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Kaila M. Kuehn

South Dakota State University


Camille M. Massmann

South Dakota State University

Natalie R. Sovell

South Dakota State University

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Cover Page Footnote

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Choline Chloride Eutectics: Low Temperature Applications

Authors: Kaila M. Kuehn, Camille M. Massmann, Natalie R. Sovell

Faculty Sponsors: Dr. Douglas R. Raynie and Amos Dwamena

Department: South Dakota State University Department of Chemistry and Biochemistry and the Van D. and Barbara B. Fishback Honors College

ABSTRACT

Deep eutectic solvents (DES) have a lower melting point than each of their individual components due to ion-dipole interactions or hydrogen bonding. Traditionally, DES are used for processing metals through plating and have many synthesis applications. DES are able to be substituted for hazardous solvents that are traditionally used for metal plating and synthesis. This, along with many other advantageous properties, appear promising for the use of DES as solvents or for use in electrochemical systems, particularly at low temperatures. Choline chloride:propylene glycol was a novel DES synthesized and analyzed for its properties, including melting point, viscosity, conductivity, heat capacity, and heat of fusion. A 1:5 ratio of choline chloride: propylene glycol was found to be most promising at low temperatures based on these results.

Keywords: *deep eutectic solvents, choline chloride eutectics, lactic acid, propylene glycol*

INTRODUCTION

In recent years, there has been a strong emphasis on developing more environmentally friendly solvents to use in the laboratory. Current research has emerged with the focus on the use of deep eutectic solvents (DES) in place of traditional organic solvents, in which eutectic solvents have a lower melting point than the melting point of any of the individual components

(Shahbaz et al., 2010). The decrease in the melting point was found to be the direct result of charge delocalization that occurred from the hydrogen bonding of a halide ion and a hydrogen bond donor (Smith et al., 2014). DES are analogues of another type of solvent classified as ionic liquids (IL) which are made from a distinct cation and anion. Ionic liquids are commonly used as solvents, but they are known to be detrimental to the environment and generally toxic (Smith et al., 2014). DES are formed from a mixture of Lewis or Brønsted-Lowry acids and bases that may have many different anionic or cationic species present. A DES is often made with a mixture of a salt and a hydrogen bond donor molecule which is able to form bonds with the halide on the salt as shown in figure 1 (Mukhtar et al., 2010). The ion-dipole interactions of choline chloride with propylene glycol and choline chloride with lactic acid are the intermolecular forces that contribute to the bonding and formation of the DES. DES can be made from quaternary ammonium salts like choline

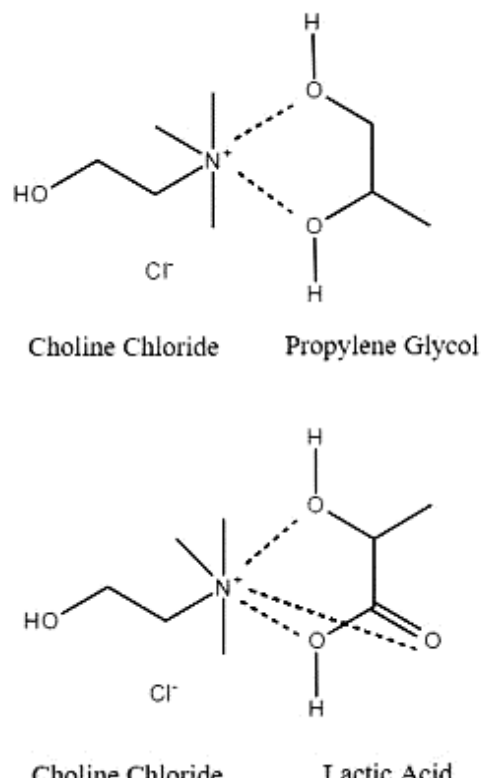


Figure 1: Ion-dipole interaction graphic representation.

