Investigated physical properties of novel type four deep eutectic solvent.

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Abstract:

A deep eutectic solvent type four was created by combining 1:4 lithium chloride and 1,2 propanediol. The physical characteristics of pure DES and $NiCl_2.6H_2O$ in DES with various additions such as H_2O, Triton X100, Boric acid, and Nicotinic acid were examined. The results reveal that H_2O and Triton X100 have a good improvement in increased conductivity and density, which is highly essential in electrodeposition applications. The UV-Vis spectra of 0.2 M $NiCl_2.6H_2O$ solutions in DES in the presence and absence of additives were measured. In the absence of additives, we observed peaks at (402, 284, and 219) nm. When we added additives, we saw a blue shift. The results showed a blue shift when additives were added. Also the physical characteristics of $CuCl_2.2H_2O$in DESs and with various additions such as Triton X100, Triton X114, Twien20 and Twien80. The results reveal that Twien80 and Triton X100 have a good improvement in increased conductivity and density, Too the UV-Vis spectra of 0.2 M $CuCl_2.2H_2O$ solutions in DES in the presence and absence of additives were measured. Show that some of additives does not effect in UV-Vis spectrum such as twin 20 rather than other additives.

Key words: lithium chloride, deep eutectic solvent, nickel, copper, electrodeposition

Introduction

Deep eutectic solvents (DESs), which are made up of two or more hydrogen bond donating and receiving molecules, are a hot topic right now[1- 4] . Following their distinctive (thermo) physical features and capacity to be "designed," many industrial uses have been proposed for such combinations [5,6]. Applications have already been suggested as green solvents with low solvent loss due to their low vapor pressure [1,7], extraction agents [8,9], catalysis [8,10], separation and synthesis of organic compounds[6], biodiesel purification [11], medication solubility [12], electrical conductivity applications [13], and surface metal deposition [14] have all been suggested. When a hydrogen bond donor (HBD) and a hydrogen bond acceptor (HBA) are mixed, the outcome is a combination with a lower freezing point than the original pure ingredients. The drop in freezing point might be as much as 200 degrees celsius in extreme circumstances.

Since DESs have the toxicological characteristics of both components, selecting benign starting materials can result in low-toxicity compounds. The majority of these substances are both inexpensive and biodegradable[6]. Choline chloride (ChCl), one of the most popular ammonium salts, is one of the most often used substances. It is a pro-vitamin, which means that it is widely utilized in a range of products, such as animal feed. It may therefore be produced from biomass, is affordable, biodegradable, and low-toxic. When choline chloride is combined with an HBD like urea, glucose, or oxalic acid, it forms a eutectic mixture.

Choline chloride, carboxylic acid, and tetra-butyl ammonium fluoride salts were used to create the first DESs [1].

The most important physical properties that have been studied for the DES are density and conductivity, Specifically, Mjalli and associates[15] proposed a technique for calculating the density of DESs at various temperatures. The average absolute relative percentage error (ARPE) for all of the tested DESs was determined to be 1.9 percent when the observed and anticipated densities were compared. Additionally, it was looked at how ARPE will be affected by the salt to HBD molar ratio in expected DES densities. The same team investigated DESs manufactured from salts based on phosphonium with various hydrogen bond donors. At various temperatures, melting temperature, density, and conductivity were all determined. Researchers found that the qualities under study were significantly influenced by the mole ratio of both compounds, as well as by the salt and HBD [8] . Compared to the majority of ionic liquids and molecular solvents, DESs have a lower conductivity. The effective polarity of choline chloride in the presence of four HBDs, 1,2-ethanediol, glycerol, urea, and malonic acid, was shown to be similarly dipolar in all four liquids[16].

The purpose of studying the physical properties of DES is to aid in our understanding of the electrical properties of DES , such as electroplating of Nickel and Copper elementes that are used in different industries.

Experimental

(DES) was prepared by combining LiCl with 1,2-Propandiol at a ratio of 1:4 each. The liquid was then put on a hotplate set to 50°C with stirring until a colorless, homogeneous electrolyte was produced. As shown in **figure1**.

