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Effect of Dissolved Salts on the Physiochemical Properties of Deep Eutectic Solvents

Eleanor Haeska
South Dakota State University

Megan Radtke
South Dakota State University

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Cover Page Footnote

We would like to acknowledge Dr. Douglas Raynie, Amos Dwamena, and Sonali Pandey for their help and support through the duration of this experiment.

INTRODUCTION

Recently within the field of chemistry, there has been increased efforts to develop and utilize safer practices and materials that have decreased effect on the environment. This interest has included opportunities to investigate different solvents such as ionic liquids, low transition temperature mixtures, and deep eutectic solvents.¹ Of particular interest are deep eutectic solvents (DES) which have been identified as an alternative to other solvents for use in industrial and biological applications. Unlike ionic liquids, DES can be non-toxic and environmentally friendly. DES consist of a hydrogen bond donor and a hydrogen bond acceptor that create a solvent that is both conductive and has a substantially depressed melting point relative to those of the two DES components.² These properties make DES potentially valuable in electrochemical applications, such as in batteries, and particularly at low temperatures. Batteries require an electrolyte source that allows electrical charge to freely move between the anode and cathode. The mobility of the electrolyte source can be difficult to maintain at low temperatures due to freezing. The depressed melting point and conductive nature of DES, however, could allow it to serve as the electrolyte source at temperatures lower than conventional electrolytes. The main objectives of the research were to determine the effects of adding aqueous salts to DES on the conductivity and viscosity of two DES (choline chloride:propylene glycol and choline chloride:lactic acid) and to measure and analyze the polarity of the DES, in order to characterize them for potential future uses.

METHODS

PREPARATION OF SOLVENTS AND SALT SOLUTIONS

A DES of choline chloride and propylene glycol (ChCl:PG) was made in a 1:5 molar ratio. An analytical balance was used to weigh the desired mass of solid choline chloride and a micropipette was used to measure the volume of liquid propylene glycol. The DES of choline chloride and lactic acid (ChCl:LA) was made in a 1:2 molar ratio. An analytical balance was used to mass the choline chloride and a micropipette was used to obtain the required volume of lactic acid. Each mixture was then heated on a hot plate with a stir bar

at 70 °C for 5 min to form the DES. Propylene glycol and lactic acid were obtained from Fisher Chemical and choline chloride was obtained from Acros Organics.

Eight aqueous solutions were prepared from the following halides: NaF, NaCl, NaBr, NaI, KCl, LiCl, MgCl₂, and CaCl₂. Calculations were performed to determine the necessary mass of salt to make 25 mL of 0.1 M solutions. The salts were weighed on an analytical balance and then placed in 50-mL screw-cap test tubes and filled to the 25-mL mark with deionized water (DI). Salts were obtained from Fisher Chemical.

CONDUCTIVITY MEASUREMENT

Conductivity of the DES and DES salt solutions was measured using an Oakton handheld conductivity probe. The DES and salt solutions were mixed in a 4:1 (DES:salt solution) volume ratio. The DES was also mixed with DI water in a 4:1 (DES:water) volume ratio. The DES-salt solutions were made in 50-mL screw-cap test tubes and then placed in a temperature-controlled coolant bath and allowed to equilibrate to the temperature of the bath for 5 min. The conductivity probe was then placed in the tube and a measurement of conductivity in $\mu\text{S}/\text{cm}$ was recorded. The conductivity probe was rinsed with DI water and ethanol prior to each measurement.

POLARITY

DES solvent polarity was determined using absorbance measurements and solvatochromic calculations. Three dye solutions, Nile Red, 4-nitroaniline, and N,N-diethyl-4-nitroaniline, were made by dissolving the desired mass of the dyes in separate test tubes with methanol to create 10-mL 0.5-mM dye solutions. A volume of 20 μL of a dye solution was pipetted into three wells for each solvent being measured in a 96-well microplate. The methanol was allowed 20 minutes to evaporate from the dye solutions, resulting in complete evaporation of the methanol in each well. After evaporation, an aliquot of 200 μL of DES was added to each well. As a control, 200 μL of methanol was added to three of the wells. The absorbance of plate was then read using a Biotek Synergy H1 Microplate Reader. This

process was repeated for measurements using 30 μL , 40 μL , and 50 μL of dye. The data obtained from the absorbance measurements was then analyzed using solvatochromic calculations giving the π^* , α , and β values, which represent dipolarity/polarizability, acidity, and basicity respectively.³ The solvatochromic values were then plotted on a solvent selectivity triangle for each solvent tested.

