarity and hydrogen bonding terms. However, all attempts to quench their flammability failed, and EL also had problems with miscibility. PFBI was a great solvent. However, it could not be used in solvent blends due to its rather rapid decomposition to form molecular iodine, and the fact that there was only a small supply of this solvent to test. Methanol was chosen, not only for its good solvency and high wetting index, but also because it tends to mix and dissolve in environments that would not be predicted by Hansen solubility parameter theory.[10] While methanol is not VOC-exempt, it is a promising molecule for low-VOC blends, because of how VOC content is measured. Methanol is a very light molecule and VOC content is measured by mass of VOC per liter of solvent. So, there will be more molecules per gram of VOC when using methanol versus most other substances. However, all attempts to quench the flammability of methanol in an azeotropic mixture have failed.

Fractional Distillation

Fractional distillation was used in this study to find seven low-boiling azeotropic solvent blends. However, no actions were taken to investigate other types of azeotropes between any of these substances. Also, there was a goal of forming non-flammable azeotropes with good solvency against hydrocarbon grease, which led to pairing substances that have high solvency with substances that are non-flammable. So, there is a possibility that more azeotropes exist between these substances, or that some of these substances actually form double azeotropes. Since the boiling points of these azeotropes were obtained by reading a mercury or alcohol thermometer on the distillation apparatus, the readings are subject to an uncertainty of a tenth of a degree Celsius. However, it is rarely the case that the temperature reading does not fluctuate some during a distillation. In cases where there were small fluctuations, such as the temperature rising and dropping slightly, the boiling temperature was chosen as the temperature that the thermometer read most often within that fraction of distillate. Some of the boiling points were confirmed with a digital reading from a thermocouple later. All of the azeotropes that were made with this method had boiling points well below the boiling point of either component, with the exception of AZ6. AZ6 was an azeotrope between Suprion and CBTF, and its boiling point was the same as the boiling point of Suprion. However, this azeotrope consisted of 20 % CBTF by volume. There are examples of low-boiling azeotropes whose boiling points are very close to the boiling point of the lowest-boiling component. The water-ethanol azeotrope is an example of this with a boiling point that is only a few tenths of a degree lower than the boiling point of ethanol.

Chemometric Analysis

Since the components of each azeotrope were known, a chemometric analysis was the easiest way to measure the ratios of the components. In this case, a Raman chemometric analysis was performed, but other methods were tested. The other methods tested include gas chromatography with a flame ionization detector (GC-FID), nuclear magnetic resonance (NMR) analysis, and infrared (IR) spectroscopy. GC-FID was unfruitful, because no separation was obtained between the components of the mixture. This method also took much more time than the Raman analysis. Another student from this research group successfully performed NMR analysis to obtain the composition of azeotropes, however, the method was much more difficult and time consuming than the Raman analysis. An IR chemometric analysis was attempted, but the high-resolution instrument was too good at seeing the peak shift between the pure substances and the mixture. This led to issues with the process of fitting the component spectra to the azeotrope spectrum. The Raman analysis was performed with a lower resolution instrument, but some of the peak shift phenomenon was apparent. The RMS difference between the spectrum of the azeotrope and the spectrum composed of the weighted average of the components sometimes had a first-derivative nature, indicating a vibrational frequency shift in the spectrum of the mixture. However, the RMS difference between the location of a peak in the azeotrope and the location of the same peak in the pure substance was always very small. Since the Solver tool in excel was being used to find the ratios of the components, the analysis was performed with different initial composition ratios to ensure that Solver was reaching the global minimum for the RMS difference. For the same sample, Solver would always reach the same composition within 0.2 %. The fact that the Raman analysis was yielding volume percentages was also verified. Two mixtures of different volume compositions were analyzed using this chemometric method. The composition from the Raman analysis was within 1 % of the volume composition for both mixtures, and was never equal to the mass, or mole percent composition. All of the Raman measurements were performed at ambient temperature. No study was performed to see if the shifts in room temperature had an effect on the volume percentages obtained from this analysis. It is expected that slight changes in temperature would change the output of the analysis, because of the dependence of density on temperature. Azeotropes are usually defined in terms of mole ratio, and while the mole ratio will always be the same the volume ratio will change slightly when the temperature changes.

As for the composition data seen in Table 3, it is only coincidence that AZ1 and AZ2 have the same composition values. This only occurred because the volume percentages were rounded to the nearest one percent. The one to one ratio of components in AZ4 was surprising, but it indicates that the intermolecular attractions that these substances share with each other are very similar to the intermolecular attractions that they share with themselves. AZ5 was very interesting, because it was a heterogenous azeotrope at room temperature. This azeotrope consisted of two immiscible layers that were each a mixture of the two components.

Flash Point

The flash point test was the first test performed on the azeotropes after determining their composition. This test was crucial to this project, because any substance that exhibits a flash point cannot be used in a vapor degreaser. The tag closed-cup flash point tester was chosen to perform the flash point test, because of its electric heater, and imitation of the environment inside of a vapor degreaser. There is a level of controversy over the flash point test, because some methods report a flash point for a substance that is reported to not have a flash point when a different method is used. In ASTM D56, a flash is defined in the following way:

> "3.1.1.1 The specimen is deemed to have flashed when a flame appears and instantaneously propagates itself over the entire surface of the fluid. 3.1.1.2 Discussion—When the ignition source is a test flame, the application of the test flame may cause a blue halo or an enlarged flame prior to the actual flash point. This is not a flash and should be ignored.".[20]

When a flash occurs during a flash point test, it is very apparent. However, when certain halogenated substances are heated in a flash point tester they participate in burning with the test flame by making the flame bigger, or changing the color of the flame. This is addressed in the standard as well by the following excerpt:

> "X1.1 A condition during flash point testing can occur with certain mixtures whereby the nonflammable component of the sample tends to inert the vapor space above the liquid, thus preventing a flash. Under this condition, the flash point of the material is masked resulting in the reporting of incorrect high flash point or no flash point.

> X1.2 This flash point masking phenomenon most frequently occurs with ignitable liquids that contain certain halogenated hydrocarbons such as dichloromethane (methylene chloride) and trichloroethylene.
>
> X1.3 Under this condition, no distinct flash as defined in 3.1.1 is observed. Instead a significant enlargement of the test flame and a change in the color of the test flame from blue to yellow-orange laminar flame is observed.”.[20]

The above information reveals that the halogenated hydrocarbons do not exhibit a flash, but will participate in burning. The flash point tests in this study were in agreement with this. The goal in this study was to use these halogenated hydrocarbons to make the vapor zone inert, thus making a mixture, with a flammable substance, that does not have a flash point. This would make the substance useable in a vapor degreaser. The substances in Table 3 that report a flash point as less than or equal to a certain temperature, are the substances that exhibited a flash at the starting temperature of the test. The case of AZ5 was particularly interesting, because the flash point of the azeotrope was a lower temperature than the flash point of ethyl lactate. Ethyl lactate was the only substance in the blend that had a flash point. It was deduced that this was the result of the increased vapor pressure of EL in the azeotrope, combined with the inability of HFE-7500 to quench the flammability of ethyl lactate.

Solvency Screening and Solvent Wetting Index

AZ 4 did not pass the solvency screening, because it had a $P_{\text{transferred}}$ of 0.37 %. The hope with this blend, was that the higher D term of HFC3 would combine with the higher P and H terms of AE3 to make a relatively good solvent. However, it can be seen in Figure 22 that the two components of this blend were both better than the azeotrope at removing hydrocarbon grease. From the data it appears that AZ6 and AZ7 were better than the components that the blends were made from, and that they were competitive with nPB and TCE. However, this was not attributed to the blends' ability to dissolve the grease. In these cases the grease fell out of the vials in clumps, indicating that it was loosened from the glass, but not dissolved. This was attributed to the azeotropes' increased wetting index compared to CBTF. The wetting index was increased because of an increased density and a decreased surface tension.

Density

The density measurements in Table 5 were all very good. The literature values were all within the uncertainty of the experimental measurements after interpolation to 25 °C. However, when the density versus temperature data was recorded, Suprion began to get cloudy at the low end of the temperature range. It was deduced that this led to a bad linear least squares fit when calculating the thermal expansion coefficient. This is the reason for the rather large uncertainty value on the thermal expansion coefficient and the density at 25 °C for Suprion. This uncertainty value for density doesn't look very large, but when you compare it to the others, it is three times as large as the next highest uncertainty value. The density values for the azeotropes seem to be the expected values when compared to the literature values of the components. This is because the density is between the values of the two components, and closer to the value of the component that makes up the majority of the blend.

Surface Tension

The surface tension measurements for the pure substances were not included, because only two ambient measurements with slightly differing temperatures were measured for these substances. The two data points were too close in temperature to establish a reliable temperature dependence, and two data points is not enough to establish a statistically acceptable relationship. This method and instrument have been used to obtain good surface tension data of well-known substances, such as water, in the past. This removes the need for validation of this method. For the azeotropic mixtures, a high temperature and a low temperature were added when measuring the surface tension of the azeotropes. This gave a good temperature span for an interpolation and enough data points to create a statically significant relationship between temperature and surface tension for the azeotropes. The surface tension values for the azeotropes seem to be what is expected when compared to the literature values of the components. This is because the values are between the values of the components, but closer to the component with the smallest surface tension. Surface tension usually behaves this way with mixtures, because the lower surface tension molecules are surface active and break the interactions of the higher surface tension component.

