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Novel castor oil – based deep eutectic solvent: Synthesis and physicochemical property determination

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ABSTRACT

The physicochemical properties of a deep eutectic solvent (DES) and thus its area of application are influenced by the nature salt or hydrogen bond acceptor (HBA), hydrogen bond donor (HBD), molar ratio, temperature and water content. The search for and discovery of new HBD would further widen the scope of DES versatility. In this study, the capacity of castor oil to serve as HBD and form DES with choline chloride (ChCl) was investigated. ChCl and castor oil were mixed in four molar ratios, namely 1:1, 1:2, 1:3, and 1:4. DES was formed at 1:3 and 1:4 molar ratios and code-named DES1 and DES2, respectively. The physicochemical properties of both DESs were measured as a function temperature from 313 K to 353 K. The results indicate that the densities of these castor oil-based DESs are uniquely low when compared to other DESs and ionic liquids. Their physicochemical properties generally follow the known trend for other DES, in terms of temperature variations. The viscosity, conductivity, surface tension and refractive index of castor oil based-based DES all fall within the known range for other choline chloride-based DESs. Based on its pH values, castor oil based DES is a Bronsted acidic deep eutectic solvent. This discovery offers significant potential to expand the possible combinations of salts and HBDs and further increase the areas of application of this solvent.

Keywords**:** Castor oil, choline chloride, deep eutectic solvent, density, viscosity, refractive index

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1. INTRODUCTION

The advent of ionic liquid has opened up new vistas in solvation and revolutionalizes problem solving or interventions in the scientific and technological world. Ionic liquids (ILs) are salts with organic cations and melting point below 100 °C (Yang et al., 2020). They have extraordinary properties such as negligible vapor pressure, high conductivity, thermal stability, ability to dissolve many different organic, inorganic and organometallic materials, and are immiscible with many organic solvents (Keskin et al., 2007). These properties can be readily tuned through careful selection of cation-anion combinations. No wonder ionic liquids are also referred to as designer solvents. Common cations used for the synthesis of ILs are pyrrolidinium, imidazolium, phosphonium, and alkylammonium, while the anions include tetra fluoroborate (BF_4^-), trifluoromethylsulfonate (TfO^-), dicyanamide (DCA^-) and chloride (Cl^-). Their solvation properties are profoundly higher than those of organic solvents due to their capability for wide range of intermolecular interactions (strong and weak ionic, hydrogen bonding, van der Waals, dispersive, n-π, and π- π interaction) (Hejazifar et al., 2020). ILs has application in wide and diverse areas including extraction, catalysis, electrochemical and microemulsion. The shortcoming of ILs that has stood on its way to replacing organic solvents in large scale is high cost.

Deep eutectic solvents (DESs) are relatively cheap and green analogues of ILs that retain most of the good properties of ILs. They are generally eutectic mixtures of two or more components that can form intermolecular forces. It is a mixture of quartenary salt and complexing molecule. The commonly used quartenary salts (hydrogen bond acceptor, HBA) are choline chloride, tetraalkylammonium and phosphonium. There are four types of DES depending on the complexing molecules, namely, type I (metal halides), type II (hydrated metal halides), type III (hydrogen bond donors, HBD), and type IV (mixed metal halide and HBD) (Majid et al., 2020). The most frequently studied DES is the type III, and in this regard the choice of HBD is crucial. Several HBD have been explored from amide, carboxylic acid and alcohol group such as glycerol (Kim and Park, 2018), ethylene glycol (Leron et al., 2012), urea (Abbot et al., 2003), malonic acid (Zhu et al., 2017), levulinic acid (Li et al., 2016), fatty acids (Silva et al., 2019), sugar (Farias et al., 2017), monoethanolamine (Mjalli et al., 2017), aspirin (Abbot et al., 2017), amylalcohol (Faraji et al., 2020) and decanoic acid or dodecanoic acid (Riveiro et al., 2020). The physicochemical and biological properties of DES depend upon the nature of HBA and HBD, molar ratio, temperature and water content. Unveiling new HBA or HBD would further increase the options available for selection and widen the versatility and diverse area of application of DES.