chloride that are mixed with metal salts such as zinc chloride which experience large depressions of freezing point (Abbott et al., 2004). Unlike traditional IL, DES have the potential of being non-toxic, environmentally benign, biodegradable, and non-reactive with water (Shahbaz et al., 2010). DES are believed to be more environmentally friendly because the components of these mixtures are all toxicologically well-characterized (Smith et al., 2014). Other advantages of DES are that they are non-flammable and they have a very low vapor pressure. These two properties make DES safer to work with as they do not volatilize like some IL do and also have a much smaller risk of explosion (Garcia et al., 2015). Additionally, DES are generally easier to produce than IL because they involve the mixing of the hydrogen bond donor and the halide ion with minor heating, and the simplicity of the methodology to form the solvents contributes to lower production costs of DES (Smith et al., 2014). These and other characteristics of DES provide an opportunity for further research into improvements to current processes and new uses for the DES.

In addition to decreasing freezing point, DES have been shown to lower lattice energy because of intermolecular forces associated with hydrogen bonds and ion-dipole interactions in the complex ions formed during construction of the DES (Abbott et al., 2004). The first example of one such solvent is the mixture of choline chloride and urea. When mixed into a 1:2 molar ratio, these reagents reached a melting point of 12°C whereas individually these reagents had melting points at 302°C and 133°C, respectively (Mukhtar et al., 2010). A depression of the melting point as previously described allows various metal salts to be dissolved into the solution.

The use of DES is applicable to many different areas of research. For example, since DES have low melting points and high conductivity, they could be used in the creation of a type of electrochemical system that works in cold temperatures because of their previously described attributes and their high electrochemical stability, which would indicate that DES could be applied as a safer electrolyte in electrochemical devices, such as batteries (Boisset et al., 2013). This is what makes DES interesting to various groups and outdoor enthusiasts. DES could also be used industrially for zinc electroplating or even in chemistry laboratories for catalysts in Diels-Alder reactions (Abbott et al., 2004).

Another possible application for DES is in the production of biodiesel. Biodiesel is created from an alcohol reacting with triglycerides in the presence of a catalyst, producing Fatty Acid Alkyl Esters (FAAE) and the by-product glycerol through a process known as transesterification (Shahbaz et al., 2010). The majority of glycerol needs to be removed for biodiesel to work properly in engines. The glycerol content can be determined to be free glycerol, the by-product, or partially reacted triglycerides, and total glycerol is the sum of the free glycerol and bound glycerol. Current purification processes that remove this glycerol are expensive and harmful to the environment, so the possibility of a cheaper and environmentally safer option is appealing.

In the study described previously regarding biodiesel, one of the DES tested was choline chloride, a low cost quaternary ammonium salt, and ethylene glycol (Shahbaz et al., 2010). Studies on choline chloride and ethylene glycol as a DES show that the hydrogen bonds form strong associations which cause very efficient depressions of melting point (Garcia et al., 2015). However, the interaction of propylene glycol with choline chloride has not been as heavily studied. With the longer carbon chain of propylene glycol compared to ethylene glycol, there is potential for a lower depression of the melting point, thus making it a more efficient solvent. Ethylene glycol still has a toxicity which is higher than desired, while propylene glycol has been approved as a less toxic solution, as it has replaced ethylene glycol in antifreeze. It would be possible to test propylene glycol in a DES to see if it would have similar properties and abilities as ethylene glycol, but with a lower toxicity level. Choline chloride combined with lactic acid in the 1:2 molar ratio has created a DES with known properties, making it a comparable solvent for novel DES.

In general, these eutectic mixtures are easily prepared, are not reactive when mixed with water, and many are biodegradable with low toxicity. Thus, DES are promising for the future of green chemistry.

Objective 1:

Synthesis of eutectics with sub-zero melting points. Choline chloride and lactic acid in a DES eutectic mixture will be created and serve as a reference point for a novel DES mixture created from choline chloride and propylene glycol.

Objective 2:

Characterization of the properties of DES mixtures created from choline chloride with lactic acid and choline chloride with propylene glycol to determine the usefulness of these solvents at low temperatures. These properties may include: melting point, conductivity, viscosity, electrochemical window, and solubility.

Hypothesis:

Does choline chloride and propylene glycol work as a DES? If so, what are its properties when compared to choline chloride and lactic acid, a known DES? If not, why does it not work as a DES?