VISCOSITY MEASUREMENT

Viscosity of the DES-salt solutions was measured using a Brookfield DV-II Ultra Programmable Rheometer. Solutions of DES and salt were made in a 4:1-mL ratio with 4 mL of DES and 1 mL of aqueous salt solution. Sample size for each trial was 0.5 mL of the 4:1 mL DES-salt solution. Measurements were performed at 20°C at a rate of 0.1, 0.2, and 0.3 rpm at 1-min intervals. Values obtained from the rheometer include viscosity (centiPoise), shear stress (dyne/cm^2), and shear rate (1/sec).

RESULTS AND DISCUSSION

EFFECT OF SALT ON DES CONDUCTIVITY

Figures 1 and 2 show the values obtained for conductivity in microSiemens (μS) per centimeter. It was predicted that conductivity would decrease with decreasing temperature.⁵ This was not observed in most of the readings for ChCl:PG and ChCl:LA. As seen in Figure 1, the conductivity for ChCl:PG in solution with aqueous halide is lower than that of the DES-water solution at 20°C. The DES-water solution is indicated in Figures 1 and 2 by the 'No Halide' column. At 0°C the addition of aqueous halide to ChCl:PG caused an increase in the conductivity of the solution when compared to the addition of DI water to the DES. At -10°C no conclusive trend could be found about the effect of halide on the conductivity of ChCl:PG. Overall, conductivity at 0°C and -10°C is higher than the data for 20°C. This result was not expected because the conductivity of the DES-salt solution was predicted to be higher at 20 °C. At higher temperatures molecules within a solution move at a faster rate than molecules are lower temperatures. Therefore, conductivity would be

higher at higher temperatures because the ions are moving at a faster pace according to the kinetic theory of matter.

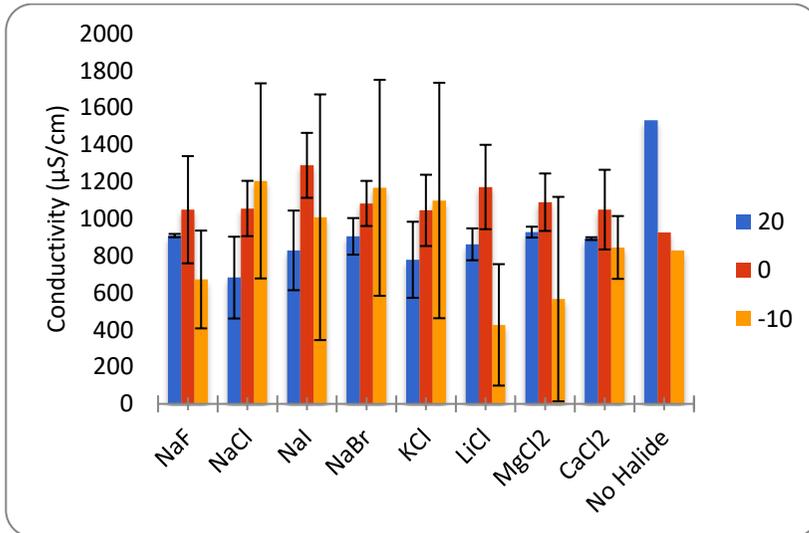


Figure 1. Conductivity of Choline Chloride:Propylene Glycol with Halide Solutions

As seen in Figure 2, the difference between the conductivity of ChCl:LA DES+salt solutions and that of the DES-water solution is not sufficiently large to conclude that adding salt increases the conductivity of the DES. Error bars indicate one standard deviation. The conductivity for ChCl:LA in solution with aqueous halide is decreased when compared to the conductivity of the DES-water solution at 20°C. At 0°C the addition of aqueous halide to ChCl:PG caused an increase in the conductivity of the solution when compared to the addition of DI water to the DES. This is consistent with the results at 0°C.