Castor oil, like any other lipid, contains an array of fatty acids in the form of triglycerides. However, the unique feature of castor oil is the presence of a predominant fatty acid (FA) in its profile, ricinoleic acid, accounting for between 87 and 95 % of the FA composition of this oil; and the presence of a hydroxyl group (OH) on carbon-12 in the ricinoleic acid (Ogunniyi, 2006; Saez-Bastante et al., 2015; Usman et al., 2017). With the presence of such strong hydrogen bonding functionality, it is reasonable to hypothesize that castor oil could serve as HBD and form a eutectic mixture with HBAs, with marked freezing point depression. To the best of our knowledge, there is no report of any previous study where castor oil is explored in this regard.

This study therefore investigate castor oil as HBD. Choline chloride was used as HBA and mixed with castor oil in different molar ratios. The resulting DESs were characterized by measuring their main physicochemical properties such as freezing point, density, viscosity, conductivity, pH, refractive index and surface tension. The effect of temperature variation on each of these physical properties was also examined.

2. EXPERIMENTALS

2. 1. Material

Choline chloride ($C_5H_{14}ClNO$) was obtained from Zigma Andrich, castor seed was procured from local market in Okene-Kogi State, Nigeria. n-hexane was bought from Finlab, Lagos State. Distilled water and ice packs were obtained from the Laboratory at the Department of Chemical and Petroleum Engineering, University of Lagos, Nigeria.

2. 2. Method

2. 2. 1. Extraction of castor oil

The castor beans were grinded using a manual grinder into a paste (cake) in order to weaken or rupture the cell walls to release castor fat for extraction. 300 ml of n-hexane was poured into round bottom flask. 10g of the sample was placed in the thimble and was inserted in the centre of the extractor. The soxhlet was heated at 60 °C. When the solvent was boiling; the vapour rises through the vertical tube into the condenser at the top.

The liquid condensate drops into the filter paper thimble in the centre, which contains the solid sample to be extracted. The extract seeps through the pores of the thimble and fills the siphon tube, where it flows back down into the round bottom flask. This was allowed for 6 hours. At the end of the extraction, the resulting mixture (miscells) containing the oil was heated to recover solvent from oil.

2. 2. 2. Preparation of DES

The DESs were prepared by mixing choline chloride salt and castor oil in four different molar ratios, namely 1:1, 1:2, 1:3, and 1:4 under atmospheric pressure and suitable temperature until homogeneous phase was obtained. A glass jacketed vessel with a mechanical stirrer, stirring at the rate of 350 rpm was used to mix the mixture for 2 hrs. The preparation was carried out in an air tight beaker. The resulting DES had a whitish-milky colour and a version – jelly form at room temperature. However, the resulting mixtures from mixing molar ratios of 1:1 and 1:2 were discarded as they turned out to be semi-solids after production.

2. 2. 3. Determination of physicochemical properties

The freezing point of the prepared DES was determined as follows: packs of ice blocks were placed in a bowl and the samples were collected in test tubes, and placed on the blocks. The temperatures at which the samples solidified were measured using a thermometer.

The densities of all the samples were measured using density bottles of volume 5 ml. The mass of the density bottle was measured when empty and after it was filled with each sample. The density bottle was also weighed with water inside and the weight collected.

The values obtained were recorded and the density of each sample was calculated using the equation (1).

$$\rho_{sample} = \frac{m_1 - m_0}{m_2 - m_0} \qquad (1)$$

m_1 = mass of density bottle and sample
m_2 = mass of density bottle and water
m_0 = mass of density bottle

The viscosity of each sample was measured using Brook Field Viscometer. The sample was put into a 50 ml beaker. The beaker was placed under the spindle of the viscometer and the viscometer was allowed to operate for 5 minutes. The reading on the dashboard of the viscometer was recorded.

The conductivity test was measured by Metroh conductivity meter. The sample was put into a 50 ml beaker. The cathode and anode of the conductivity meter were inserted into the beaker and the conductivity of the sample was read from the dashboard of the conductivity meter.

The pH test was measured by Metroh pH meter. The sample was put into a 50 ml beaker. The cathode and anode of the pH meter were inserted into the beaker and the pH of the sample was read from the dashboard of the pH meter.

The refractive index of the samples was read by 60/95 ABDE Refractometer. A drop of the sample was placed on the lens of the refractometer and the refractive index of the sample was read from the dashboard of the refractometer.