METHODS

Preparation of the Deep Eutectic Solvents:

Before creating the solvents, the molar ratios were calculated. The choline chloride was massed on an analytical balance while a micropipette was used to measure the lactic acid and propylene glycol. The choline chloride: 85% lactic acid 1:2 ratio DES dissolved with a little stirring. The choline chloride: propylene glycol 1:1 and 1:2 ratios did not form homogenous mixtures, so testing could not be performed on these samples. With heat and stirring, choline chloride: propylene glycol 1:3, 1:4, 1:5, 1:6, and 1:7 ratios were formed although the 1:3 and 1:4 ratios fell out of solution while in a freezer at about -20°C for a week, so testing was discontinued with these two samples.

Viscosity of Lactic Acid 1:2 and Choline Chloride: Propylene Glycol 1:5, 1:6, and 1:7:

A Brookfield viscometer model number M/98-211-C0310 was used to measure viscosity. The information gathered included temperature (°C), viscosity (cP), percent torque (dyne*cm), shear stress (SS; dyne/cm²), shear rate (SR; sec⁻¹), rotations per minute (RPM), and the time it was measured over. Each sample was tested at five temperatures: -20°C, -10°C, 0°C, 10°C, and 20°C, and five RPMs were used: 0.1, 0.2, 0.3, 0.4, and 0.5, each for one minute. In order to obtain the -20°C temperature, a beaker containing dry ice and acetone was placed into the cooling bath.

Conductivity of Lactic Acid 1:2 and Choline Chloride: Propylene Glycol 1:5, 1:6, and 1:7:

A Vernier LabQuest with temperature and conductivity probes was used to determine the conductivity of each sample and the use of the temperature probe ensured the temperature was in the desired range for each measurement. To keep the temperature

constant, the samples were placed in the cooling bath used on the viscometer, and conductivity was determined for each of the same five temperatures as listed above for viscosity.

Differential Scanning Calorimetry (DSC): Determination of Thermodynamic Properties:

A Shimadzu DSC-50 was used to gather data on the approximate melting point, heat of fusion (J/mol), and heat capacity (J/mol*K). Figure 2 shows a basic layout of the DSC instrument.

Two tests were run to standardize the instrument before sample could be run. First, two empty pans were placed in the instrument and the instrument was heated to drive out any water.

Next the reference pan was run with a sapphire crystal. These values were compared to known values to ensure the instrument was performing accurately. The samples were then run. One at a time, each sample was placed in the sample pan

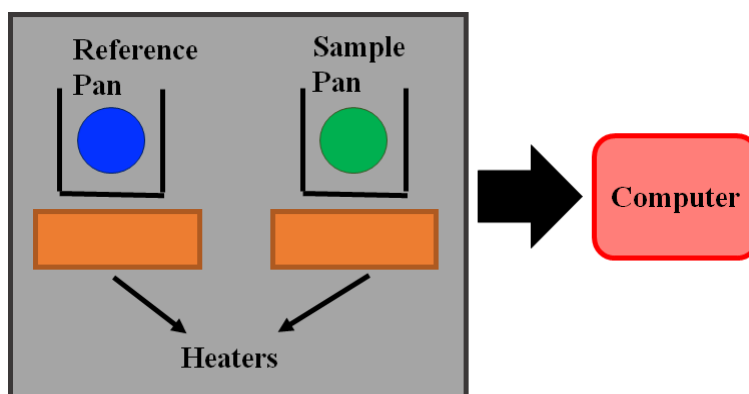


Figure 2: Graphic representation of the differential scanning calorimetry instrument set up

and the reference pan was generally an empty cell. Before starting the instrument, the samples were cooled to the desired temperature, then the heaters raised the temperature as the instrument transferred measurements to the computer for analysis. The approximate melting points were gathered by cooling the DSC to -90°C with liquid nitrogen and heating it to -50°C to measure the peak where the melting point exists. Heat of fusion and heat capacity were found by using the DSC from 0°C to 60°C with a temperature hold at 20°C . Propylene glycol was also tested as a comparison to ensure the technique was accurate, and when compared to the NIST value, the heat capacity was comparable (NIST). The temperature range used to determine the heat of fusion and heat capacity was chosen to allow comparisons with the NIST value.