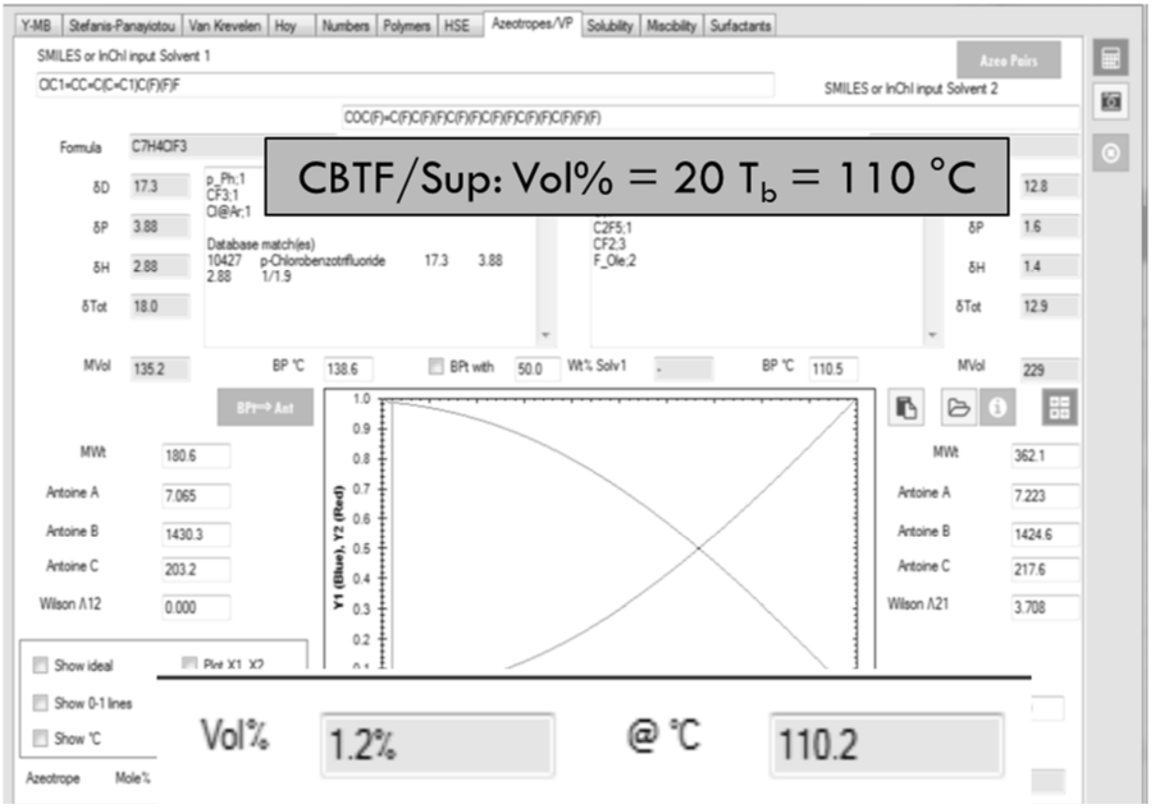
Viscosity

The viscosity measurements were performed using the method with the most modifications. However, the modifications that were made only had the possibility of making the measurement better for substances that were stable in the temperature range of the density measurements. “Stable”, in this case, means that the substance does not undergo phase changes or other changes that could have a large effect on the density data.

This excludes Suprion, because of the cloudy phenomenon that occurred at the low end of the temperature range. If this is taken into consideration, the use of interpolated densities in the calculation of viscosity should make the measurement more reliable, because it is difficult to ensure that the density and viscosity measurements take place at the same temperature without temperature-controlled environments. The use of well-known standards to calibrate an instrument reduces error by removing the need to measure the dimensions of the viscometer, and allowing the temperature dependent viscometer constant to account for any changes in the viscometer's dimensions when the temperature is varied. Also, a 30-frames per second video camera was used to time the ball-drop. This led to an uncertainty of ±1 frame or ±0.03 seconds in the timing, which is much better than any human could consistently do with a stopwatch. The literature value for HFE-7500 is far from being within the uncertainty of the measurement for unknown reasons. The measurement for Suprion is surprisingly close to the literature value, considering the suspect density data. However, the uncertainty value is quite large, which may be related to the cloudiness in the density measurement. The CBTF literature value is within the uncertainty of the measurement. Also, this measurement has a reasonably low uncertainty value. The azeotropic viscosity values seem to be reasonable, because they are between the literature viscosity values of the components. However, AZ6 seems to close to the center of the values of its components, while AZ7 is more than twice as close to the value for the component with the lower viscosity than it is to the other component.

Azeotrope Prediction

The HSPiP software has an azeotrope prediction model. Using this model, it is apparent that the boiling point prediction is very good, but the volume percent composition prediction does not work very well for the two examples shown in Figure 23 and Figure 24. In these two figures the volume composition and boiling point prediction using the HSPiP azeotrope prediction model is blown up at the bottom, and are compared to the experimental values located near the top.



CBTF/Sup: Vol% = 20 T_b = 110 °C

SMILES or InChI input Solvent 1: OC1=CC=C(C=C1)C(F)(F)F

SMILES or InChI input Solvent 2: COC(F)=C(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F)

Formula: C7H4ClF3

δD: 17.3
δP: 3.88
δH: 2.88
δTot: 18.0

p_Ph;1
CF3;1
Cl@Ar;1

Database match(es)
10427 p-Chlorobenzotrifluoride 17.3 3.88
2.88 1/1.9

C2F5;1
CF2;3
F_Ole;2

δD: 12.8
δP: 1.6
δH: 1.4
δTot: 12.9

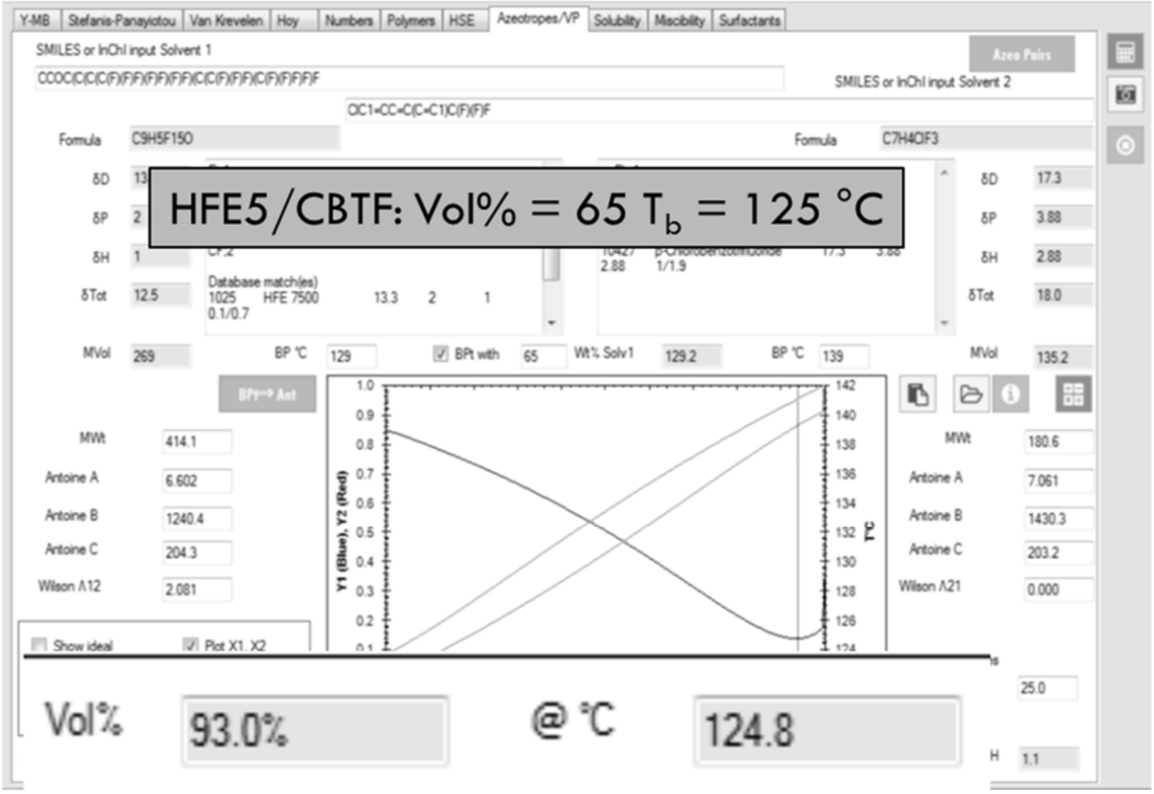
MVol: 135.2
BP °C: 138.6
☐ BPt with 50.0 Wt% Solv1 -
BP °C: 110.5
MVol: 229

MWt: 180.6
Antoine A: 7.065
Antoine B: 1430.3
Antoine C: 203.2
Wilson Λ12: 0.000

MWt: 362.1
Antoine A: 7.223
Antoine B: 1424.6
Antoine C: 217.6
Wilson Λ21: 3.708

Vol% 1.2% @ °C 110.2

Figure 23. AZ 6 HSPiP volume composition and boiling point prediction compared to experiment.



