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Phase Equilibria and Heat Capacities for Tetraarylphosphonium-based Ionic Liquids

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A thesis submitted in partial fulfillment of the requirements of the University of South Alabama Honors Program and the Bachelor of Sciences degree in the Chemical & Biomolecular Engineering Department

University of South Alabama
Mobile
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Approved by:

Mentor: Dr. Kevin West

Committee Member: Dr. Grayson Dennis

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ABSTRACT

Climate change is one of the most pressing issues facing humanity in the 21st century. A major contributing factor to this problem is the continued use of fossil-fuel based sources for energy. Concentrated solar power (CST) with thermal energy storage (TES) provides a potential opportunity to support this transition away from fossil fuels but suffers from high costs and extended downtimes. Current heat transfer fluids used in these processes often consist of a mixture of alkali metal nitrates with melting points above 200°C. For CST and TES to be viable, a thermally stable, low melting fluid is needed. Ionic liquids (ILs) provide a very feasible form of TES due to their high heat capacities and low melting points. Thermally robust ILs can be synthesized by limiting the structural diversity of the species to thermally stable moieties on the cation and coupling these cations with a thermally stable anion. However, these synthetic restrictions result in salts with melting points at or above 100°C. Mixtures of these salts, with each other or with structurally similar molecular species, can yield fluids with melting temperatures low enough to be effective thermal storage fluids. In this project, the phase equilibrium of a binary mixture of tetraphenyl phosphonium bistriflimide (TPP) and benzanilide was examined to provide valuable information on eutectic behavior for organic ionic liquids with aromatic compounds. The use of digital scanning calorimetry (DSC) (Solid/Liquid Equilibrium, SLE) along with cloud-point analysis (Liquid/Liquid Equilibrium, LLE) was used to study this behavior. The phase transitions, including eutectic behavior, are expressed on a binary T-x diagram and show how the phase behavior varies with temperature and composition. Solid/liquid equilibrium behavior is compared to the ideal solution model to aid in understanding molecular-level interactions in the mixture. The study showed a minimum eutectic melting temperature of below 100 °C and liquid-liquid interactions in compositions having high amounts of TPP compared to benzanilide. The findings of this study can be used to develop further ILs and their mixtures as viable thermal energy storage fluids that could dramatically reduce the cost and difficulty of operating CST at scale.

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LIST OF ABBREVIATIONS

CSP: Concentrated Solar Power

DSC: Differential Scanning Calorimetry

IL: Ionic Liquid

TES: Thermal Energy Storage

TPP: Tetraphenyl phosphonium bistriflidmide

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INTRODUCTION

Human influences on the environment over the past century have been drastic and damaging to both human health and the ecosystems across the planet. The damage done to the environment has been done through several means, but greenhouse gas pollution has been a major cause of the observed warming of the planet in recent history with carbon emissions having the most significant impact.[1] In the United States, energy related carbon emissions are projected to increase through the year 2040 despite a projected dip in the mid-2030s.[2] A major component of carbon emissions is the way energy is produced with 25% of all carbon emissions being from the energy and heat sector.[3] Internationally, Renewables are only projected to account for 15% of energy by 2040 while Liquid, Coal, and Gas based fuels are not expected to decrease output at all in the same time frame.[4] The lack of expectation in the adoption of renewable energy shows the need for innovation in the field to make renewables a more viable and used form of energy production.

A major problem with many of the renewables widely used in the United States is that they are intermittent energy sources that cannot produce energy whenever needed like coal, natural gas, or liquid fuels can. There is however a solar power based renewable energy that has the ability to provide dispatchable energy in the same way that the fossil fuel power plants widely used do. This technology is termed Concentrated Solar Power (CSP) with thermal energy storage. CSP concentrates the thermal energy from the sun to use it to heat a process fluid which can then be used to heat steam and run a generator. Although this technique has a lot of potential in being a renewable and carbon friendly way to generate dispatchable energy many of the power plants that use this thermal concentration and then store this heat energy have struggled with the challenges that are presented by generating energy this way.[5] A major challenge is finding a good compound to use as the thermal energy storage device.

Ionic liquids present themselves as a wonderful option to use for thermal energy due to their high heat capacities and thermal stability, but the compounds that have the most beneficial of these properties often come instead in the form of a molten salt which is a solid at room temperature.[6] Not only are they a solid at room temperature but they often need to be heated to extremely high temperatures to enter the liquid phase where their ionic liquid properties can be fully utilized in storing thermal energy.[7] This presents a significant opportunity for improvement within thermal energy storage as a compound that retains the advantages of high heat capacity and thermal stability but also melts at a much lower temperature would be a much more viable form of storage that would make CSP a much better investment. The study of solid-liquid phase equilibria between potentially useful molten salts and other compounds is therefore a pathway into finding a way to reduce the melting point of a molten salt without greatly sacrificing the properties that make them such a good option for thermal energy storage.