RESULTS

Viscosity of Lactic Acid 1:2 and Choline Chloride: Propylene Glycol 1:5, 1:6, and 1:7:

Figure 3 and Figure 4 show the trends for viscosity over a temperature range from approximately -20°C to 20°C with the temperature measured in degrees Celsius and the viscosity measured in centipoise. Each of the samples followed an exponential regression because the R^2 values were higher than 0.94. The strongest exponential correlation was seen for choline chloride: propylene glycol 1:5 was 0.99, which suggests a very high correlation. The viscosity increases exponentially as the

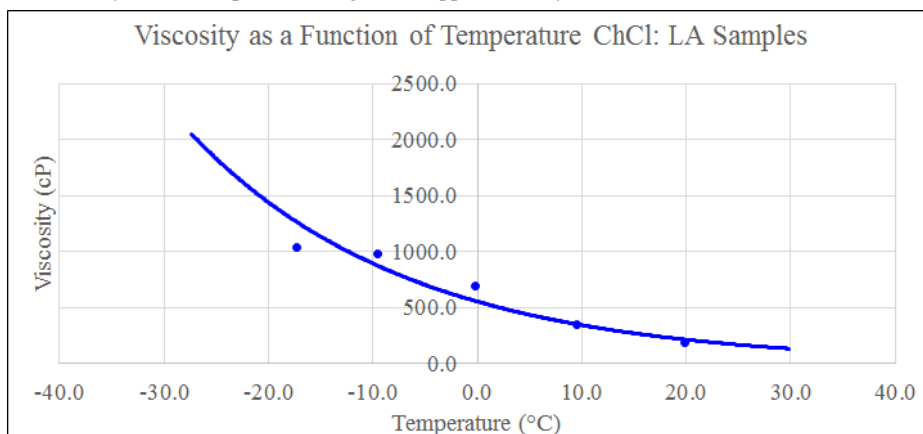


Figure 3: Viscosity graph for Choline Chloride: Lactic Acid sample as a reference.

temperature decreases for all samples. The choline chloride: lactic acid 1:2 sample had a significantly elevated viscosity for each temperature. Each of the choline chloride: propylene glycol solvents were comparable to each other at each temperature.

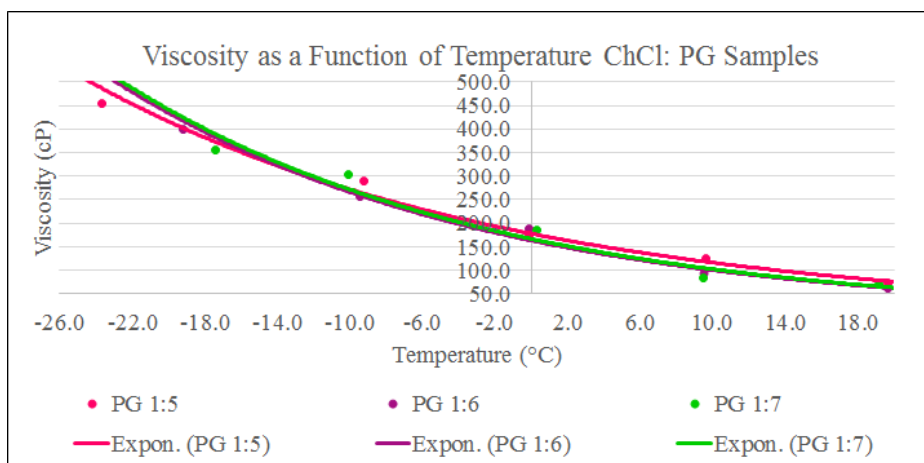


Figure 4: Viscosity graph for choline chloride: propylene glycol sample as a reference.