HFE5/CBTF: Vol% = 65 T_b = 125 °C

SMILES or InChI input Solvent 1: CCOC(C(C(C(F)(F)F)(F)F)(F)F)(C(C(F)(F)F)(C(F)(F)F)F)F

SMILES or InChI input Solvent 2: ClC1=CC=C(C=C1)C(F)(F)F

Formula: C9H5F15O

Formula: C7H4ClF3

δD: 13

δP: 2

δH: 1

δTot: 12.5

Database match(es)
1025 HFE 7500 13.3 2 1
0.1/0.7

10427 p-Chlorobenzotrifluoride 17.3 3.88
2.88 1/1.9

δD: 17.3

δP: 3.88

δH: 2.88

δTot: 18.0

MVol: 269

BP °C: 129

☑ BPt with: 65 Wt% Solv1: 129.2

BP °C: 139

MVol: 135.2

MWt: 414.1

Antoine A: 6.602

Antoine B: 1240.4

Antoine C: 204.3

Wilson Λ12: 2.081

MWt: 180.6

Antoine A: 7.061

Antoine B: 1430.3

Antoine C: 203.2

Wilson Λ21: 0.000

☐ Show ideal ☑ Plot X1, X2

25.0

H 1.1

Vol% 93.0% @ °C 124.8

Figure 24. AZ 7 HSPiP volume composition and boiling point prediction compared to experiment.

HSPiP acknowledges in the “help” documents that the results from the azeotrope prediction for fluorinated compounds may be unreliable due to a lack of data for fluorinated compounds. The two azeotropes that were tested in the HSPiP prediction model contained fluorinated compounds.

The azeotrope prediction method that was produced in this study was tested on the seven azeotropes that were discovered in this project, which all contained fluorinated compounds. In these examples, the data needed to calculate the azeotropic point was taken from the HSPiP database. This data consists of values that were predicted based on the structures of the molecules. This could have had an effect on the prediction model’s ability to accurately predict the azeotropic composition, and this effect could be removed by using data from a database of experimental data. Also, the assumption that the volumes of the two components are additive when mixed, could cause much of the error with this prediction method. This error could be removed if a model could be found to accurately predict the real volume upon mixing, and how much of that volume each component would make up.

CHAPTER V

Conclusions

The goal of this thesis was to provide methods that can be used to search for new azeotropes with specific desired properties, and methods to characterize these new azeotropes. All azeotrope possibilities that were examined in this study were low-boiling azeotropes composed of non-aqueous solvents, and the desired properties were for the azeotropes to be non-flammable and have good solvency against hydrocarbon grease. This is because the azeotropes were meant for use in a vapor degreaser as drop-in replacements for TCE and nPB. A secondary goal of this thesis was to discover a method for predicting if an azeotrope will form between two substances using the Hansen Solubility Parameters.

This research uncovered seven new azeotropic solvent blends. In four of these azeotropes, the flammability was not quenched by the amount of flame retardant solvent in the blend. This means that these blends are failed attempts at producing azeotropes with the first desired property using the method outlined in this thesis. However, three of the azeotropes that were produced, were non-flammable. Out of these three, one did not pass the solvency screening against hydrocarbon grease. So, this one failed to meet the requirements of the second desired property. This still leaves two azeotropes that were non-flammable, and had some solvency against hydrocarbon grease. These solvents were not able to compete with TCE and nPB in terms of solvency though. The azeotropes in this study show that while the search method outlined in this thesis is not perfect, it is capable of producing azeotropic blends with the desired properties.

The modified characterization methods that were produced in this study, were definitely improved from their original state, and the wholly-new Raman chemometric analysis was perfect for its purpose. The original characterization methods assumed that the density measurement was taken at the same temperature as the surface tension and viscosity measurements. However, in this study it was quickly realized that this is usually false unless all three measurements are performed on the same sample at the same time, which is impossible. The Raman analysis was quick, easy, and provided readily useable volume fractions for mixing the identified azeotropes in larger quantities.

The implementation of property versus temperature relationships made the measurements of density, surface tension, and viscosity much more accurate due to the dependence of all of these properties on temperature. Surface tension and viscosity are dependent on density and these relationships helped to avoid the difficulty of implementing precise temperature control on the tests in order to achieve the same temperature between these tests and the density test. These relationships also helped to extrapolate or interpolate experimental values to 25 °C for reporting purposes, and comparisons to literature. Video-assisted data collection for flash point and viscosity, had a huge impact on these two methods. In the flashpoint test, the video served as visual evidence, and as reassurance in situations where the flash was not immediately obvious. In the viscosity measurements, the video was used to obtain more accurate timing for the ball-drop. Since this was traditionally done using a stopwatch, the timing was made much more reproducible and less reliant on the individual who performs the timing, or human reflexes. All the methods used in this thesis are inexpensive, and can be easily implemented with little budgetary impact.

An azeotrope prediction model that relates the HSPs to azeotrope formation was discovered in this thesis. This model works fairly well for the azeotropes discovered in this project despite using predicted data and an assumption that is definitely not true in all cases. This azeotrope prediction method could save companies and researchers massive amounts of time and resources, because it provides a way to predict if two substances will form an azeotrope before going to the lab and attempting to make an azeotrope. A graduate student from the Department of Computer Science at SHSU, Nathan Thompson, has been contracted to write a program using this prediction model. With this program, it will be possible to take a giant list of compounds and find every combination of two substances that is predicted to form an azeotrope. If this program was available at the beginning of the SERDP project, there is a good chance that a better solution to the problem could have been found in the amount of time that was available for that project.

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APPENDIX A

FRACTIONAL DISTILLATION

SCOPE

This procedure outlines fractional distillation setup as well as instructions for the distillation process.

PURPOSE

This procedure provides instructions for performing a fractional distillation.

SAFETY REQUIREMENTS

1. Before beginning this procedure, read all of the Safety Data Sheets for the chemicals at hand.

2. Contact your supervisor for information regarding the proper personal protection equipment (PPE) to be used in this procedure.

3. Personnel engaged in the handling of chemicals that could present a hazard due to splashing are required to wear safety eyewear with side-shields, or work in a hood, or wear a safety face shield.

NOTE

Nitrile or equivalent gloves are used for incidental contact only.

4. Wear nitrile or equivalent gloves when handling chemicals. In case of an incidental spill, wear nitrile gloves during cleanup. Do not use latex gloves for organic solvent work.

GENERAL INSTRUCTIONS

1. The sequence of operations in this procedure is not mandatory.

2. Waste Disposal

NOTE

Segregation of halogenated and non-halogenated waste streams is vital to the management of waste disposal costs. Likewise, recycling of solvent is a priority. Do not mix solvents if you do not have to!

   2.1. Dispose of halogenated solvents in a properly labeled halogenated solvent waste container.

   2.2. Dispose of non-halogenated solvents in a properly labeled non-halogenated solvent waste container.

   2.3. Dispose of aqueous waste containing heavy metal waste in a properly labeled heavy metal aqueous waste container.

- 2.4. Dispose of contaminated PPE and laboratory expendables into the laboratory regulated solid waste container.
- 2.5. Dispose of uncontaminated PPE and laboratory consumables in the laboratory nonregulated solid waste container.

OPERATIONS FOR PERFORMING A FRACTIONAL DISTILLATION

1. Setting up the distillation apparatus.
   - 1.1. Choose an appropriately sized boiling flask and heating mantle for the distillation that needs to be performed.
     - 1.1.1. The flask should be large enough so that the liquid that needs to be distilled does not fill the boiling flask more than 75 percent of its maximum capacity.
     - 1.1.2. The flask should be small enough so that the liquid that needs to be distilled does not fill the boiling flask less than 50 percent of its maximum capacity.
     - 1.1.3. The heating mantle should be the appropriate size for the heating flask that you have chosen.
     - 1.1.4. The heating mantle should cover the lower 50 percent of the flask with good contact between the inside of the heating mantle and the boiling flask.
   - 1.2. Pour the liquid that needs to be distilled into the boiling flask.
   - 1.3. Add some boiling chips to the flask.
   - 1.4. Place the flask into the heating mantle inside of the fume hood.
   - 1.5. Attach a fractionating column to the boiling flask.
     - 1.5.1. Remember to either use stopcock grease or a Teflon sleeve on this connection because it will get very hot.
     - 1.5.2. Remember to clamp the fractionating column to a ring stand to hold it up right during the distillation.
   - 1.6. Attach a three way distilling head to the top of the fractionating column.
     - 1.6.1. Remember to either use stopcock grease or a Teflon sleeve on this connection because it will get very hot.
   - 1.7. Attach a thermometer adaptor to the top of the distilling head.
   - 1.8. Place a thermometer in the thermometer adaptor.
   - 1.9. Lower the thermometer until the end of the thermometer is just below the fork in the distilling head.
   - 1.10. Attach a condenser to the distilling head.
     - 1.10.1. Remember to secure the condenser to the distilling head using a clamp on the connection, a tightly wrapped rubber band from the water outlet on the condenser to the distilling head, or by clamping the condenser to another ring stand.
     - 1.10.2. The water outlet is the one closest to the distilling head.
     - 1.10.3. The water inlet is the one farthest from the distilling head.

- 1.11. Attach a vacuum adaptor to the end of the condenser.
    - 1.11.1. Remember to secure the vacuum adaptor to the condenser using a clamp on the connection, or a tightly wrapped rubber band from the water inlet on the condenser to the vacuum adaptor.
- 1.12. Attach an appropriately sized receiving flask to the vacuum adaptor.
    - 1.12.1. Remember to secure the receiving flask by clamping it to another ring stand.
- 1.13. Run a rubber tube from the water tap to the water inlet on the condenser.
- 1.14. Run a rubber tube from the water outlet on the condenser to the drain.
- 1.15. Plug the heating mantle into a power regulator.
- 1.16. Plug the power regulator into an electrical outlet.