Literature Review

The impact that human activity has on the environment has been a heavily researched topic over the last few decades. There are many facets to the ways that the needs of human society can impact the environment but one that has had extra attention given to it is the emission of various compounds into the air that can produce several negative effects. Since 1900, the amount of carbon emissions has increased dramatically with about a 90% increase since 1970 alone.[8] This is not the only form of air pollution that is potentially harmful however with both SO_2 and NO_X being two non-carbon compounds which provide a negative impact to the environment. The negative impacts that these compounds have when in the air have been well documented through several different studies and committees. These compounds have been found to have a negative impact on vegetation and are especially impactful in regard to forest trees.[9] They are also a significant part of the air pollution that negatively impacts human health and therefore a contributor to the 4.2 million deaths attributed to outdoor pollution every year.[10] The negative impact that these pollutants have on both the environment and on human health have therefore made them a major focus in the effort to combat human caused climate change and pollution.

Production of easily accessible energy is a major factor in the quality of life and in the advancements made in the last century in human society. However, the energy sector is a significant producer of air pollution and accounts for much of the SO2 and NOX emissions currently being produced.[11] They are also a large component of greenhouse gas emissions which is another key area that is being focused on to diminish human caused damage to the environment.[3] The negative impacts that the pollution from the energy sector can cause, along with several other factors, have driven the investment and research into cleaner renewable sources of energy production. This has led to rapid cost reduction in the sector and a large increase in the development of energy plants that use renewable energy. Despite this, the current rate of investment is proving to not be near enough as renewables will need to grow at triple the current rate to meet the pledged climate change guidelines for many countries.[12] This means that the pace at which energy production is changed from the current dominant methods of oil, natural Gas, and coal must be hastened through increased investment. Continued advances in the field of renewable energy are also likely needed to increase the adoption of renewable energy sources.

The viability of renewable energy in comparison to the established fossil fuel-based power plants depends directly on the type of renewable energy used, the area it is in, and economic factors that can vary wildly from region to region. The economic benefits of renewable energy sources in comparison to both different renewable energy sources and fossil fuel use is an often-debated topic that has wide reaching impacts on the policy that many governments along with power companies use to determine investment in new renewable energy plants. In recent years, it has been shown that wind plants and traditional solar power plants are on average more cost-effective in terms of energy produced per dollar than either coal or natural gas plants.[12] This also does not factor in the large human health concerns that fossil fuel plants contribute to which increase their actual economic impact. The health impact that these plants can have could be up to 30% of the cost of their energy production.[13] This further shows the pure price advantage that solar, and wind have over traditional fossil fuel plants. Despite this, adoption of renewables has been slower than needed which points to other factors besides just cost per megawatt hour slowing down the creation of new renewable energy plants.

If renewables are most cost effective on average, then there must be other concerns which are slowing down the needed pace of renewable energy adoption. One of these is likely the environmental concerns that can come with new renewable energy power sources. It is important to note however that almost every new renewable energy or nuclear plant with the exception of a few potential hydropower plants has significantly less lifecycle emissions than fossil fuel plants.[3] There has also been discussion on the other environmental issues that could arise with the creation of new solar, wind, hydro, or geothermal energy plants although many of these issues are much less drastic that the effects current power generation technologies create. Wind power for instance, does not seem to cause significant harm in terms of noise pollution or bird fatality although direct comparisons to other energy sources' environmental impact are rare.[14] The lack of large environmental concerns on the same level of the current use of fossil fuels points to there being another cause for concern in the adoption of renewable energies.

There are other problems outside the realm of environmental impact that arise with the heavy use of wind and solar power. The most discussed and troubling of these concerns would be the swap from dispatchable sources of energy (Coal, Oil, Natural Gas) to intermittent energy sources (Solar, Wind) that cannot change output based on the needs of the energy grid. This leads to an imbalance not in total energy produced but instead the time it is produced which can lead to the dreaded "Duck Curve" where the net load on a power grid fluctuates much more rapidly due to high penetration of solar based renewable energy which has been a major issue in the wide adoption of solar renewable energy.[15] There are several ways that this curve can be flattened but many of them would require lifestyle changes that may be difficult to enforce or encourage with a public that has historically been resistant to changes in quality of life to improve environmental impact. There is however a clean, renewable energy source that has the potential to provide dispatchable energy without greatly increasing the cost of production. This technology is termed Concentrated Solar Power (CSP) and has been shown to reduce the system operating cost in areas that have a large amount of renewable energy generation.[16,17] There are many forms of CSP with many still being rapidly developed. In general, a CSP plant uses a series of arrays which concentrate the thermal energy of the sun to heat up a process fluid which is then used to drive a conventional generator to produce energy.[18] According to the same source, there are four main types of CSP plants which are Parabolic Trough Collectors, Linear Fresnel Collector, Tower Solar Power, and Stirling Dish. These all use the same base technology but with many large differences in terms of design, cost, area needed, running temperature, and efficiency. All of them, however, can use a form of storage termed Thermal Energy Storage (TES). Concentrated Solar Power is very easily coupled with TES despite what type of CSP is being used in any given plant.[19] The use of this energy storage is what actually makes CSP a dispatchable energy source as the TES deployed alongside the plant allows for the short-term storage of energy throughout the day to then be deployed during peak consumption hours. The ease of deploying CSP alongside a TES system is what separates it from other renewable energies as it allows the storage of energy without having to use a battery system.