Conductivity of Lactic Acid 1:2 and Choline Chloride: Propylene Glycol 1:5, 1:6, and 1:7:

Figure 5 displays the graph for the conductivity data with the temperature in degrees Celsius and the conductivity in micro Siemens per centimeter. A linear relationship was predicted for each of the solvents based off of R² values. Each of the R² values was higher than 0.98, which suggests a strong linear correlation between the temperature and conductivity of the samples. The

highest R² was reported for choline chloride: lactic acid 1:2, with a value of 0.9884. Figure 5 demonstrates that the choline chloride: propylene glycol 1:5 has the highest overall conductivity. At lower temperatures, the choline chloride: lactic acid 1:2 solvent had the lowest conductivity. The choline chloride: propylene glycol 1:5 was expected to have the highest conductivity because it has the most ions in solution when compared to the other choline chloride: propylene glycol ratios.

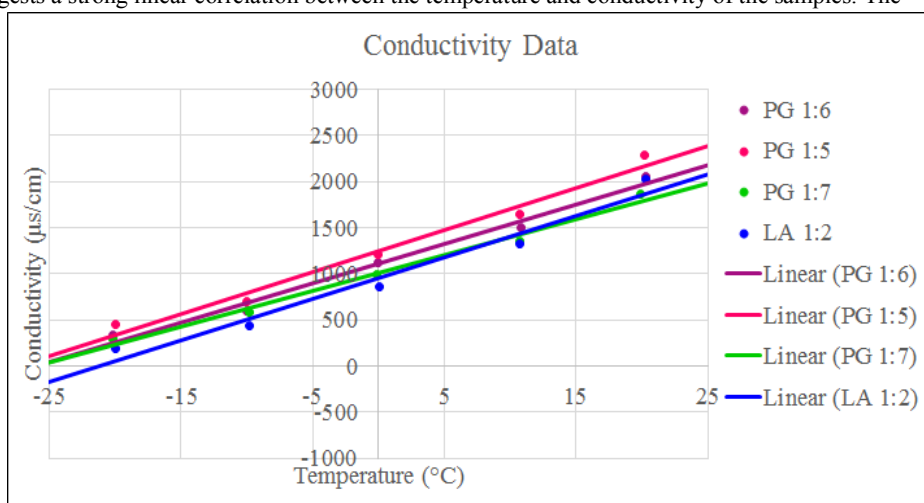


Figure 5: Conductivity graph for all samples tested.

Differential Scanning Calorimetry (DSC): Determination of Thermodynamic Properties:

Heat of Fusion and Heat Capacity of Lactic Acid 1:2 and Choline Chloride: Propylene Glycol 1:5, 1:6, and 1:7:

Table 1 and table 2 display the heat capacity and heat of fusion of each of the samples. The choline chloride: propylene glycol samples had comparable heat capacities and heat of fusions. These values were all much lower than the lactic acid but higher than the propylene glycol sample. Due to the hydrogen bonds between the choline chloride and propylene glycol, the heat capacity and heat of fusions were expected to be higher than that of the 100% propylene glycol sample where applicable. This is because of the extra energy needed to break the hydrogen bonds, as suggested by the highly exothermic heat of fusion value for choline chloride: lactic acid 1:2. The same can be said for the heat capacity of the choline chloride: lactic acid being higher than the propylene glycol samples. There are more hydrogen bonds in the choline chloride: lactic acid sample and since the ratio is 1:2 there is a greater amount of choline chloride in the sample when compared to the choline chloride: propylene glycol samples, explaining why they were much lower values for heat capacity and heat of fusion.

Heat Capacity Analysis	
Sample	C _p (J/g*K)
PG	2.439
ChCl:LA (1:2)	2.588
ChCl:PG (1:5)	2.606
ChCl:PG (1:6)	2.596
ChCl:PG (1:7)	2.656

Table 2: Data for heat of fusion obtained from differential scanning calorimetry

Heat of Fusion Analysis	
Sample	ΔH
PG	N/A
ChCl:LA (1:2)	-9540.67
ChCl:PG (1:5)	-7797.32
ChCl:PG (1:6)	-7820.99
ChCl:PG (1:7)	-7539.59

Table 1: Heat capacity data obtained through analysis of differential scanning calorimetry

Melting Point of Lactic Acid 1:2 and Choline Chloride: Propylene Glycol 1:5, 1:6, and 1:7:

Table 3 displays the melting point data for the samples along with a control of propylene glycol. The known melting point for propylene glycol is -59 °C. With a value of -59.05 °C the percent difference is 0.085% (DOW). This then ensures the melting point can be accurately measured despite the lack of crystal formation. When compared to 100% propylene glycol the choline chloride: propylene glycol solvents had depressed melting points, which was expected. Of all the samples, choline chloride: propylene glycol 1:7 saw the greatest melting point depression. This is expected to be because there is less choline chloride per mole of propylene glycol however, all the solvent samples were very comparable in melting point, making them all viable options as a DES.