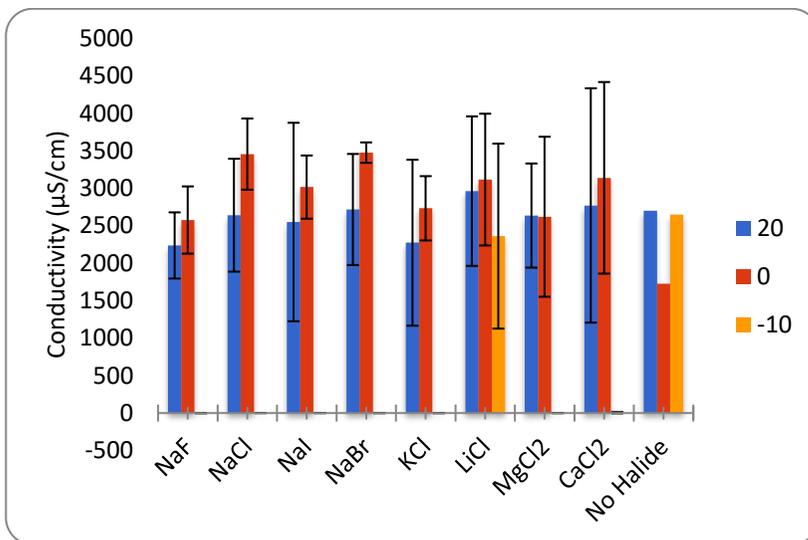


Figure 2. Conductivity of Choline Chloride:Lactic Acid with Halide Solutions

At -10°C, the addition of halide salt decreased the conductivity of the ChCl:LA solution. The measured conductivity taken for all samples, with the exception of LiCl, was so low in comparison that they do not appear in Figure 2. This result was expected because ions tend to move less when temperature is extremely low.^{5,6} Overall, the 0°C conductivity data is higher than the data for 20°C. Error bars indicate one standard deviation.

POLARITY

Figure 3 shows a solvent selectivity triangle with points marking methanol and ChCl:PG. These plots are based off the π^* , α , and β values found in Table 1. The π^* value indicates the dipolarity or polarizability of a molecule, which shows the separation of charge in a molecule and the ability of a molecule to form instantaneous dipoles. The α value indicates the acidity of a solvent or the effects of the hydrogen bond donor. The β value indicates the basicity of a solvent or the effects of the hydrogen bond acceptor.

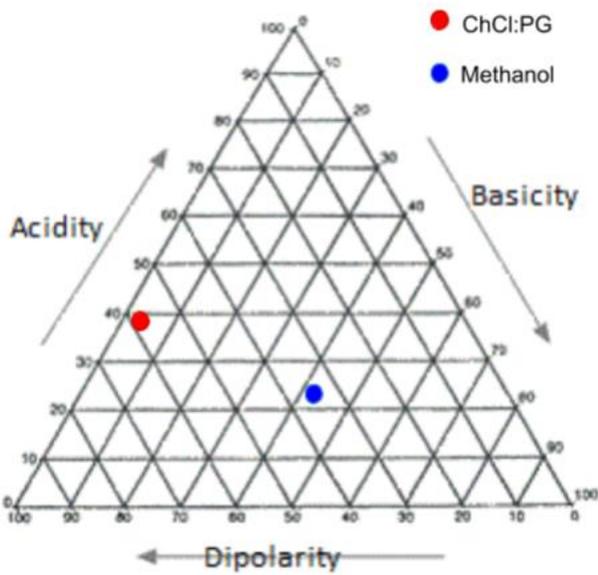


Figure 3. Solvent Selectivity Triangle

Table 1. Solvatochromic Calculation Data

| | π^* | α | β |
|----------|---------|----------|---------|
| ChCl:PG | 1.05 | 0.421 | 0.531 |
| Methanol | 0.731 | 0.798 | 0.636 |

Solvents with similar properties plotted on a solvent selectivity triangle will end up within the same area on the triangle. This results in grouping of properties, such as alcohols, ethers, aromatic hydrocarbons. Methanol was plotted on the solvent selectivity triangle and was determined to be in the alcohol range, while ChCl:PG was plotted in the polar protic range of solvents. Polar protic solvents are notable because of the large effect of dipolarity on the solution as well as acidity. Alcohol solutions are found within the middle of the

triangle, as the effect of dipolarity, acidity, and basicity are all equal in affect.⁴ The polarity for the DES solution of ChCl:LA was not calculated due to reactivity of the solvent with the Nile Red dye solution, preventing a clear maximum wavelength from being obtained.

VISCOSITY

Figures 4 and 5 show the results for viscosity measurements at 0.1 rpm at 20°C. Viscosity data was measured in centiPoise (cP).