The addition of a TES system to a CSP plant also makes it an excellent option for providing energy in industrial plants and processes. 33% of US energy consumption comes from the industrial sector which makes it a key contributor to carbon emissions.[20] Cogeneration of electrical power and thermal energy is a common practice among energy intensive industrial processes such as petroleum or pulp processing. CSP could be a way to transition these processes away from carbon emitting sources. As of 2018, Natural gas and hydrocarbon has liquids are the energy source for 53% of industrial consumption.[21] The dependency of many industrial processes on carbon emitting sources of energy pose a significant challenge with decarbonization of energy generation. The use of CSP in these industries could increase efficiency by expanding the use of cogeneration while also reducing the carbon footprint of energy generation at sites. However, this would require a significant capital investment to install the needed equipment to operate these smaller scale CSP facilities. Around 93% of natural gas used in the industrial sector cannot be easily switched.[21] This means that any new technology that would be implemented would need to recoup the costs of the capital investment needed to construct that technology. The flexibility of TES could provide a way of increasing the use cases of a new onsite generation plant by integrating multiple systems within the TES system.

Although concentrated solar power (CSP) is already used in many functional plants across the world there are still many future developments that could improve the viability and ease of use of CSP. A large part of the potential future developments in the field of CSP involve improvements in the techniques of thermal energy storage that pairs with the solar plants. Many of the issues with currently existing CSP facilities involve their TES or heat transfer fluid systems.[22] The crucial technical requirements for the design of a thermal energy storage (TES) system are:[23]

1) High Energy Density
2) Good heat transfer between heat transfer fluid and storage medium
3) Mechanical and Chemical stability of storage material
4) Chemical compatibility between heat transfer fluid, heat exchanger, and storage medium
5) Complete reversibility for a large number of charge/discharge cycles
6) Low thermal losses
7) Ease of control

Additional factors include the material both having a low economic and environmental cost associated with their production and use.[19] The significant improvement of any one of these factors without a loss in another could provide a much more viable TES solution that could drastically improve the viability of both thermal storage and CSP. This creates a delicate balancing act between the different factors that create a good TES fluid. For instance, molten salts are typically considered one of the more viable forms of TES, but they often possess high melting temperature. This is not ideal as a low melting temperature is needed to reduce the freezing risk of the liquid which is being used as a TES fluid.[24] Many methods of decreasing the melting temperature of a molten salt would help alleviate the freezing problem that could cause enormous problems for a CSP plant but would likely also cause negative impacts to either the thermal stability or heat capacity of the molten salt. This is problematic as both high energy density and stability are some of the crucial technical requirements that are outlined above. There are two other types of TES besides the one that uses molten salts (sensible heat storage). These are latent heat storage and thermochemical heat storage and although both have shown potential, they are more complex than sensible heat storage and are further away from maturity.[25] This means that at least for plants currently being designed with a TES system this balance between the different components of a thermal storage fluid is a vital one to reach the best possible outcome in terms of economic viability.

Molten salts have been shown to possess many of the factors that are needed in a good TES fluid. These can include the ability to discharge at constant rates, lack of corrosion issues, eliminating the need for pressurized tanks, and several others.[7] Currently, nitrate-based molten salts position themselves as being a high-efficiency option for thermal energy storage but have high melting temperatures.[26] Melting temperatures of the pure components used for nitrate-based molten salt mixtures in TES can exceed 280 °C.[27] This high melting temperature requires additional freeze protections to operate in a TES system which increases the challenge of operating a CSP plant.[28] Due to this, finding a material that has similar advantages to the current molten salts while allowing for a lower melting temperature would increase the viability of the CSP technology. There are several materials that have the potential to meet these requirements with the focus material for this paper being a tetraarylphosphonium-based ionic liquid called tetraphenyl phosphonium bistriflidmide. Several traits of tetraarylphosphonium-based ionic liquids could be particularly useful in the field of TES. The most important of which being their extremely high thermal stability for an organic material.[29] The materials in this family of ionic liquids also possess significantly lower melting temperatures than the pure components utilized in molten salt mixtures for TES.[30]

A potential eutectic mixture between an ionic liquid and another compound that has similarities in the desired qualities for TES could provide a more efficient means of storing thermal energy by lowering the melting temperature of the ionic liquid without severely limiting the positive qualities of the fluid. A deep eutectic solvent is one that presents a significant negative deviation from its thermodynamically ideal behavior.[31] Many of the same principles used to form these deep eutectic solvents can be applied to the formation of eutectic solvents with ionic liquids. Much work has been done on the factors that can impact the melting point depression of a eutectic which can include crystal packing as well as hydrogen bonding factors.[32] The specifics of how and what effects tetraarylphosphonium-based ionic liquid's solid-liquid equilibria is an area that still needs a significant amount of work. However, the study of the equilibria behavior between different compounds and these ionic liquids could lead to a much lower melting point through the use of a eutectic solvent. Currently, the molten salt mixtures used in TES utilize this technique to greatly reduce their melting temperature; mixtures of these salts achieve further melting temperature reductions (over 100 °C lower than the binary mixture) by adding additional components.[33] By studying the binary interactions of tetraarylphosphonium-based ionic liquids a similar mixture of several materials could be created that greatly reduces melting temperature without sacrificing thermal stability.