2. Performing a distillation.
    - 2.1. Turn on the water tap so that the pressure is sufficient to rid the condenser water jacket of air.
        - 2.1.1. The water can usually be turned down some after the air has been forced out.
    - 2.2. Power on the power regulator and set it to about 50 percent of its maximum.
        - 2.2.1. The regulator may need to be set to a lower setting for liquids with low boiling points, or a higher setting for liquids with high boiling points.
        - 2.2.2. When the setting is correct, the liquid will be at a gentle rolling boil after it has had time to heat.
        - 2.2.3. If the liquid doesn’t boil or barely boils after giving it time to heat, the setting on the power regulator can be increased.
        - 2.2.4. If the liquid boils up into the column after giving it time to heat, the setting on the power regulator should be decreased.
    - 2.3. Never leave the distillation unsupervised for more than a few minutes.
    - 2.4. The distillation should be checked about every five minutes after the liquid starts to boil to ensure that the liquid is boiling at the proper rate, and to ensure that the process is proceeding safely.
        - 2.4.1. In small distillations, it may need to be constantly observed or checked more often.
    - 2.5. After the first drop of distillate is captured in the receiving flask, record the temperature reading on the thermometer.
    - 2.6. From this point forward, check the temperature every time that the distillation is observed.
    - 2.7. In some cases, low boiling azeotropic mixtures are formed. If the temperature reading is lower than the boiling temperature of any of the components in the original mixture, then this has probably occurred. If this has occurred:
        - 2.7.1. If the purpose of the distillation was to create a low boiling azeotropic mixture, then continue the distillation until the temperature starts to increase to the boiling temperature of one the components.
        - 2.7.2. If the purpose of the distillation was to separate the components of the original

mixture, then stop the distillation and report that the mixture cannot be separated by distillation.

- 2.8. If the temperature reading is close to the literature boiling point of one of the components of the mixture, then continue the distillation.
  - 2.8.1. If the purpose of the distillation was to create a low boiling azeotropic mixture, then it is still possible that an azeotropic or near-azeotropic mixture was formed.
  - 2.8.2. If the purpose of the distillation was to separate the components of the original mixture, then the distillation is on track to fulfill its purpose.
- 2.9. If separation is the goal, then the receiving flask needs to be changed each time the temperature starts to increase to the boiling temperature of the next lowest boiling component.
  - 2.9.1. If the component that needs to be purified is the lowest boiling component of the mixture, then the distillation can be stopped the first time that the temperature starts to increase to the next lowest boiling temperature.
  - 2.9.2. If several components need to be purified, then change the receiving flask each time the temperature starts to increase to the next lowest boiling temperature.
    - 2.9.2.1. Label each flask with the small temperature range at which it was collected.
- 2.10. Always stop the distillation before the boiling flask is dry.

3. Stopping the distillation.
   - 3.1. Power off the power regulator.
   - 3.2. Allow the boiling flask to cool until it can be handled comfortably.
   - 3.3. Turn off the water tap.
   - 3.4. Remove the flask from the heating mantle.
   - 3.5. Allow the flask to continue to cool until it reaches room temperature.
   - 3.6. Pour the remaining liquid from the flask into a waste bottle.
   - 3.7. Label the waste bottle with the names of the remaining components of the distilled mixture, the words “Still Bottoms”, and the date.

APPENDIX B

RAMAN SPECTROSCOPIC AND CHEMOMETRIC ANALYSIS

SCOPE

This procedure outlines sample preparation, Raman spectrophotometric data collection, and chemometric analysis for determining the volume percent composition of liquid solvent mixtures.

PURPOSE

This procedure provides instructions for performing Raman spectrophotometric data collection, and chemometric analysis using Microsoft Excel's Solver Tool.

SAFETY REQUIREMENTS

1. Before beginning this procedure, read all of the Safety Data Sheets for the chemicals at hand.

2. Contact your supervisor for information regarding the proper personal protection equipment (PPE) to be used in this procedure.

3. Personnel engaged in the handling of chemicals that could present a hazard due to splashing are required to wear safety eyewear with side-shields, or work in a hood, or wear a safety face shield.

NOTE

Nitrile or equivalent gloves are used for incidental contact only.

4. Wear nitrile or equivalent gloves when handling chemicals. In case of an incidental spill, wear nitrile gloves during cleanup. Do not use latex gloves for organic solvent work.

5. The Raman instrument contains a 785 nm laser that is not visible. Do not aim the laser probe at any part of your body, especially the eye.

GENERAL INSTRUCTIONS

1. The sequence of operations in this procedure is not mandatory.

2. Waste Disposal

   NOTE

   Segregation of halogenated and non-halogenated waste streams is vital to the management of waste disposal costs. Likewise, recycling of solvent is a priority. Do not mix solvents if you do not have to!

   2.1. Dispose of halogenated solvents in a properly labeled halogenated solvent waste container.

   2.2. Dispose of non-halogenated solvents in a properly labeled non-halogenated solvent waste container.

- 2.3. Dispose of aqueous waste containing heavy metal waste in a properly labeled heavy metal aqueous waste container.
- 2.4. Dispose of contaminated PPE and laboratory expendables into the laboratory regulated solid waste container.
- 2.5. Dispose of uncontaminated PPE and laboratory consumables in the laboratory nonregulated solid waste container.

OPERATIONS FOR RAMAN SPECTRAL DATA COLLECTION ON CLEAR SOLUTIONS

1. Prepare instrument.
    - 1.1. Check the Raman probe to see if the liquid standoff cap is in place. (This positions the beam so the focus will be inside the wall of a standard glass vial.)
        - 1.1.1. Screw the standoff cap stamped “L” onto the Raman probe, if necessary.
        - 1.1.2. Store the solids standoff cap “S” near the spectrometer with the verification cap “V” that contains a teflon insert.
2. Start instrument and computer.
    - 2.1. Turn on instrument and computer.
        - 2.1.1. Flip the rocker switch to on “1” on the Raman Systems RS-3000 Raman spectrometer.
        - 2.1.2. Turn the key to turn the laser on.
        - 2.1.3. Turn on the PC near the Raman spectrometer.
        - 2.1.4. Ensure that a USB cable connects the PC to the spectrometer.
        - 2.1.5. Start the Raman Desktop software
    - 2.2. Record any error messages, and discuss with your supervisor.

NOTE

Instrument validation only needs to be performed at the beginning of a series of tests.

3. Validate instrument performance.
    - 3.1. Install the verification cap “V” on the Raman probe OR place a vial of solvent that will exhibit a familiar Raman spectrum into the black aluminum sample chamber.
    - 3.2. Insert the probe into the sample chamber till it is gently pressing against the vial.
    - 3.3. Place the aluminum sample cover over the sample chamber.
    - 3.4. Open the data collection toolbox in the Raman Desktop Software.
    - 3.5. Set the integration mode to “Integration Mode Standard”.
    - 3.6. Set the integration time to 10 s.
        - 3.6.1. Adjust the integration time if necessary to produce peaks in the range of 1000 counts.
    - 3.7. Set the dark spectrum mode to “Automatic Dark Subtract”.

- 3.8. Set the measurement mode to “Single Measurement”.
- 3.9. Set the maximum frame time to 10 s.
- 3.10. Set the total frames to 1.
- 3.11. Collect a sample spectrum.
- 3.12. Inspect it to see if the instrument is performing correctly.

NOTE

The instrument is now validated to be in good working order unless errors occurred. Discuss any errors with your supervisor.

OPERATIONS FOR ANALYSIS OF LIQUIDS AND SOLUTIONS

1. Collect data for solvent blend composition analysis.
    - 1.1. Place pure components into separate vials.
    - 1.2. Collect Raman spectra of pure components
        - 1.2.1. Data format = Raman Shift in Wavenumber
            - 1.2.1.1. Insert the following calibration equation to make the software convert pixels (P) to wavenumbers Raman shift (cm^{-1}). All of the decimal places from excel were kept here to ensure that the conversion is as precise as possible.

$$cm^{-1} = -0.000393424633127776(P)^2 + 2.17982010968675(P) - 98.6447924612422$$

            - 1.2.1.2. Set the integration mode to “Integration Mode Standard”.
            - 1.2.1.3. Set the dark and sample integration times to 10 s.
            - 1.2.1.4. Set the dark spectrum mode to “Automatic Dark Subtract”.
            - 1.2.1.5. Set the measurement mode to “Single Measurement”.
            - 1.2.1.6. Set the maximum frame time to 10 s.
            - 1.2.1.7. Set the total frames to 1.
        - 1.2.2. Integration Time = 10 s
            - 1.2.2.1. Modify the integration time to produce a maximum peak height near 1000 counts for the components with the strongest Raman signal.
            - 1.2.2.2. Use this SAME INTEGRATION TIME for both components AND the mixture.
    - 1.3. Place the blended solvent into a vial.
    - 1.4. Collect a Raman spectrum of the blended solvent.
2. Export data as an Excel-compatible (csv) file.

OPERATIONS FOR DATA ANALYSIS OF LIQUIDS AND SOLUTIONS

1. Chemometric Analysis of solvent blend spectrum. The following steps provide information on making a Microsoft Excel spreadsheet to perform the data analysis.

1.1. Create a sheet and name it “Raman Data”, and label a column for the wavenumber data, each component and the mixture using the top row.