Figure 1: The Deep Eutectic Solvent used in this Thesis 1:4 (LiCl: 1,2-Prop)

Then the 0.2M nickel chloride solution was prepared by added 2.37g from nickel chloride ($NiCl_2.6H_2O$) (Aldrich99.5%) to (DES) which has been prepared. Then it is added other materials such as (10% H_2O), (0.16M Nicotinic acid) (Aldrich 98%) , (0,4M Boric acid)(Aldrich99.8%), and (0.02M Triton X100) (Sigma Aldrich, ≥ 99.5%). Also the 0.2M copper chloride solution was prepared by added 1,704g from copper chloride (CuCl2.6H2O) (Aldrich99. %) to (DES) which has been prepared. Then it is added other materials such as (0.01M Twien20) (Sigma Aldrich 98%) , (0.025Twien80)(Aldrich99%), (0.02M Triton X114) (Sigma Aldrich, ≥ 99%) and (0.02M Triton X100) (Sigma Aldrich, ≥ 99.5%). The conductivity of the liquids was measured using different temperature using a Digital Conductivity SeriesIno.Lab.720 conductivity meter fitted with an inherent temperature probe (cell constant = 1.01 cm-1). As shown in **figure2**.

Figure2. Device of conductivity meter

Also examinations of the samples of nickel and copper solutions with and without additions were conducted using a (Spectro UV-VIS Double Beam PC Scanning Spectrophotometer UVD-2950) UV-visible spectrophotometer equipment. As shown in **figure3**.

Figure3. Device of UV-Visible Spectroscopy.

Results and Discussion

Density

Density of Nickel Solutions

It is important to study the density of the coating electrolyte because it has a substantial impact on coating qualities when metals are electrodeposited from ionic liquids. The density data for the DES pure are shown in **figure 4** with increasing temperature the density decreases. Also we observed increase in density when adding $NiCl_2.6H_2O$ to DES. Too when increasing temperature the density of the nickel chloride solution additives solutions decreases as shown in **figure4**.