The viability of ionic liquids as energy storage devices along with their ability to form deep eutectics with a variety of compounds shows the potential of utilizing these qualities to produce a better energy storage fluid. In particular, the eutectic formed from the mixing of TPP with benzanilide shows promise and could lead to further research on the behavior of tetraarylphosphonium-based ionic liquids as a storage fluid for thermal energy. As previously discussed, the measuring of eutectics using Differential Scanning Calorimetry (DSC) is quite established and shows promise in being able to chart the behavior of the solid-liquid equilibrium of TPP and benzanilide. Additionally, the work done on the solid-liquid equilibrium for these two compounds should allow for a more accessible starting point for potential future work in tetraarly-phosphonium based ionic liquids solid-liquid equilibrium studies. Due to the need to reduce costs and increase feasibility of concentrated solar power and thermal energy storage the behavior of lower melting temperature ionic liquid mixtures must be studied to determine whether they can prove to be a viability alternative to the current thermal energy storage fluids being used today.

Experimental Methods

Materials

Benzanilide was produced by Alfa Aesar, USA with a 98+% purity. Tetraphenyl phosphonium bistriflidmide (TPP) was produced according to methods previously described in literature.[30] Samples were combined into TA Tzero Pan before being sealed with TA Tzero Hermetic Lid and mixed through at least 10 melt/freeze cycles in the DSC.

Differential Scanning Calorimetry

All Differential Scanning Calorimetry (DSC) measurements were taken using a TA Instruments DSC 2500. The program that was used to acquire and analyze the data was TA Instruments TRIOS 5.1. The rate of the ramp in the runs in which data was taken was 10° C/Min with a range of -80 °C to 180 °C. The "onset" analyze function built into TRIOS was used to find the temperature used for the eutectic point. The "endset" analyze function built into TRIOS was used to find the melting point of the specific mixture being sampled. The "peak integration" analyze function was used to find the enthalpy of the sample to build the Tamman's triangle to find the expected eutectic composition value. For that analysis, only the curve that represented the eutectic melt was measured, if the two curves were indistinguishable then analysis was not done.

Sample DSC Curves

Figure 1 shows a sample DSC curve generated by ramping pure TPP 10 °C/min from 0°C to 180 °C.

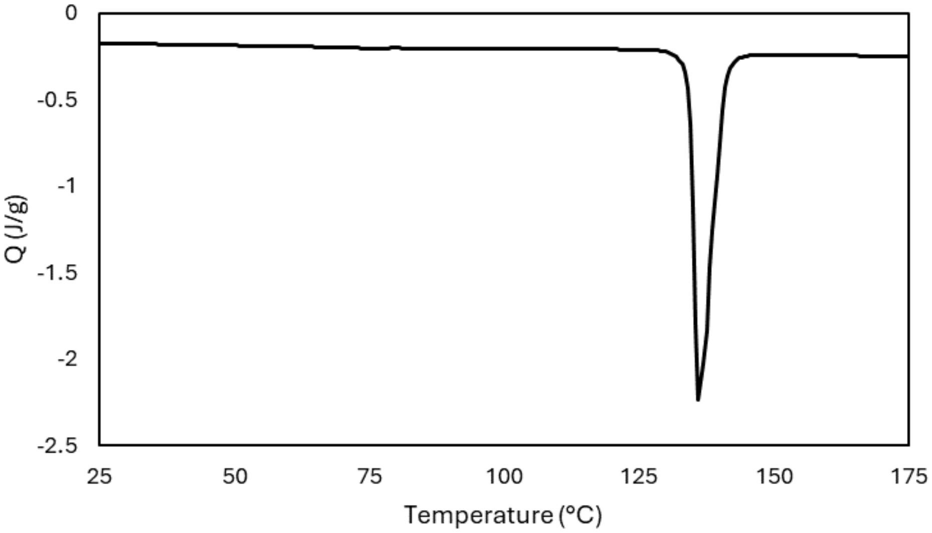

Figure 1. DSC curve produced from ramping TPP from 0°C to 180 °C by 10 °C/min**.**

As seen in **Figure 1**, a pure compound produces a single large curve that can be measured to provide the melting temperature of the compound from its onset point and the ΔH^{fus} of the compound through integration of the area of the curve. The observed behavior changes when a mixture of compounds is measured which is shown in **Figure 2** where a mixture of 40 mol% TPP and 60 mol% benzanilide is ramped from 0°C to 180 °C by 10 °C/min. The mixture produces a curve with two endothermic events in the plot which reflect two different melts occurring within the sample. The first melt is the eutectic melting point, or the point where some material in the sample starts to melt to create solid-liquid phase behavior. The second melt is the liquidus melting point, or the point where the remaining solid in the sample melts to create a completely liquid sample. This melt is measured by taking the endset of the second endothermic event and produces a solubility point that can be plotted. By plotting this point at different compositions of TPP, a line can be created that describes the liquidus behavior of the TPP:benzanilide binary system.