1.2. Insert the wavenumber data and the counts data from the Raman spectral data starting in row 2 of each of the corresponding columns.

1.3. Create a new sheet and name it “Analysis”, and in the first row type the labels of each of the components and the mixture. These will be referred to as the label cells.

  1.3.1. In the second row, type a number between 1 and 0 below each component as a “guess” of what the composition of the mixture is in respect to each component. The number that is typed in these cells are not important. However it is important that the sum does not exceed 1. These will be referred to as the composition cells.

  1.3.2. For the last component, insert an equation that subtracts the compositions in respect to the other components from 1.

  1.3.3. In a lower row, create columns that perform horizontal look ups to obtain the mixture data and the counts data for all of the components using the labels in the top row.

  1.3.4. Create a separate column that calculates a spectrum using the weighted average of the component spectra.

  1.3.5. Create a column that calculates the difference in each data point between the mixture spectrum and the calculated spectrum. These are the residuals.

  1.3.6. Create a column that squares the residuals.

  1.3.7. Create a cell that takes the square root of the sum of the squared residuals.

2. The following steps provide information on performing the data analysis.

2.1. Type the label of the mixture and each component of the mixture that is to be analyzed in the label cells. If the mixture only contains two components, leave the other label cells blank. This automatically updates the component data on this sheet.

2.2. Select “Solver” under the “Data” tab of Excel.

2.3. For a two component mixture, enter the following parameters into the “Solver Parameters” window:

  2.3.1. “Set Objective” = [the Sum of the Squares of the Residuals] (ex: “$H$2”)

  2.3.2. “To:” = “Min”

  2.3.3. “By Changing Variable Cells:” = [composition cells] (ex: “$D$2”)

  2.3.4. “Subject to the Constraints:” = [composition cells] <= 1 and >= 0 (ex: “$D$2:$F$2 <= 1”; “$D$2:$F$2 >= 0”) Volume fractions should always be less than or equal to one, and they cannot be negative by definition.

  2.3.5. “Select a Solving Method:” = “GRG Nonlinear”

2.4. For a three component mixture, enter the following parameters into the “Solver Parameters” window:

  2.4.1. “Set Objective” = [the Sum of the Squares of the Residuals] (ex: “$H$2”)

  2.4.2. “To:” = “Min”

  2.4.3. “By Changing Variable Cells:” = [composition cells] (ex: “$D$2:$E$2”)

  - 2.4.4. “Subject to the Constraints:” = [composition cells] <= 1 and >= 0 (ex: “$D$2:$F$2 <= 1”; “$D$2:$F$2 >= 0”) Volume fractions should always be less than or equal to one, and they cannot be negative by definition.
  - 2.4.5. “Select a Solving Method:” = “GRG Nonlinear”
- 2.5. Click “Solve”. The percentage of each component in the mixture will appear in the cell below the label of the corresponding component.
- 2.6. This method can be extrapolated to mixtures with more components.

APPENDIX C

CLOSED CUP FLASH POINT DETERMINATION

SCOPE

This procedure outlines all of the steps for determining the flash point of a liquid sample with a kinematic viscosity of less than 9.5 cSt at 25 degrees Celsius, using a closed cup flash point tester.

PURPOSE

This procedure provides instructions for determining the flash point of a liquid sample using a closed cup flash point tester.

SAFETY REQUIREMENTS

1. Before beginning this procedure, read all of the Safety Data Sheets for the chemicals at hand.

2. Contact your supervisor for information regarding the proper personal protection equipment (PPE) to be used in this procedure.

3. Personnel engaged in the handling of chemicals that could present a hazard due to splashing are required to wear safety eyewear with side-shields, or work in a hood, or wear a safety face shield.

NOTE

Nitrile or equivalent gloves are used for incidental contact only.

4. Wear nitrile or equivalent gloves when handling chemicals. In case of an incidental spill, wear nitrile gloves during cleanup. Do not use latex gloves for organic solvent work.

GENERAL INSTRUCTIONS

1. The sequence of operations in this procedure is not mandatory.

2. Waste Disposal

   NOTE

   Segregation of halogenated and non-halogenated waste streams is vital to the management of waste disposal costs. Likewise, recycling of solvent is a priority. Do not mix solvents if you do not have to!

   2.1. Dispose of halogenated solvents in a properly labeled halogenated solvent waste container.

   2.2. Dispose of non-halogenated solvents in a properly labeled non-halogenated solvent waste container.

2.3. Dispose of aqueous waste containing heavy metal waste in a properly labeled heavy metal aqueous waste container.

2.4. Dispose of contaminated PPE and laboratory expendables into the laboratory regulated solid waste container.

2.5. Dispose of uncontaminated PPE and laboratory consumables in the laboratory nonregulated solid waste container.

OPERATIONS FOR DETERMINING THE FLASH POINT OF A LIQUID USING A CLOSED CUP FLASH POINT TESTER.

1. Prepare the flash point tester.
    - 1.1. Fill the bath of the flash point tester.
        - 1.1.1. Fill the bath with ethylene glycol, because the flash point of the sample is not known. The top pipe is the in pipe (for connection to a water tap when water is used), and the bottom pipe is the out pipe.
        - 1.1.2. The bath is full when ethylene glycol is expelled from the out pipe on the back of the flash point tester into the waste container.
    - 1.2. Connect the tester to a natural gas outlet using a rubber hose.
    - 1.3. Wipe out the test cup with a lint-free wipe.
    - 1.4. Place the test cup into the tester slowly allowing for any excess ethylene glycol to be expelled into a waste container through the overflow path built into the tester, and allowing the bath to remain completely full.
    - 1.5. Measure 50 mL of the sample in a graduated cylinder.
    - 1.6. Pour the sample into the cup without getting the cup wet above the liquid level.
    - 1.7. Pop any bubbles in the liquid.
    - 1.8. Place the lid on the tester.
2. Performing the flash point determination.
    - 2.1. Perform the test with a fresh sample each time.
    - 2.2. Perform the test under dim lighting.
    - 2.3. Perform the test with a draft shield 18 inches long on each side, 24 inches high, and open in front.
    - 2.4. Turn on the natural gas.
    - 2.5. Barely turn the natural gas adjustment knob on the tester to allow the gas to reach the flame tip.
    - 2.6. Light the natural gas coming from the flame tip to obtain the test flame.
    - 2.7. Compare the size of the test flame to the flame size bead on the tester lid.
        - 2.7.1. If the test flame is smaller than the bead, adjust the natural gas adjustment knob to make the flame the same size as the bead.

  - 2.7.2. If the test flame is bigger than the bead, completely close the adjustment knob. Once the flame has gone out, try to open the adjustment knob less than it was opened previously. Light the gas to see the size of the flame. Repeat this process if necessary.
- 2.8. Start recording the test with a video camera.
- 2.9. At the beginning of the recording state the name of the sample along with the boiling point if it is known.
- 2.10. Before each application of the test flame to the sample, state the temperature reading from the thermometer of the test cup.
- 2.11. Apply the flame to the sample.
  - 2.11.1. Turn the knob connected to the flame tip counter clockwise. This will pull open a sliding door and apply the flame to the hole closest to the flame tip.
  - 2.11.2. Apply the flame to the sample for approximately one second.
- 2.12. Watch the hole farthest from the flame tip during application of the flame.
  - 2.12.1. If the flame can be seen instantaneously propagating itself across the entire surface of the liquid, then the sample has flashed. The lowest temperature at which this occurs is the flash point.
  - 2.12.2. An increase of the size, or a change in color of the test flame is not considered a flash.
- 2.13. If the sample flashes at this starting temperature, then the test needs to be performed at lower temperatures. In cases of extreme cooling being needed it is acceptable to report the flash point as being less than a certain temperature instead of trying to obtain the actual flashpoint.
  - 2.13.1. To obtain temperatures lower than the ambient temperature, the tester along with the ethylene glycol bath can be placed in a chemical only laboratory refrigerator. Also, place a closed container of the sample in the refrigerator.
  - 2.13.2. Lower temperatures can also be obtained by using an ice water bath instead of ethylene glycol. This bath can only cool down to zero degrees Celsius.
- 2.14. The starting temperature of the test should always be at least ten degrees Celsius below the flashpoint.
  - 2.14.1. If the sample flashes less than ten degrees above the starting temperature, the test should be performed again with a lower starting temperature.
- 2.15. If the sample does not flash at the starting temperature, then power on the heater by flipping the switch on the side of the tester base.
- 2.16. Adjust the control knob to attempt to make the temperature raise by one degree Celsius per minute.
  - 2.16.1. The control knob may need to be adjusted during the test to maintain the temperature rise of one degree Celsius per minute.
  - 2.16.2. During the test, periodically check the temperature and time the rise of the temperature to ensure that the rate of temperature rise is correct.
- 2.17. Apply the flame to the sample after every one degree of temperature rise.

2.18. If the boiling point of the sample is reached and the sample has yet to flash, then the sample is said to have no flash point.

SOURCE DOCUMENTS

External Documents:

1. ASTM Standard D56 - 05, 1995 (2010), "Standard Test Method for Flash Point by Tag Closed Cup Tester," ASTM International, West Conshohocken, PA, 2000, DOI: 10.1520/D0056-05R10, www.astm.org.

APPENDIX D

SOLVENT COMPARISON FOR CLEANING GREASE

SCOPE

This procedure outlines the method used for comparing the ability of different solvents to remove grease.