3. RESULTS AND DISCUSSION

As stated in sub-section 2.2.2, the mixture resulting from molar ratios 1:1 and 1:2 were discarded since they were semi-solids and no further analysis was done for them. The determination of physicochemical properties such as freezing point, density, viscosity, conductivity, pH, and refractive index for the DES obtained at 1:3 and 1:4 molar ratios of ChCl : castor oil, code-named DES1 and DES2 respectively, are presented and discussed in this section.

3. 1. Freezing point

Freezing point depression is the defining feature of DES. The obtained freezing points for DES1 and DES2 are 8 °C and 6 °C, respectively. Considering that the freezing point for castor oil and ChCl are 263.2 K (-10 °C) and 575 K (302 °C), respectively, the values obtained for the two DESs in this study does not meet the typical definition of being below the freezing point of the constituents. However, similar finding has also been reported for other DES. For example, DES synthesized using benzyltripheny phosphonium chloride (HBA) and glycerol or ethylene glycol (HBD) were reported to have freezing points of 50.36 °C and 47.91 °C (Smith et al., 2014), respectively. These values are higher than the freezing points of the respective HBD, glycerol (17.8 °C) and ethylene glycol (-12.9 °C). Also, for DES synthesized using ChCl and ethylene glycol in 1:2 molar ratio, Ibrahim et al. (2019) reported 236.86 K (-36.29 °C) which is lower than the freezing point of both components but another study reported a value of about 10 °C for 1:2.5 molar ratio (Manurung et al., 2019). The disparity in both studies can be attributed to both difference in molar ratio and the presence of water content of 6.504 mg/g in the former. It can be reasonably inferred that higher molar ratio of castor oil : ChCl could sufficiently depress the freezing point below -10 °C. The values reported in this study are sufficiently low for wide area of applications.

3. 2. Density

Density is an important physical property of DES that enables determination of its suitable area of application. **Figure 1** show the variation of DES density with increase in temperature. It is observed that the densities of the studied DES generally decrease with increase in temperature, similar to the behavior of other DESs.

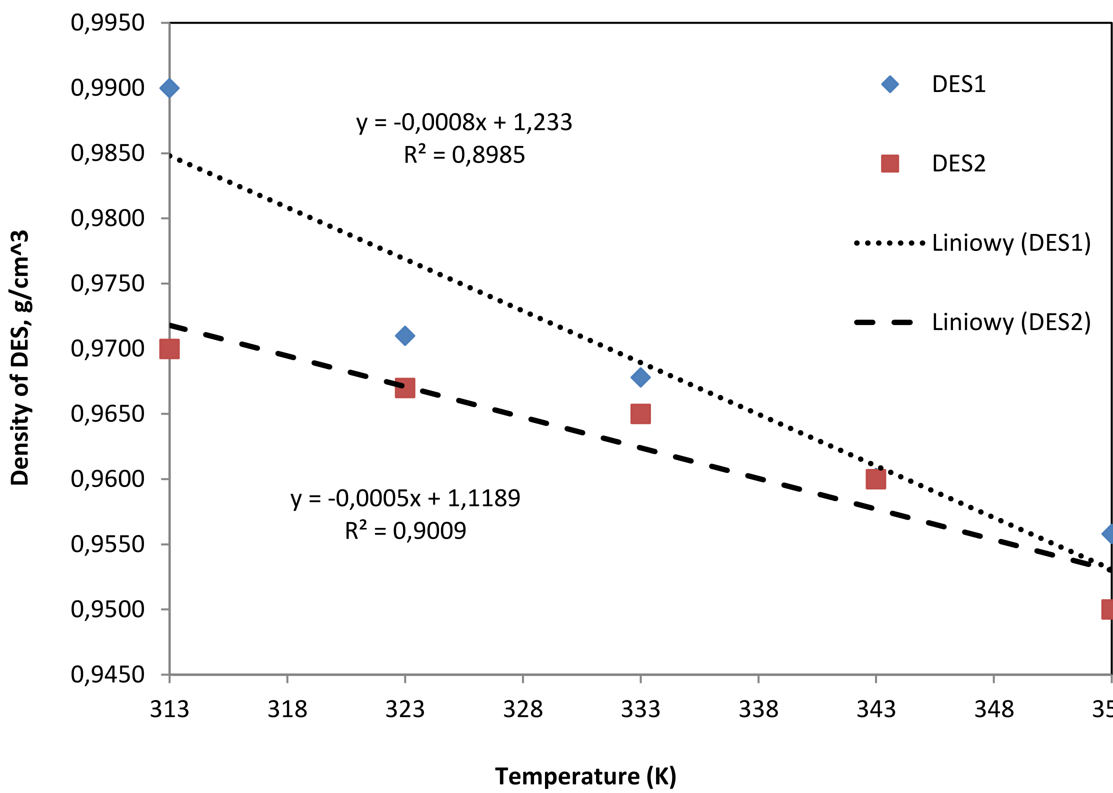

Figure 1. Densities of castor oil based deep eutectic solvents as a function of temperature