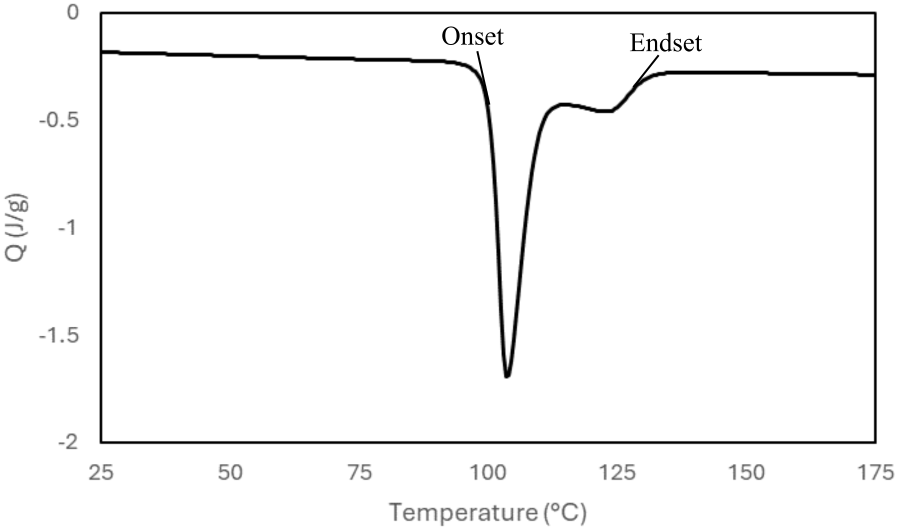

Figure 2. DSC curve generated from ramping a 40 mol% TPP mixture with benzanilide from 0°C to 180 °C by 10 °C/min**.** Onset and endset tags are estimates to demonstrate area on curve each analysis is used.

Procedure

The preparation for mixtures of the TPP and benzanilide was done in pan to prevent unequal mixing from producing inaccurate results. The Tzero aluminum pans were first weighed using a Mettler-Toledo XP26 DeltaRange with a max weight of 5.1g/22g and an error of .002mg/.01mg (which was also used to make all measurements for this experiment). The two materials used were massed directly into the Tzero pan and then sealed with the Tzero hermetic lid. The exact weights of the two materials were then used to find the mole fraction composition of the sample. This sample was then mixed in pan by using the freeze-thaw behavior of the material to promote mixing. The sample is ramped up to 180 °C and then down to 0 °C before being equilibrated to 0 °C. This is done 10 times to achieve a well-mixed sample that provides data accurate to the composition of the sample. Five additional runs of the same procedure are then done to generate DSC curves for data collection. As seen in **Figure 3**, the 10 mixing cycles are necessary to properly integrate the two components together and synchronize the sample's thermal history. The use of 10 of these cycles provided data collecting runs that were highly uniform amongst one another which is also shown in **Figure 3**.

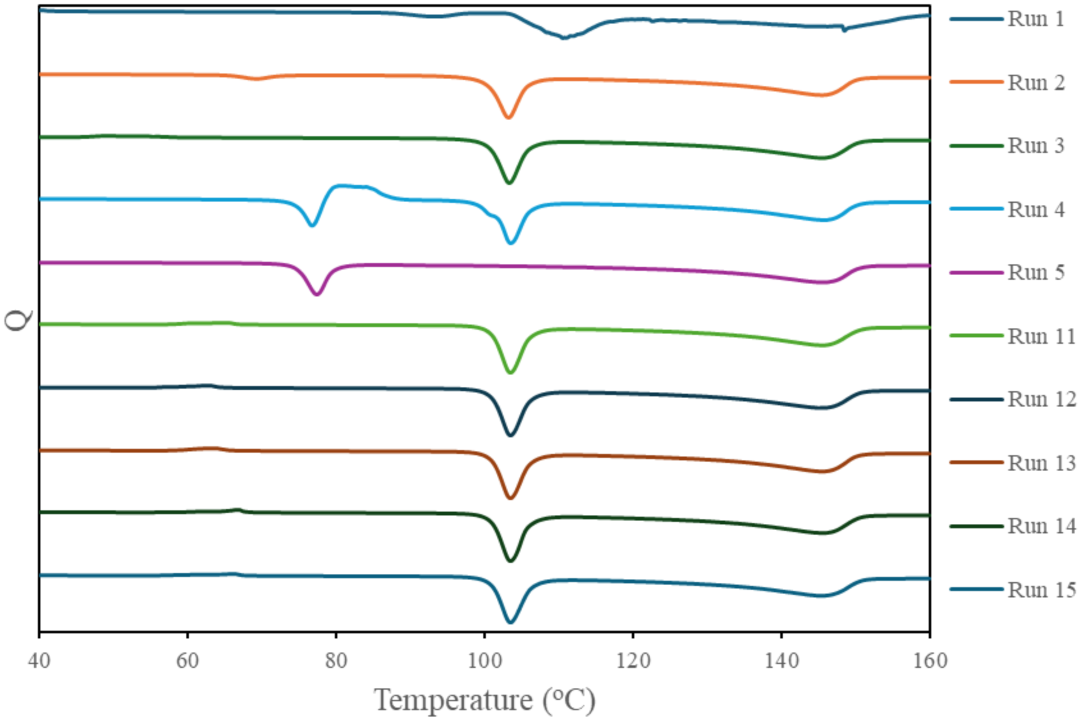

Figure 3. DSC Curves produced from ramping a 20 % TPP - 80 % benzanilide mixture 0°C to 180 °C by 10 °C/min**.** The first 5 and last 5 cycles are displayed to demonstrate mixing effect.