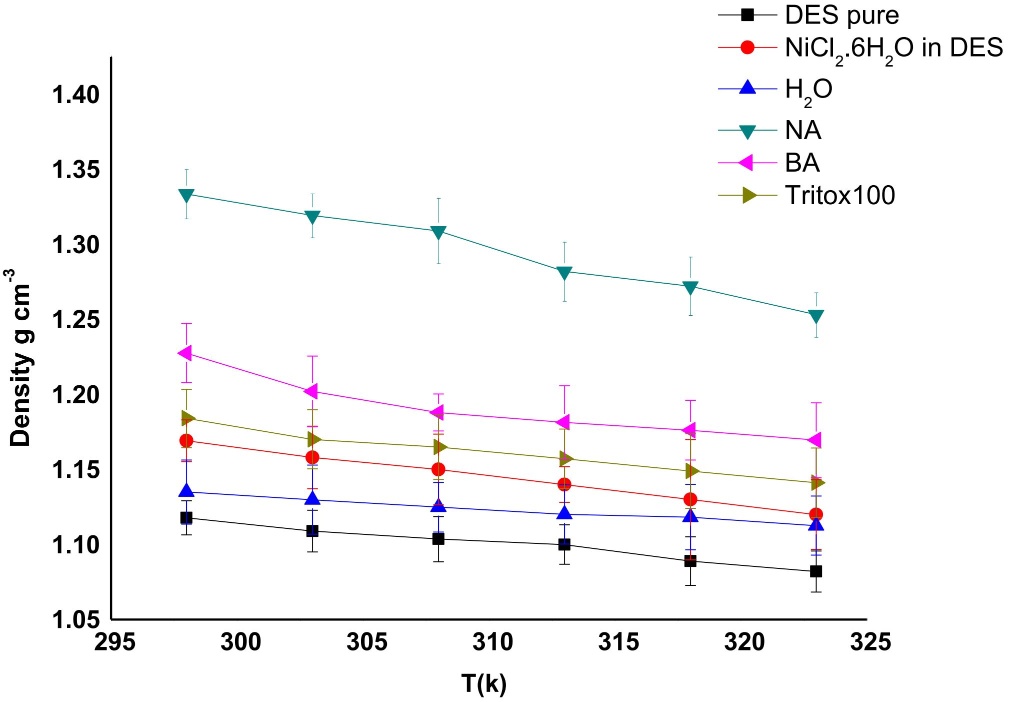

Figure 4. The Density of 0.2 M $NiCl_2.6H_2O$ in DES as a Function of Temperatures and Different Additive.

Density of copper Solutions

In **figure 5** we observed when increasing temperature the density of the copper chloride solution additives solutions decreases and the reason is with increasing temperature , viscosity decreases and the free volume increases.

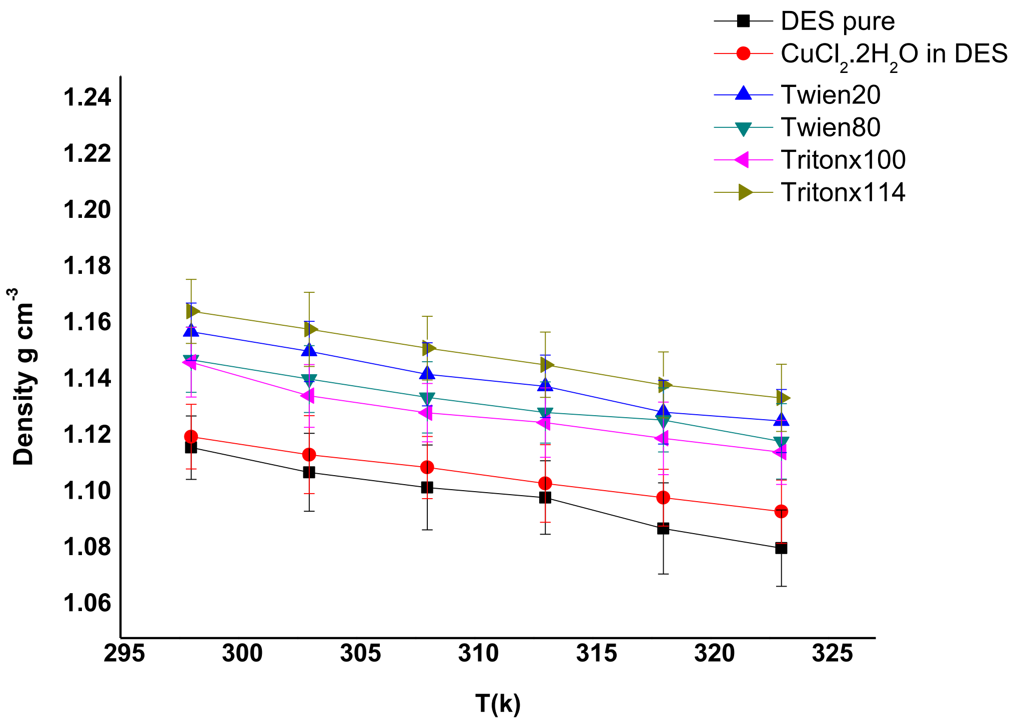

Figure 5. The Density of 0.2 M $CuCl_2.6H_2O$ in DES as a Function of Temperatures and Different Additive.

Conductivity

1. Conductivity of Nickel Solutions

It is crucial to research the conductivity of the coating electrolyte because it has a substantial impact on coating qualities when metals are electrodeposited from ionic liquids. Using a conductivity meter, the conductivities of the DESs used in this study were measured as follows: the probe of the conductivity meter was submerged in a liquid at temperatures ranging from 25°C to 80°C, the conductivity of each sample was measured at least three times at each temperature, and the average was calculated. We observed in DES an decrease in viscosity with increasing temperature , which leads to increase in conductivity. such (BA , NA) it causes decrease in conductivity while some additives cause a decrease in viscosity such (H_2O , Tritonx100) which leads to increase in conductivity[17]. as is clear from **figure6**.