This is attributed to the increased activity and molecular mobility, which increase the molar volume and reduces the density (Hayyan et al., 2012). There is an observed decrease in density with increase in molar ratio of castor oil:ChCl. For example, at 313 K, the density of DES1 is 0.99 g/cm^3 while that of DES2 is 0.97 g/cm^3. The densities of most DES previously studied are higher than 1 g/cm^3 at 298 K and remain so even as it decreases with increasing temperature. For example, the densities of ChCl based DES with different HBD at 298 K are as follows: 1.24 g/cm^3 (urea), 1.12 g/cm^3 (ethylene glycol), and 1.18 g/cm^3 (glycerol) (Smith et al., 2014). The finding from this study is in sharp contrast with the previous trend. It is noted that the densities of DES1 and DES2 are higher than the measured density of castor oil used for the study (0.9 g/cm^3). This relatively lower density of castor oil based DES make suitable for many applications without need for a co-solvent.

The experimental data of the density as a function temperature were fit into a linear expression (Equation 2):

$$\rho = a + bT \tag{2}$$

where ρ is the density in g/cm^3, T is the temperature in Kelvin, and a and b are constants that represent the molar ratio of ChCl : castor oil. The values of and b for DES1 and DES2 are shown in **Figure 1**. The R^2 was found to be greater than 0.99, indicating that the density-temperature relationship for the studied DES is indeed linear.

3. 3. Viscosity

Viscosity is a vital property for application of DES, especially in separation and catalysis, since it influences achievable mass transfer and cost of pumping. **Figure 2** show the viscosities of the prepared DESs as a function of temperature. It can be seen that viscosity decrease with increase in temperature for both DES1 and DES2. The viscosities of DES1 are higher than those of DES2 at all temperatures. The viscosities of the prepared DESs are remarkably higher than of castor oil (42.6 cP) as measured in this study. Generally, DESs have high viscosities due to the presence of extensive hydrogen network between the components, which cause lower mobility of free species within the DES (Zhang et al., 2012; Zainal-Abidin et al., 2017).

Table 1 show a comparison of the viscosities of some choline chloride-based DES. It is clear from this table that the castor oil-based DES has a high viscosity comparable to urea and malonic acid based DESs. This is evidence of the strong hydrogen bond network between choline chloride and castor oil.

Table 1. Comparison of viscosity of choline chloride-based DES.

DES	Molar ratio	Viscosity (cP)	Temperature (K)	Reference
ChCl : Glycerol	1:2	281	298	AlOmar et al. (2016)
ChCl : Urea	1:2	750	298	Yue et al. (2012)
ChCl : Ethylene glycol	1:2	42	298	Ibrahim et al. (2019)
ChCl : Malonic acid	1:2	721	298	Qin et al. (2020)
ChCl : Castor oil (DES1)	1:3	411.6	313	This study
ChCl : castor oil (DES2)	1:4	401.6	313	This study
ChCl : Glycerol (control)	1:3	126	313	This study

The Arrhenius-like behavior exhibited by DES1 and DES2 in this study has similarly been reported for other formulations of DES (Aroso et al., 2017; AlOmar et al., 2016; Silva et al., 2019; Ibrahim et al., 2019). The viscosity-temperature relationship is accordingly described by equation 3:

$$\mu = \mu_o e^{-\frac{E_\mu}{RT}} \tag{3}$$

where μ is the dynamic viscosity, μ_o is the pre-exponential factor, E_μ is the activation energy, R is the universal gas constant, and T is the temperature in K.