The onset temperature is recorded for the first curve on the plot and the endset temperature is recorded for the second. These values are used for the eutectic temperature and the liquidus temperature respectively. Data was not used in several circumstances due to various reasons. Some samples did not properly melt and refreeze during data collecting runs which prevented the sample from producing curves to be measured. Several different operating procedures were attempted to induce melt in these problematic samples, but no procedure was found that could reliably create a melt/freeze repeatably with these samples. The collection of data around the eutectic point proved to be problematic due to the slow melting of the eutectic mixture that caused the two curves (eutectic and liquidus) to be too close to distinguish between them. To prevent the reporting of inaccurate liquidus data all compositions within 10 °C of the predicted eutectic composition do not have liquidus data reported.

For the Tamman analysis, the enthalpy of the eutectic melt was measured using the "peak integration" analysis function present on the software. The enthalpies were then plotted to create a linear regression model for both the hypo- and hyper-eutectic sides of the plot so the intersection could be used to estimate the molar composition of a eutectic mixture. Compositions that contained high amounts of TPP or benzanilide produced eutectic enthalpies that were small enough to have substantial deviation between samples. For this reason, all enthalpies that were recorded under 10 J/g were excluded from the plot.

Results

The main objective of this experiment was to create a solid-liquid phase equilibrium chart for TPP and benzanilide. Creation of this chart was accomplished through the measurement of liquidus and eutectic DSC peaks at various compositions. An example run for measured compositions throughout the entire composition range is included in **Figure 4**. The data for the 70 mol% TPP sample was not included as consistent data could not be achieved in this region. Two-phase liquid-liquid behavior has been observed experimentally with these compounds at this composition and temperature which provides a reasonable explanation for this abnormal DSC behavior. On the 50 mol% curve the liquidus and eutectic curves combine into a single curve. This behavior occurs on all sample compositions sufficiently close to the eutectic composition which prevents the accurate measurement of liquid curve data in these samples. For these runs, the eutectic measurement is reported without the accompanying liquids measurement.

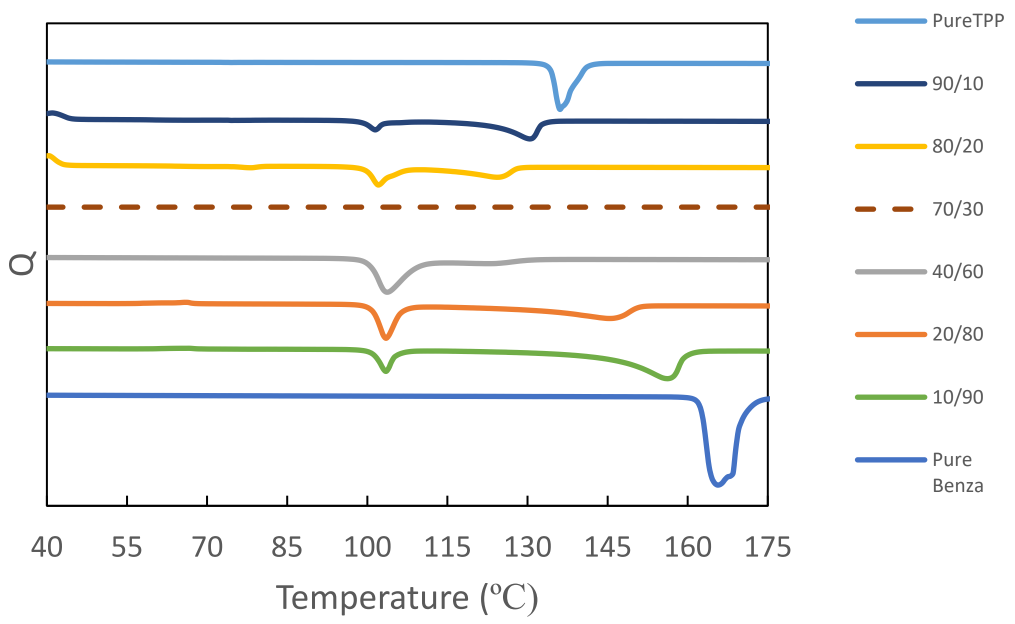

Figure 4. DSC curves for mixtures of TPP and benzanilide. Curves are offset for visibility but not rescaled and are labeled by their molar composition. The dotted line represents the data point influence by observed liquid-liquid phase behavior.

The full solid-liquid equilibrium curve is shown in **Figure 5**. The ideal solution model is overlayed on top of the experimental data. As seen by this overlay, the two compounds behave close to what is predicted by ideal behavior in high compositions of either TPP or benzanilide. However, there are significant deviations from ideal behavior as the samples approach the eutectic composition. A thermodynamic model cannot currently be fit to the given data as the absence of measurements for two-phase behavior prevent the model from maintaining accuracy throughout the entire composition range. As previously stated, it is not possible to use solely DSC analysis to find near-eutectic composition liquidus curve information. There is also detected two-phase liquid-liquid phase behavior that has not yet been measured well enough to be included in the phase equilibrium chart. This is the suspected reason for the abnormal behavior seen near the 70 mol% TPP composition. **Table 1** shows the exact measurements of eutectic and liquidus melts.