PURPOSE

This procedure provides instructions for performing a test to compare the ability of various solvents to remove grease.

SAFETY REQUIREMENTS

1. Before beginning this procedure, read all of the Safety Data Sheets for the chemicals at hand.

2. Contact your supervisor for information regarding the proper personal protection equipment (PPE) to be used in this procedure.

3. Personnel engaged in the handling of chemicals that could present a hazard due to splashing are required to wear safety eyewear with side-shields, or work in a hood, or wear a safety face shield.

NOTE
Nitrile or equivalent gloves are used for incidental contact only.

4. Wear nitrile or equivalent gloves when handling chemicals. In case of an incidental spill, wear nitrile gloves during cleanup. Do not use latex gloves for organic solvent work.

GENERAL INSTRUCTIONS

1. The sequence of operations in this procedure is not mandatory.

2. Waste Disposal

   NOTE
   Segregation of halogenated and non-halogenated waste streams is vital to the management of waste disposal costs. Likewise, recycling of solvent is a priority. Do not mix solvents if you do not have to!

   2.1. Dispose of halogenated solvents in a properly labeled halogenated solvent waste container.

   2.2. Dispose of non-halogenated solvents in a properly labeled non-halogenated solvent waste container.

   2.3. Dispose of aqueous waste containing heavy metal waste in a properly labeled heavy metal aqueous waste container.

2.4. Dispose of heavy metal waste into the laboratory regulated solid waste container.

2.5. Dispose of contaminated PPE and laboratory expendables into the laboratory regulated solid waste container.

2.6. Dispose of uncontaminated PPE and laboratory consumables in the laboratory nonregulated solid waste container.

OPERATIONS FOR COMPARISON OF THE ABILITY OF SOLVENTS TO REMOVE GREASE

1. Producing grease contamination.
    - 1.1. Number enough clean, empty vials to have five replicate vials as blanks, and five replicate vials for each test solvent.
        - 1.1.1. Blanks are empty vials.
        - 1.1.2. Make sure that the caps are also numbered.
    - 1.2. Weigh all of the vials with the caps on.
    - 1.3. Add a small amount of grease to the bottom of every vial, except for the five blank vials, using a syringe.
        - 1.3.1. Take note of which numbers correspond to the blank vials.
        - 1.3.2. Do not to get grease on the top half of the vial!
    - 1.4. Weigh all of the vials again with the caps on.
2. Cleaning the grease from the vials.
    - 2.1. Remove the caps of all of the vials except for the blank vials.
    - 2.2. Fill each vial that contains grease three quarters full with a test solvent. Five vials per solvent.
        - 2.2.1. Take note of which numbered vials contain which solvent.
        - 2.2.2. Do not add solvent to the blank vials.
    - 2.3. Place the caps back on the vials as they are filled.
    - 2.4. Weigh all of the vials again.
    - 2.5. Shake all of the vials for one hour at a high setting on a shaker.
    - 2.6. Number 5 clean aluminum weigh pans for each test solvent for use as transfer pans.
        - 2.6.1. Make sure the numbers correspond to the numbers that are on the vials on the shaker.
    - 2.7. Weigh all of the transfer pans.
    - 2.8. When the shaking period is over, pour the solvent from the vials on the shaker into the corresponding transfer pans.
    - 2.9. Place the vials that were transferred from (without the caps), and the pans that were

transferred to, in the GC oven at 100 °C to evaporate the solvent.

- 2.10. Take vials out of the oven as they get dry.
    - 2.10.1. Do not allow the residue to get cooked to the vials or pans!
- 2.11. Allow the vials and pans to cool to room temperature.
- 2.12. Place the caps back onto the vials.
- 2.13. Weigh the dry transfer pans.

3. Qualitative data collection of the extracted grease contamination.
    - 3.1. Take pictures of the resulting residue in the bottom of the vials that were transferred from, and the pans that were transferred to.
    - 3.2. Examine the vials and pans and make note of any interesting observations.

GRAVIMETRIC DATA ANALYSIS

1. Analysis of the grease contamination data.
    - 1.1. Calculating the percent of the grease removed from the vials.
        - 1.1.1. Subtract the mass of the empty vials from the mass of the vials with grease to obtain the mass of grease added to each vial.
        - 1.1.2. Subtract the mass of the transfer pan from the mass of the pan with the transferred residue to obtain the mass of the grease residue that was transferred.
        - 1.1.3. Divide the mass of the grease residue that was transferred by the mass of grease added to each vial to obtain the fraction of grease that was transferred by the solvent.
        - 1.1.4. Multiply the fraction of grease that was transferred by the solvent by 100 to obtain the percentage of grease that was transferred by the solvent.

APPENDIX E

LIQUID DENSITY AND SURFACE TENSION MEASUREMENT AND DATA ANALYSIS

SCOPE

This procedure outlines tensiometer preparation, density and surface tension data collection, and data analysis for determining the density and surface tension of liquid samples using a DuNuoy ring tensiometer.

PURPOSE

This procedure provides instructions for performing density and surface tension measurements, data collection, and data analysis using Microsoft Excel.

SAFETY REQUIREMENTS

1. Before beginning this procedure, read all of the Safety Data Sheets for the chemicals at hand.

2. Contact your supervisor for information regarding the proper personal protection equipment (PPE) to be used in this procedure.

3. Personnel engaged in the handling of chemicals that could present a hazard due to splashing are required to wear safety eyewear with side-shields, or work in a hood, or wear a safety face shield.

> **NOTE**
> Nitrile or equivalent gloves are used for incidental contact only.

4. Wear nitrile or equivalent gloves when handling chemicals. In case of an incidental spill, wear nitrile gloves during cleanup. Do not use latex gloves for organic solvent work.

GENERAL INSTRUCTIONS

1. The sequence of operations in this procedure is not mandatory.

2. Waste Disposal

> **NOTE**
> Segregation of halogenated and non-halogenated waste streams is vital to the management of waste disposal costs. Likewise, recycling of solvent is a priority. Do not mix solvents if you do not have to!

   2.1. Dispose of halogenated solvents in a properly labeled halogenated solvent waste container.

- 2.2. Dispose of non-halogenated solvents in a properly labeled non-halogenated solvent waste container.

- 2.3. Dispose of aqueous waste containing heavy metal waste in a properly labeled heavy metal aqueous waste container.

- 2.4. Dispose of contaminated PPE and laboratory expendables into the laboratory regulated solid waste container.

- 2.5. Dispose of uncontaminated PPE and laboratory consumables in the laboratory nonregulated solid waste container.

OPERATIONS FOR DENSITY AND SURFACE TENSION MEASUREMENT

1. Construction of the apparatus.
    - 1.1. Find a flat material, such as ply wood, for an upper platform that is big and sturdy enough for a digital laboratory balance to be supported by it.
    - 1.2. Cut a hole in the upper platform where the under-hook of a balance sitting on top of the material could be accessed from the underside of the material.
    - 1.3. Find a raising and lowering platform, such as a hydraulic jack, that is capable of lowering at a very slow rate.
    - 1.4. Mount the upper platform with the hole over the raising and lowering platform in a way that would allow it to support the weight of a laboratory balance with minimal vibration.
    - 1.5. Place a digital laboratory balance on the upper platform so that the under-hook of the balance is over the hole.
    - 1.6. Hang a small bead chain from the under-hook of the balance.
    - 1.7. Bend or cut a small hook connector so that the open side of the hook is lower than the other side.
    - 1.8. Attach the hook connector to the bead chain hanging from the under-hook of the balance.
    - 1.9. Connect the balance to a computer with data collection software such as Hyperterminal.
    - 1.10. Make the balance level.
2. Measure density.
    - 2.1. Tare the balance.
    - 2.2. Obtain a small Pyrex sinker with a volume of 10 cm^3.
    - 2.3. Place the sinker on the hook connector.
    - 2.4. Allow the mass reading to stabilize.
    - 2.5. Record the stable mass as the dry mass (m_d).
    - 2.6. Obtain a container of the sample liquid large enough so that the sinker can be submerged in the liquid without touching the bottom of the container.

   2.7. Place the sample container under the hanging sinker.
   2.8. Raise the platform so that the sinker enters the liquid sample.
   2.9. Keep raising the platform until the sinker is completely submerged and only one side of the hook connector is breaking the surface of the liquid.
   2.10. Allow the mass reading to stabilize.
   2.11. Record the stable mass reading as the wet mass (m_w).
   2.12. Lower the platform to remove the sinker from the sample.
   2.13. Remove the sinker from the hook connector.
   2.14. Measure the temperature of the sample with a thermocouple.
   2.15. Repeat to obtain a duplicate measurement.
3. Measure surface tension.
   3.1. Obtain a platinum iridium tensiometer ring with a ring radius of 0.9537 cm, and a wire thickness of 0.01779 cm.
   3.2. Make sure that the ring is perfectly circular and flat, and that the part that the ring hangs from is perfectly perpendicular to the ring.
   3.3. Clean the ring by applying fire to it until it glows red.
      3.3.1. Always remove the ring from the fire immediately when it starts glowing red.
   3.4. Hang the ring from the hook connector hanging from the under-hook of the balance.
   3.5. Obtain a container of your sample. The liquid does not have to be very deep in the container. However, the container should have a large enough diameter for the meniscus in the container to not affect the liquid's surface in the center of the container.
      3.5.1. A 400 or 600 mL beaker has a good diameter for this purpose.
   3.6. Place the sample container on the platform directly below the ring.
   3.7. Raise the platform until the ring is just below the surface of the sample.
   3.8. Make sure that the ring is in the center of the container.
   3.9. Bend a thermocouple over the wall of the sample container in a way that allows the thermocouple to be submerged in the sample but close enough to the wall of the container to not interfere with the surface tension measurement. This allows constant measurement of the temperature.
   3.10. Tare the balance.
   3.11. Begin capturing data with the data collection program on the computer.
   3.12. Make the platform begin lowering at a slow and steady rate.
   3.13. The ring should begin slowly rising through the surface of the sample.
   3.14. The ring will pull the surface of the liquid upward with it.
   3.15. The mass lifted should increase, and just before the ring disconnects from the liquid's surface, the mass lifted should begin decreasing.
      3.15.1. If the mass lifted doesn't start to decrease before the ring disconnects from the surface of the liquid, then the platform was probably lowering too fast. If this

happens, restart the measurement.