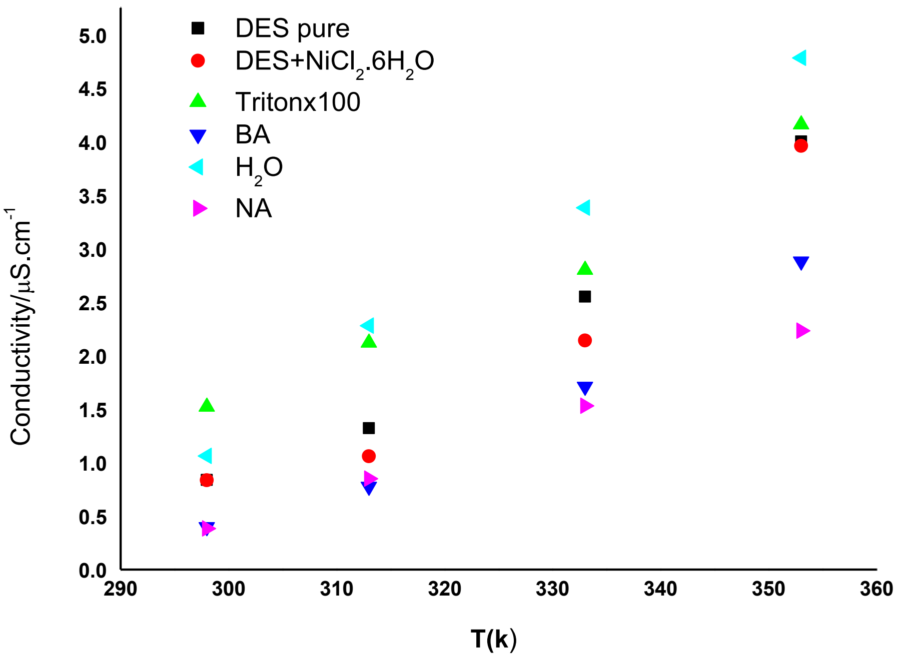

Figure 6. The Conductivity of 0.2 M $NiCl_2.6H_2O$ in DES as a Function of Temperatures and Different Additive.

2. Conductivity of copper

Likewise, the conductivity of the copper solution and its additives was measured in the same way. In both the presence and absence of additives**, Figure 7** depicts the conductivity of $CuCl_2.2H_2O$ in DES as a function of temperature[18]. We observed an increase in conductivity with increasing temperature and that because decrease in viscosity of solutions with increasing temperature. As the viscosity of the Cu solution was increased with some the additives such (Twien20, Tritonx114) it causes decrease in conductivity while some additives cause a decrease in viscosity such (Twien80 , Tritonx100) which leads to increase in conductivity. as is clear from **figur7.**