Melting Point Analysis	
Sample	°C
PG	-59.05
ChCl:LA (1:2)	-63.99
ChCl:PG (1:5)	-64.19
ChCl:PG (1:6)	-64.26

Table 3: Melting point data obtained from analysis of differential scanning calorimetry data.

DISCUSSION

According to the results from viscosity, conductivity, thermodynamic properties, and melting point, it can be determined that the most viable DES depends on the application, although each choline chloride: propylene glycol sample could be used as a DES. Since each of the choline chloride: propylene glycol samples had a lower viscosity than the choline chloride: lactic acid 1:2 sample, it would be more beneficial to use the choline chloride: propylene glycol samples since a lower viscosity is desired for electrochemical systems. At the lower temperatures, the choline chloride: propylene glycol 1:5 sample had the lowest overall viscosity, making this a valuable candidate for low temperature applications.

When analyzing conductivity data, it is evident that the sample with the highest conductivity at each temperature was the choline chloride: propylene glycol 1:5. One noticeable trend with conductivity was that as the molar ratios increased, the conductivity decreased since the choline chloride: propylene glycol 1:5 had slightly higher conductivity values than choline chloride: propylene glycol 1:6 and the choline chloride: propylene glycol 1:6 sample had slightly higher conductivity values than choline chloride: propylene glycol 1:7 which could be due to a higher proportion of choline chloride in the lower molar ratio samples. Since the choline chloride: lactic acid 1:2 sample had a lower conductivity at the lower temperatures, it would be more advantageous to use the choline chloride: propylene glycol samples for electrochemical systems. To send an electrical impulse through a system it is very important to have efficient means to do so. Thus, the solvent with the highest conductivity is the most desirable in such systems.

For the heat of fusion and heat capacity the propylene glycol sample behaved as expected (NIST) thus the values obtained for our samples are likely accurate. The propylene glycol samples, all three ratios, had higher heat capacities and lower heat of fusions than those of the choline chloride: lactic acid sample. These are important in characterizing the choline chloride: propylene glycol samples as solvents.

A trend seen with melting point was that as the molar ratios of the solvents increased, the melting point tended to increase. In terms of melting point, the sample with the lowest overall melting point was choline chloride: propylene glycol 1:7. Since each of the samples had melting points lower than each of their individual components, each sample satisfied the basic requirement for a DES.

CONCLUSION

Based on analysis of the current data, each of the choline chloride: propylene glycol solvents would be a practical DES, especially at low temperatures. The choline chloride: propylene glycol solvents were also found to be more conductive and have a lower depression of melting point than the choline chloride lactic acid 1:2 sample, thus making them a better fit for use in low temperature electrochemical systems. Based on viscosity and conductivity results, the choline chloride: propylene glycol 1:5 mixture would be the most viable DES, especially at sub-zero temperatures. Further testing and analysis could be conducted to measure the conductivity of the solvents with and without the addition of ions, such as lithium chloride or lithium fluoride, which would determine if the conductivity also depended on the radius of the ion. Due to the slight differences between the solvents as the molar ratios increased, including further depression of the melting point, testing could be performed by creating higher ratios of the choline chloride: propylene glycol solvents. The choline chloride: propylene glycol solvents could be further characterized

by thermogravimetric analysis, which measures the mass of a substance as a function of either temperature or time. Additionally, the solvents could continue to be tested at even lower temperatures, past -20°C . Currently, the majority of these results focus on the ability of the choline chloride: propylene glycol DES to work in electrochemical systems at cold temperatures, but further testing could also be done to determine their properties as a solvent. Different ways to test the solvent properties include analyzing the saturation levels and the ability to dissolve ionic, polar covalent, and non-polar covalent compound.

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