3.16. When the ring disconnects from the liquid's surface, the measurement is complete. The temperature should be recorded at the time this occurs.

3.17. Stop the data collection.

3.18. Save the data.

3.19. Obtain at least two measurements.

3.20. Always refresh the surface of the sample by removing the surface with a disposable pipet between measurements.

DENSITY AND SURFACE TENSION DATA ANALYSIS

1. Analysis of density data.

1.1. The following equation can be used to calculate the hydrostatic density. Where, dry mass is represented by m_d, the density of the sinker is represented by ρ_1 (this is calculated by dividing the dry mass in grams by the volume of the sinker in mL), the liquid density is represented by ρ_2, the wet mass is represented by m_w, and the density of the air is represented as ρ_3 (this value is kept constant at 0.00118 g/mL in all calculations, because the changes in this value are insignificant).

$$\rho_2 = \left(\frac{m_d - m_w}{m_d}\right)\rho_1 + \left(\frac{m_w}{m_d}\right)\rho_3$$

1.2. This density value can be interpolated to 25 °C.

1.2.1. Take a density measurement at a temperature lower than 25 °C that is also lower than the temperature of the density measurement that needs to be interpolated.

1.2.2. Take a density measurement at a temperature higher than 25 °C that is also higher than the temperature of the density measurement that needs to be interpolated.

1.2.3. The span of these two temperatures should be about 10 to 20 °C.

1.2.4. Convert the high and low temperature density measurements and the two ambient temperature density measurements to Kg/m^3.

1.2.5. Use the following equation and the four density measurements to do a regression to obtain the volumetric temperature expansion coefficient (β).

$$\frac{\rho_L}{\rho_H} - 1 = \beta(T_H - T_L)$$

In this equation, ρ_L is the density at the lowest temperature in Kg/m^3, ρ_H is the density at a higher temperature in Kg/m^3, T_L is the lowest temperature in °C, and T_H is the higher temperature in °C.

1.2.5.1. Create a column in excel that calculates the left side of the equation for all four measurements where the low temperature density stays constant at the lowest temperature value for each calculation. These are the y-values for the regression. Keeping the low temperature value constant creates a zero intercept.

1.2.5.2. Create a column in excel that subtracts the lowest temperature from each temperature. These are the x-values for the regression.

            - 1.2.5.3. The slope obtained from the regression analysis is β.
        - 1.2.6. The low temperature density and β can be used to determine the density at 25 °C with the use of the equation from the previous step.
            - 1.2.6.1. The constant β is unique to every liquid. If a different sample is used, then a new β will need to be calculated.
        - 1.2.7. Use the information in the regression output to obtain an uncertainty value for the interpolated density value.

2. Analysis of surface tension data.
    - 2.1. In an Excel workbook, plot all of the mass lifted versus time data. This will be referred to as a force curve.
    - 2.2. Towards the end of the force curve, the mass lifted should reach a maximum and decrease for a small amount of time to create a rounded curve downward before the meniscus breaks and the mass lifted drops almost vertically to zero.
        - 2.2.1. If the mass lifted drops sharply to zero without first decreasing in small increments to create a curve downward, then the data is bad and the procedure needs to be performed again.
    - 2.3. Find the maximum mass lifted (m) in grams for each set of data by using the maximum function in Excel.
    - 2.4. The maximum mass lifted (m) is used to calculate the maximum liquid volume lifted (V).

$$V = \frac{m}{\rho_2 - \rho_3}$$

    - 2.5. The maximum mass lifted can also be used to calculate the maximum equilibrium force of detachment (F).

$$F = mg$$

    - 2.6. In this equation, g is the gravitational acceleration ($g = 980.665\ \text{cm/s}^2$). This force and the radius of the ring (R) can be used to calculate a first approximation of the surface tension (γ)

$$\gamma = \frac{F}{4\pi R}$$

    - 2.7. Two consecutive corrections are applied to this approximation. The sources of these corrections are discussed further in the Williams paper. The first correction term is for the interface between phase 2 and phase 3, the liquid and the air. This correction (f_{23}) is a function of R^3/V and R/a where a is the wire radius of the ring. This correction term is applied as seen in the following equation.

$$\gamma_{23} = \frac{F}{4\pi R} f_{23}$$

2.8. The second correction term is calculated using the shape of the interface between phases 2 and 3. The corrected surface tension from the previous equation is used to calculate a scaling factor (C_{23}) for R and V as seen in the following equation.

$$C_{23} = \frac{(\rho_2 - \rho_3)g}{\gamma_{23}}$$

2.9. This scaling factor is applied to the radius of the ring as seen in the following equation.

$$R' = R\sqrt{C_{23}}$$

2.10. The scaling factor is applied to the volume lifted as seen in the following equation.

$$V' = VC_{23}^{3/2}$$

2.11. R' and V' are used to calculate the second correction to the surface tension (*f'*) as seen in the following equation

$$f' = \frac{4\pi R'}{V'}$$

2.12. The final surface tension value is calculated using the following equation.

$$\gamma' = \left(\frac{F}{4\pi R}\right) f'$$

2.13. Use a density value that has been corrected to the temperature of the surface tension measurement when performing these calculations.

  2.13.1. Correct the density value using the method given in the density data analysis section replacing 25 °C with the temperature of the surface tension measurement.

2.14. The surface tension value can be interpolated to 25 °C.

  2.14.1. Take a surface tension measurement at a temperature lower than 25 °C that is also lower than the temperature of the surface tension measurement that needs to be interpolated.

  2.14.2. Take a surface tension measurement at a temperature higher than 25 °C that is also higher than the temperature of the surface tension measurement that needs to be interpolated.

  2.14.3. The span of these two temperatures should be about 10 to 20 °C.

  2.14.4. A plot of the hot, cold and ambient measurements should reveal a strong linear relationship between temperature and surface tension. The surface tension should decrease as temperature increases.

  2.14.5. Perform a regression on the data to decide if the coefficients in the linear equation given are statistically significant.

2.14.6. If the coefficients are statistically significant (p-value < 0.05), use the equation to interpolate the surface tension measurement to 25 °C.

2.14.7. Calculate an uncertainty value for the surface tension using the standard error values from the regression output.

SOURCE DOCUMENTS

External Documents:

1. Darren L. Williams; et. al., *An Inexpensive, Digital Instrument for Surface Tension, Interfacial Tension, and Density Determination*, Ind. Eng. Chem. Res. 2008, 47 4286-4289.

APPENDIX F

FALLING BALL VISCOSITY MEASUREMENT AND DATA ANALYSIS

SCOPE

This procedure outlines viscometer preparation, viscosity data collection, and viscosity data analysis for determining the viscosity of liquid samples using a falling ball viscometer.

PURPOSE

This procedure provides instructions for performing falling ball viscosity measurements, data collection, and data analysis using Microsoft Excel.

SAFETY REQUIREMENTS

1. Before beginning this procedure, read all of the Safety Data Sheets for the chemicals at hand.

2. Contact your supervisor for information regarding the proper personal protection equipment (PPE) to be used in this procedure.

3. Personnel engaged in the handling of chemicals that could present a hazard due to splashing are required to wear safety eyewear with side-shields, or work in a hood, or wear a safety face shield.

NOTE

Nitrile or equivalent gloves are used for incidental contact only.

4. Wear nitrile or equivalent gloves when handling chemicals. In case of an incidental spill, wear nitrile gloves during cleanup. Do not use latex gloves for organic solvent work.

GENERAL INSTRUCTIONS

1. The sequence of operations in this procedure is not mandatory.

2. Waste Disposal

   NOTE

   Segregation of halogenated and non-halogenated waste streams is vital to the management of waste disposal costs. Likewise, recycling of solvent is a priority. Do not mix solvents if you do not have to!