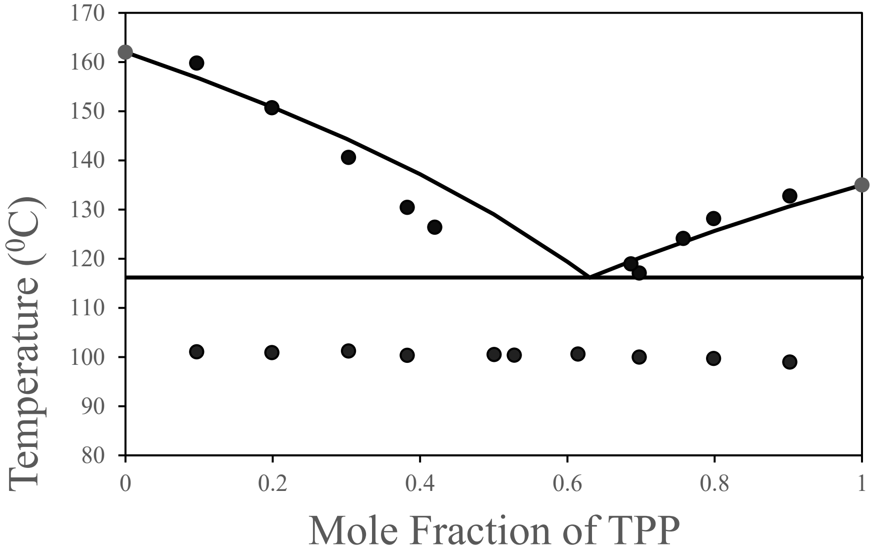

Figure 5. Plot of solid-liquid equilibria curve. The experimental data is shown with solid dots along with the predicted data based on ideal components shown in solid lines. The values for both the liquidus curve and eutectic point are shown for experimental values.

Table 1. Eutectic and liquidus melting temperatures for various compositions of a binary TPP-benzanilide mixture.

TPP (mol %)	T_{eu} (°C) (±0.1)	T_{li} (°C) (±0.1)
0.097	101.0	159.8
0.199	100.9	150.7
0.303	101.2	140.6
0.383	100.3	130.4
0.420	100.1	126.4
0.686	100.5	118.9
0.698	100.0	117.1
0.757	99.7	124.1
0.799	99.7	128.2
0.902	99.0	132.7

The previously described inability to produce accurate data around the eutectic composition creates a difficulty in determining the viability of these compounds as TES materials. The eutectic composition has the lowest possible melting point for a full sample of these two compounds and so that mixture's physical properties have special relevance in the comparison to current TES materials. To estimate the exact eutectic composition, a Tamman's plot was created which is shown in **Figure 6**. This plot shows the enthalpy of fusion of the eutectic melt for both the TPP-rich and benzanilide-rich sections of the solid liquid equilibrium diagram. As the relative enthalpy of fusion for the eutectic decreases as you move further away from the eutectic composition, two linear lines can be created from the two sections which will intersect where the eutectic enthalpy of fusion is at its maximum. This intersection point can be used as an approximation for eutectic composition as the eutectic enthalpy of fusion should be greatest when the entire mixture is at the eutectic composition. The equations to the linear fit lines are both provided within the chart. When using this method, the predicted eutectic composition is 54 mol% TPP. This aligns with what is expected both through the phase behavior previously displayed as well as preliminary modeling.

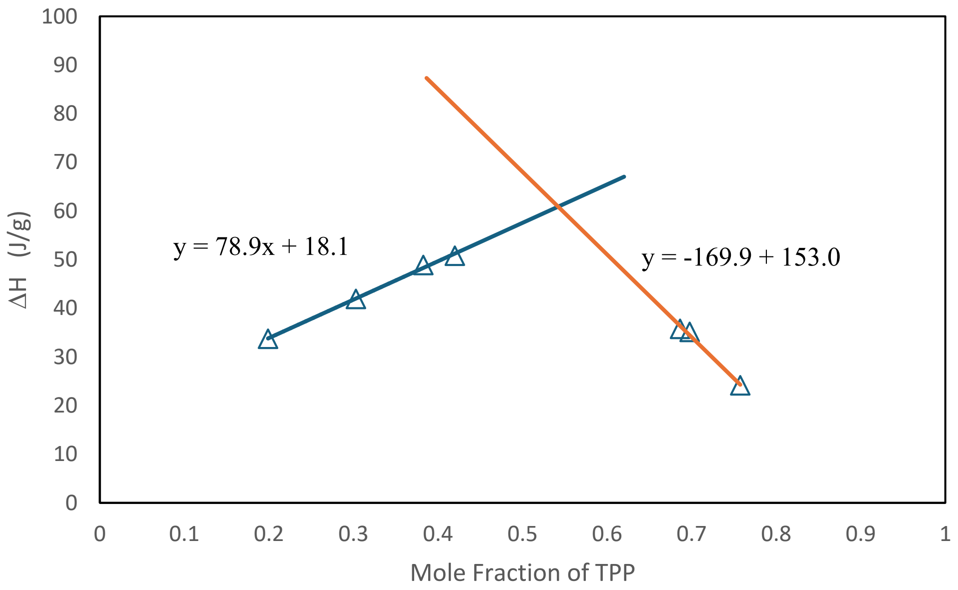

Figure 6. Plot of the relationship between concentration of TPP and enthalpy. The experimental data is shown using dots while the solid lines are linear fits to the data.

This plot was overlayed on to the solid-liquid equilibrium curve to provide visual confirmation of the accuracy of the methodology. **Figure 7** contains this overlay as well as the predicted eutectic composition as found with the Tamman's plot.