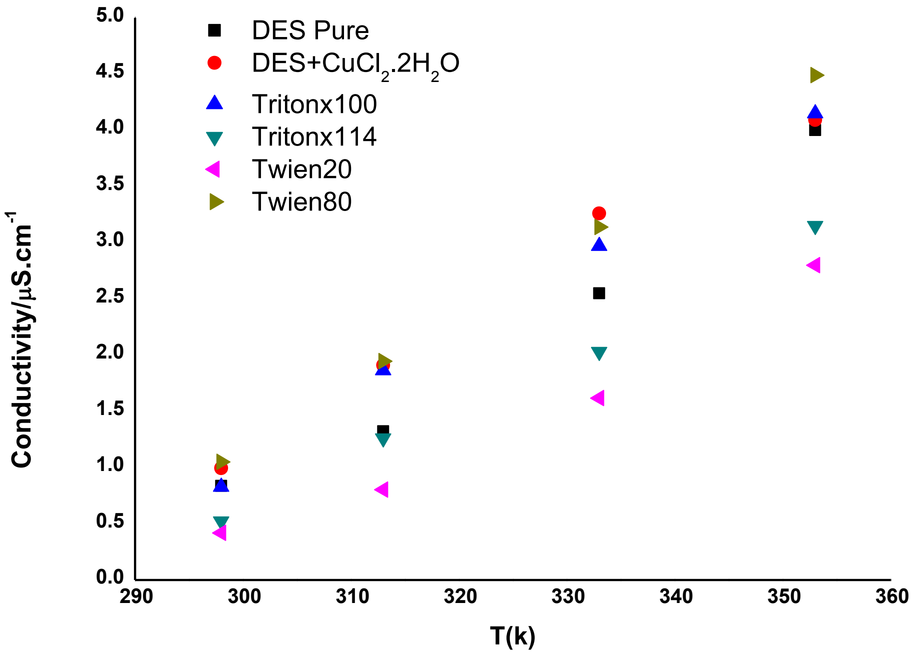

Figure 7. The Conductivity of 0.2 M $CuCl_2.6H_2O$ in DES as a Function of Temperatures and Different Additive.

UV – Vis measurement

1.UV-Vis of Nickel Solutions

The ability to learn how much an addition influences the metal speciation is provided by UV-Vis studies. The spectra for $NiCl_2$ solution in DES are compared in **Figure 8** to solutions with additions such (NA), (H_2O), (Tritonx100), and (BA). The peak locations of bands 1 and 2 are constant at room temperature, indicating that Ni speciation in the presence of these additions is unaffected despite their relatively high concentration[19]. Indicating that Ni^{2+} is the structure pertaining to this peak, the peak in band 1 is still present for all additions and appears at a comparable intensity and peak location for the solutions including H_2O and BA. However, the peak location has changed for those solutions containing NA and Tritonx100, shifting to a somewhat lower wavelength/higher energy as well as having a greater intensity. The peak's continued roughly constant location and intensity indicate that it still results from an octahedral complex's $^3A_{2g}$ (F)→ $^3T_{1g}$ (P) transition.

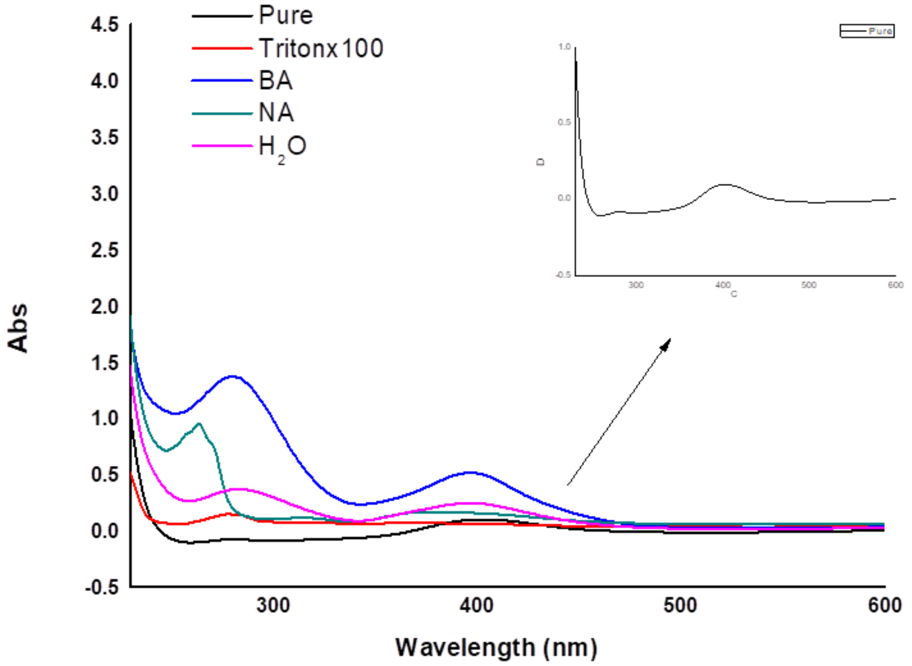

Figure 8: UV-Vis spectra of 0.02 M $NiCl_2$ in DES in the Absence and Presence of additives at λ=(200-600)nm