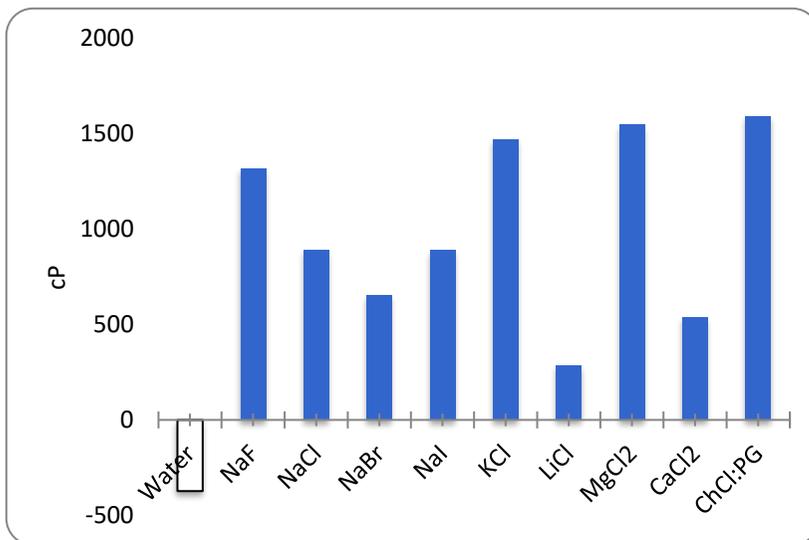


Figure 4. Viscosity of Choline Chloride:Propylene Glycol with Halide Solutions

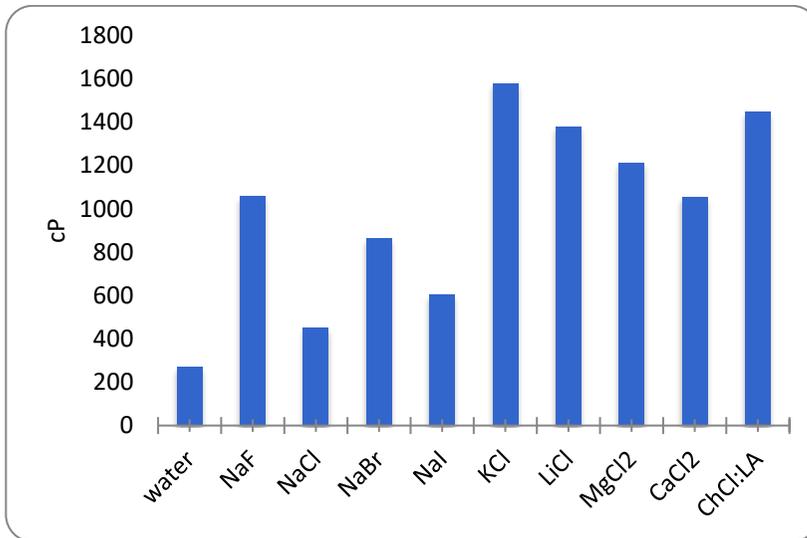


Figure 5. Viscosity of Choline Chloride:Lactic Acid with Halide Solutions

Both solutions of ChCl:PG and ChCl:LA show lower viscosities when combined with DI water than when combined with aqueous halides. This indicates that the presence of halides increases the viscosity of the DES solution when compared to the DES-water solution. The data do not show that addition of larger halides increases viscosity more than the addition of smaller halides. The DES-salt solutions had lower viscosity than the DES without halide, with exception to ChCl:LA in combination with KCl, which had a higher viscosity than ChCl:LA. The addition of water to the DES from the aqueous halides was expected to make the solution less viscous in comparison to the DES without halide. The solution of KCl was the largest monovalent cation analyzed in this research and had the highest viscosity of all halides tested for ChCl:LA and the second highest viscosity for ChCl:PG.

CONCLUSIONS

The measurement results show that the addition of aqueous halides does not improve conductivity, but does decrease viscosity of DES. Conductivity of DES-salt solutions measured at 0°C had higher measurements than values obtained at 20°C. However,

conductivity of DES-no halide solution had higher values than the measurements taken at 0°C and -10°C for the same solutions. Additionally, the polarity of choline chloride: propylene glycol can be likened to the solvent classes of polar protic or aqueous solvents. Polarity of choline chloride: lactic acid was unable to be measured. It may be concluded that the addition of aqueous halides to DES would not make DES better suited for electrochemical applications.

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