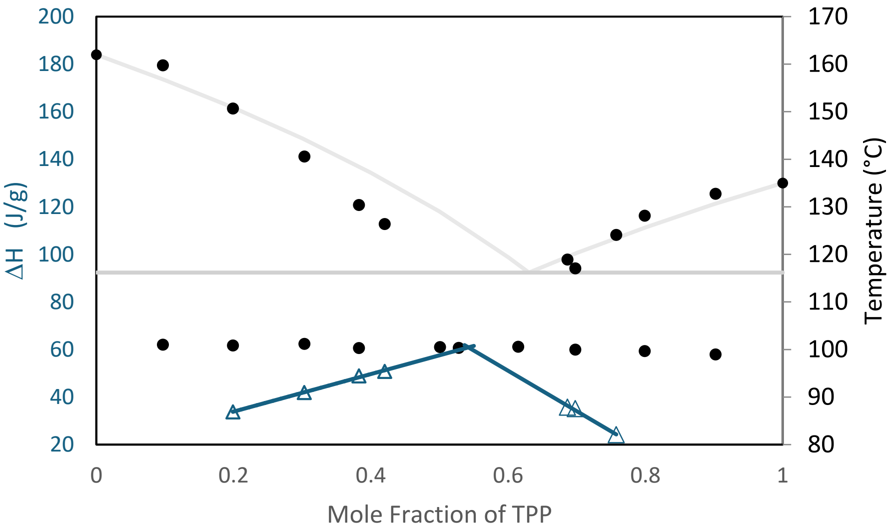

Figure 7. Enthalpy of eutectic melt, solid-liquid equilibrium curve, and ideal solid-liquid equilibrium curve for TPP:benzanilide system based on concentration of TPP.

Conclusion and Future Work

The solid-liquid equilibrium for TPP and benzanilide proved to show many interesting behaviors that can aid or start further research with TPP and other tetraarylphosphonium-based ionic liquid compounds. The eutectic temperature for the TPP: benzanilide mixture is likely not low enough to make the compound truly viable in a TES environment. However, the behavior of the two compounds does suggest that TPP has the potential to greatly decrease its melting temperature while in a eutectic mixture. This can be further studied through the use of other compounds that might provide similar interactions with TPP as benzanilide. Compounds like terphenyl and other thermally stable compounds with aromaticity should be considered for further solid-liquid equilibrium studies. If these compounds behave similarly to benzanilide in mixtures with TPP they present a potential pathway towards creating a viable TES fluid. The tertiary and quaternary behavior of TPP with various other aromatic compounds is also of great interest to the future work of this project. Many currently used ionic liquids in TES use more than just two compounds in order to create an optimal mixture. Replacing TPP with other tetraarly-phosphonium based ionic liquid compounds is also a major future step in this project. Some of these compounds provide higher thermal stability at lower melting temperatures which suggest they would serve as a more viable compound in TES.

The results of the hypereutectic side of the solid-liquid equilibrium plot led to the discovery of liquid-liquid phase separation behavior in certain regions. This behavior needs to be explored further before the behavior between TPP and benzanilide is fully understood. Understanding this behavior is needed in order to determine the usability of benzanilide with tetraarly-phosphonium based ionic liquid compounds in TES. Although it would be possible to utilize a TES with liquid-liquid phase separation, this adds an additional complexity to the operation of an already problem prone operation. Determining what might be causing this phase separation could be important in determining which compounds would be most helpful in studying the solid-liquid equilibrium behavior of.

Analysis of the heat capacity of TPP: benzanilide mixtures is also a key piece of future research for this project. It is expected that the heat capacity of this mixture would be higher than currently used TES fluids. Confirmation of this and understanding of the change in heat capacity with temperature could prove useful in determining the viability of similar compounds in TES applications. The analysis of the thermal stability of TPP is also not completed. Understanding the differences in thermal stability between TPP and competing ionic liquids could help determine the needed qualities in other compounds used in mixtures with TPP. The differences in thermal stability between TPP and other tetraarly-phosphonium based ionic liquid compounds could also determine which is the best organic ionic liquid to use in future TES studies.

Fossil fuel use needs to be reduced throughout the twenty first century to prevent significant environmental, human health, and economic impacts across the world. To do this, novel clean energy technologies must be developed that can replace fossil fuel's role in energy generation. This energy transition must be done through many different sectors without causing significant disruption to current processes which limits the role any one technology can have in replacing fossil fuel-based power generation. CSP presents itself as a developing technology that can help alleviate the reliance on carbon emitting energy production methods. Despite this promise, CSP has significant challenges that must be addressed before wide-scale adoption of the technology is possible. Many of these problems stem from the TES materials currently used to eliminate the intermittent nature of solar power production. An improved TES material could significantly increase the viability of CSP. The purpose of this project is to explore the potential of tetraarylphosphonium-based ionic liquids as an alternative to nitrate molten salts for use in

CSP. These ILs have the potential to be applicable in a wide range of applications including both TES and as a heat exchange fluid. This report details the binary phase interactions between TPP and benzanilide to better understand the melting and freezing behavior of tetraarylphosphonium-based ILs. The knowledge gained from this survey of two materials can be applied to futures studies of similar compounds to move closer towards the goal of creating a novel material mixture that could increase the viability of TES.

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