2.UV-Vis of Copper

$CuCl_2.2H_2O$ species in DES have been identified using UV-Vis spectroscopy in both the absence and addition of additives. **Figure 9** displays the $CuCl_2.2H_2O$ absorption spectra in DES with Tritonx100, Tritonx114, Twien20, and Twien80. **Figure 9** shows three absorption bands at 406, 291 and 225nm[18]. Additionally, Figure 6 shows that some of additives does not effect in UV-Vis spectrum such as twin 20 rather than other additives.

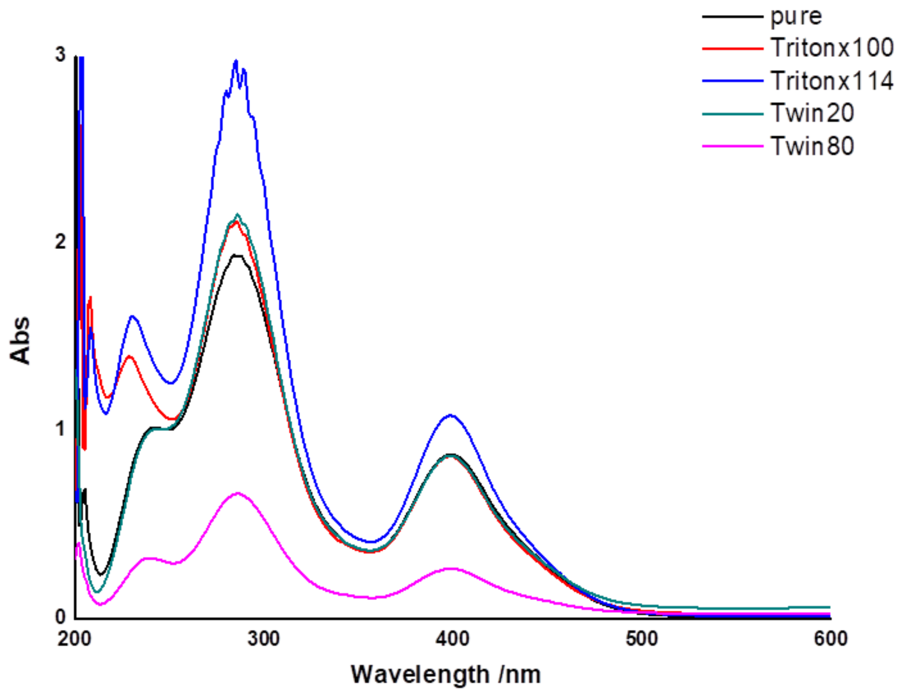

Figure 9: UV-Vis spectra of 0.02 M $CuCl_2$ in DES in the Absence and Presence of additives at λ=(200-600)nm

Conclusions

The purpose of this study was prepare a new deep eutectic solvent and studying its physical properties. Examined were the physical properties of pure DES and NiCl2.6H2O in DES with several additives, including water, Triton X100, boric acid, and nicotinic acid. The findings show that the conductivity and density of H2O and Triton X100 have significantly improved, which is very important for electrodeposition applications. In both the presence and absence of additives, the UV-Vis spectra were measured. Peaks at (402, 284, and 219) nm were seen in the absence of additives. We saw a change to blue as we added chemicals. When additives were introduced, the results displayed a blue shift. Additionally, the physical properties of CuCl2.2H2Oin DESs and with different additives as Triton X100, Triton X114, Twien20, and Twien80 According to the findings, Twien80 and Triton X100 have significantly improved conductivity and density. UV-Vis spectra were also examined in both the presence and absence of additives. demonstrate that some additives, such as twin 20, have no influence on the UV-Vis spectrum when compared to other additives.

Results of this fundamental study will be useful for studies electrical properties of DES such as electrodeposition.

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