   2.1. Dispose of halogenated solvents in a properly labeled halogenated solvent waste container.

   2.2. Dispose of non-halogenated solvents in a properly labeled non-halogenated solvent waste container.

2.3. Dispose of aqueous waste containing heavy metal waste in a properly labeled heavy metal aqueous waste container.

2.4. Dispose of contaminated PPE and laboratory expendables into the laboratory regulated solid waste container.

2.5. Dispose of uncontaminated PPE and laboratory consumables in the laboratory nonregulated solid waste container.

OPERATIONS FOR FALLING BALL VISCOMETER PREPARATION AND VISCOSITY DATA COLLECTION ON LIQUID SAMPLES

1. Prepare viscometer.
    1.1. Clean viscometer.
        1.1.1. Rinse, all viscometer parts that come in contact with the sample, twice with HPLC or spectrophotometry grade methanol. This includes the tube, top, cap, and ball.
        1.1.2. Rinse, all viscometer parts that come in contact with the sample, twice with the sample liquid. This includes the tube, top, cap, and ball.
    1.2. Fill viscometer. Always test fresh type I deionized water before any series of measurements, so that the viscometer constant can be calculated later.
        1.2.1. Fill the tube with the sample liquid until the liquid level is about ¼ of an inch from the top of the tube.
        1.2.2. Add the steel ball to the tube.
        1.2.3. Fill the tube to the top with the sample liquid.
        1.2.4. Attach the top to the tube using the Teflon screw. The liquid will fill the capillary vent in the top and some of the sample liquid will be expelled from the capillary vent.
        1.2.5. Close the tube by screwing the cap onto the capillary vent in the top.
        1.2.6. Dry the outside out the tube and top using a paper towel if needed.
        1.2.7. Invert the tube a few times, allowing the ball to fall from one end to the other.
        1.2.8. Check the tube for air bubbles during 1.2.7.
        1.2.9. If air bubbles are observed, empty the tube and repeat all steps from 1.2.
        1.2.10. If air bubbles are not observed and the steel ball passes through the timing zone in less than one second, empty the tube and repeat all steps from 1.2 using a glass ball.
    1.3. Insert viscometer into the rotating viscometer holder on the viscosity apparatus.
    1.4. Wait about 20 minutes for the viscometer and liquid to reach thermal equilibrium with the room.
2. Use of the viscosity apparatus for data collection.
    2.1. Prepare the video camera attached to the apparatus.

        - 2.1.1. Power on the video camera.
        - 2.1.2. Ensure that the video camera is aligned with the starting timing lines to avoid parallax errors.
    - 2.2. Measuring the temperature.
        - 2.2.1. Unscrew the cap from the capillary vent.
        - 2.2.2. Insert the end of a thermocouple into the capillary vent just far enough to be submerged in the liquid.
        - 2.2.3. After the temperature reading has stabilized, record the temperature.
        - 2.2.4. Replace the capillary vent cap.
    - 2.3. Taking a viscosity measurement.
        - 2.3.1. Rotate the viscometer up using the rotating viscometer holder until the ball is at rest in the top of the viscometer.
        - 2.3.2. Start recording with the video camera
        - 2.3.3. State the name of the sample, the trial number, and the temperature aloud for the recording.
        - 2.3.4. Rotate the viscometer down so that it rests vertically in front of the camera.
        - 2.3.5. After the ball passes through the first set of timing lines, shine a light behind the second set of timing lines on the viscometer. This will cause the camera to focus on the second set of timing lines.
        - 2.3.6. After the ball passes through the second set of timing lines, stop the recording.
        - 2.3.7. Repeat all steps from 2.2. and 2.3. until a sufficient number of measurements have been performed.

FALLING BALL VISCOSITY DATA ANALYSIS

1. Obtain the starting and finishing times for each measurement. These times will be in seconds and fractions of seconds. The fractions depend on how many frames per second are achieved by the video camera.
    - 1.1. Open the viscosity videos in Adobe Premiere Pro or other video software that allows frame-by-frame control.
    - 1.2. Watch the video of each measurement frame by frame to obtain the correct time stamps.
    - 1.3. The starting time is obtained by watching as the ball passes through the first set of timing lines. When the ball is exactly between the two lines, record the time stamp for that frame.
    - 1.4. The finishing time is obtained by watching as the ball passes through the second set of timing lines. When the ball is exactly between the two lines, record the time stamp for that frame.
2. Analysis of the viscosity measurement data.
    - 2.1. Use the following regression equations from the NIST data on water to calculate the density (ρ) and viscosity (η) of water at the temperature (T) of each water measurement.

$$\rho_{water} = -0.00000500(2)T^2 - 0.0000056(7)T + 1.000271(9)$$

$$\eta_{water} = 0.000430(2)T^2 - 0.042(1)T + 1.668(1)$$

2.2. Use the time (t) of the ball drop, the density of the ball (ρ_b) (steel = 8.020 g/mL and glass = 2.530 g/mL), the viscosity of water, and the density of the sample (ρ_s) (water in this case) to calculate the viscometer constant (K) at each water measurement temperature.

$$\eta = K(\rho_b - \rho_s)t$$

2.3. Perform a regression analysis on the viscometer constant versus temperature data for water to produce a temperature-dependent viscometer constant equation.

2.4. Interpolate the density values to the temperature of each sample measurement according to the method given in the density and surface tension SOP.

2.5. Use the temperature-dependent viscometer constant equation to calculate the viscometer constant at the temperature of each sample measurement.

2.6. Use the viscosity equation and the time of the ball drop to calculate the viscosity for each measurement of each sample.

3. The viscosity can be interpolated to 25 °C.

3.1. Perform a regression of the temperature versus viscosity data for each sample to obtain an equation that can be used to interpolate the viscosity to 25 °C.

SOURCE DOCUMENTS

External Documents:

1. ASTM Standard D1343, 1995 (2000), "Standard Test Method for Viscosity of Cellulose Derivatives by Ball-Drop Method," ASTM International, West Conshohocken, PA, 2000, DOI: 10.1520/D1343-95R00, www.astm.org.
2. Gilmont, Roger, “Falling Ball Viscometer Directions for Use”, Roger Gilmont Instruments, Inc.

Internal Documents:	NONE
Generated Forms:	NONE
Related Forms:	NONE

VITA

Jacob David Perry

Education

Master of Science student in Chemistry at Sam Houston State University, August 2015 – present. Thesis title: "Identification and characterization of non-flammable azeotropic mixtures for precision cleaning."

Bachelor of Science (May 2015) in Chemistry with a concentration on professional chemist and a minor in mathematics, Sam Houston State University, Huntsville, Texas.

Academic Employment

Research Assistant to Dr. Darren L. Williams, Department of Chemistry, Sam Houston State University, January 2015 – present.

Teaching Assistant, Department of Chemistry, Sam Houston State University, August 2013 – present. Labs taught include: General Chemistry I (2 sections), General Chemistry II (4 sections), Physical Chemistry I (4 sections), Physical Chemistry II (3 sections), and Advanced Integrated Laboratory (1 section). Responsibilities include: Preparing materials for laboratory exercises, presenting pre-lab lecture materials, assisting and supervising students during laboratory excercises, grading, and tutoring.

Head Teaching Assistant to Dr. Paul A. Loeffler, Department of Chemistry, Sam Houston State University, August 2014 – May 2015. Responsibilities include: all responsibilities of a teaching assistant, in addition to assisting the professor by preparing the other teaching assistants to teach lab, and co-leading teaching assistant meetings.

Research Experience

Research Assistant to Dr. Darren L. Williams, Department of Chemistry, Sam Houston State University, August 2014 – present. Research topics include: azeotropic solvent blending, Hansen Solubility Parameters, solder flux / ionic contamination removal & quantification, gravimetric analysis, and method development.

Research Assistant to Dr. Rick C. White, Department of Chemistry, Sam Houston State University, summer 2013 & summer 2014. Research topics include: organic synthesis, and photochemistry.

Laboratory Instrument Experience

Instrumental / technique familiarity includes: nuclear magnetic resonance, differential scanning calorimetry, atomic absorption spectroscopy, mass spectrometry, infrared spectroscopy, inductively coupled plasma spectroscopy, UV/VIS spectroscopy, fluorescence spectroscopy, dynamic light scattering, gas chromatography, high performance liquid chromatography, capillary electrophoresis, and gel electrophoresis.

Instrumental / technique proficiency includes: constant pressure calorimetry, bomb calorimetry, Raman spectroscopy, DuNouy ring tensiometry, tag closed-cup flash point, ball-drop viscometry, vapor degreasing, ion probe, and photochemical reaction vessel.

Certifications

The SHSU chemistry degree with a concentration on professional chemist is an ACS certified degree program.

Publications and Papers

"Photolysis of a cyclic carbonate ester and a cyclic sulfite ester: radical intermediates and ionicintermediates in an advanced laboratory experiment"

Arney, B. E.; Perry, J.; Thompson, N.; White, R.W. Photolysis of a cyclic carbonate ester and a cyclic sulfite ester: radical intermediates and ionic intermediates in an advanced laboratory experiment. *Chem. Educator* **2014**, 19, pp330-332.

This paper was the result of research in organic photochemistry under Dr. Rick C. White.

"Ionic pathways in the photochemistry of cyclic sulfite esters"

White, R. C.; Arney, B. E.; Perry, J.; Thompson, N.; Pithan, P. M.; von Gradowski, S.; Ihmels, H. Ionic Pathways in the Photochemistry of Cyclic Sulfite Esters. *J. Heterocyclic Chem.* **2016**. (submitted to be published)

This paper was also the result of research in organic photochemistry under Dr. Rick C. White.

"Using 3-Component Azeotropic Solvent Blends in Cleaning Processes"
Not a published work.
Authors: Jacob D. Perry*, Darren L. Williams.

This paper was submitted as a research proposal to NASA NSPIRES NSTRF15

Academic Awards

Dean's List (6 semesters)
President's List (2 semesters)
Robert Welch Foundation Summer Research Grant 2013, 2014, and 2016
Jeffrey E. Zagone Scholarship 2012-2013
Ray E. Humphrey Scholarship 2013-2014
Burrough Scholarship 2015