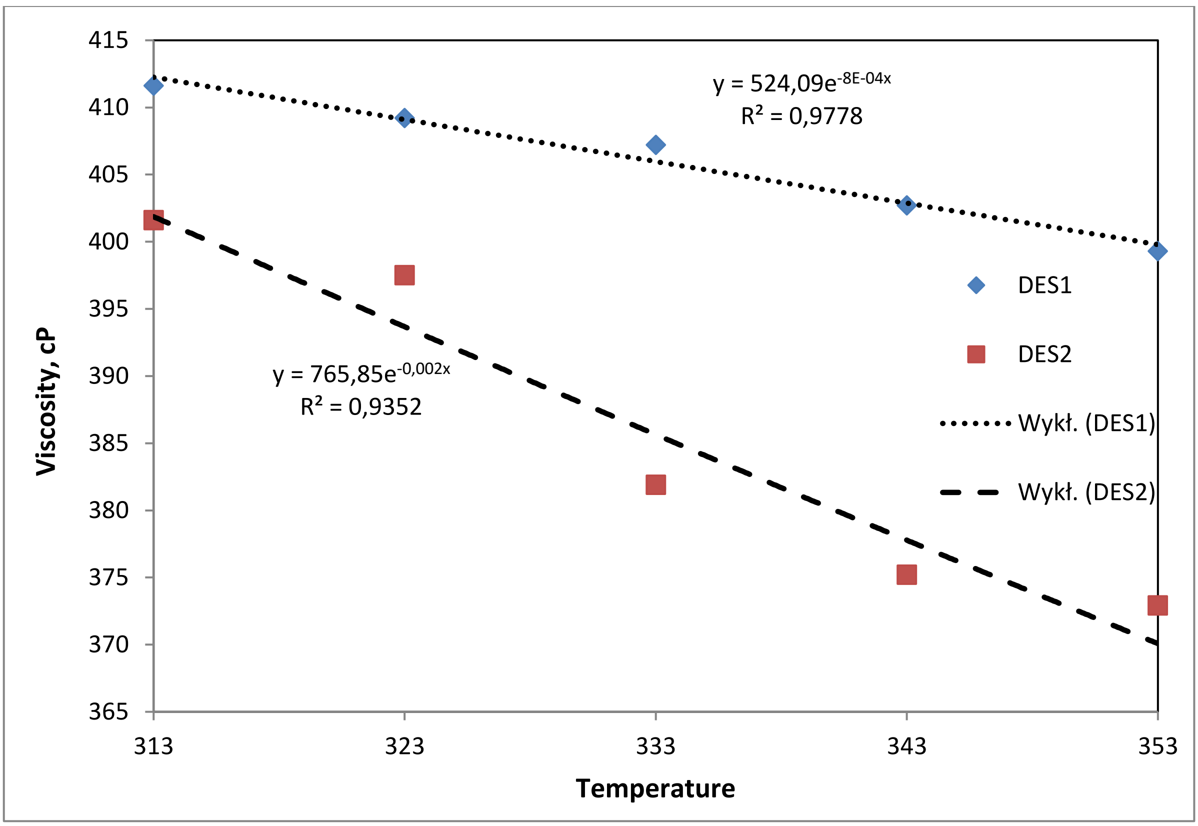

Figure 2. Viscosities of castor oil based deep eutectic solvents as a function of temperature

3. 4. Conductivity

Conductivity of DES play crucial in such area of application like electrochemistry, semiconductors, lithium batteries, electroplating, petroleum, iron and steel industries. The conductivity of DES1 and DES2 were measured as a function of temperature and plotted in **Figure 3**. It can be seen that conductivity increase as temperature increases for both DES1 and DES2. An inverse relation is observed between viscosity and conductivity against temperature. Similar trend have been reported for other DESs and it has been attributed to the free mobility of ionic species as the hole mobility increase with temperature (Zhang et al., 2012; Smith et al., 2014; Aroso et al., 2017; Al Omar et al., 2016; Ibrahim et al., 2019). In comparison with other choline chloride based DES, the castor-based DES has low conductivity. For example, the conductivity of ChCl : glycerol (1:2) vary from 985 μScm^{-1} to 4880 μScm^{-1} as temperature increase from 298 K to 348 K (AlOmar et al., 2016), while that of DES1 increase from 108.1 μScm^{-1} to 650.8 μScm^{-1} as temperature increased from 313 K to 353 K.

This again is consistent with the hole mobility theory as the viscosity of castor-based DES is relatively higher compared to glycerol-based DES. It is however observed that the conductivity of DES1 is higher than that of DES2; the expectation is the reverse considering their viscosities. This may be attributed to the higher weight ratio of ChCl in DES1 compared to DES2.

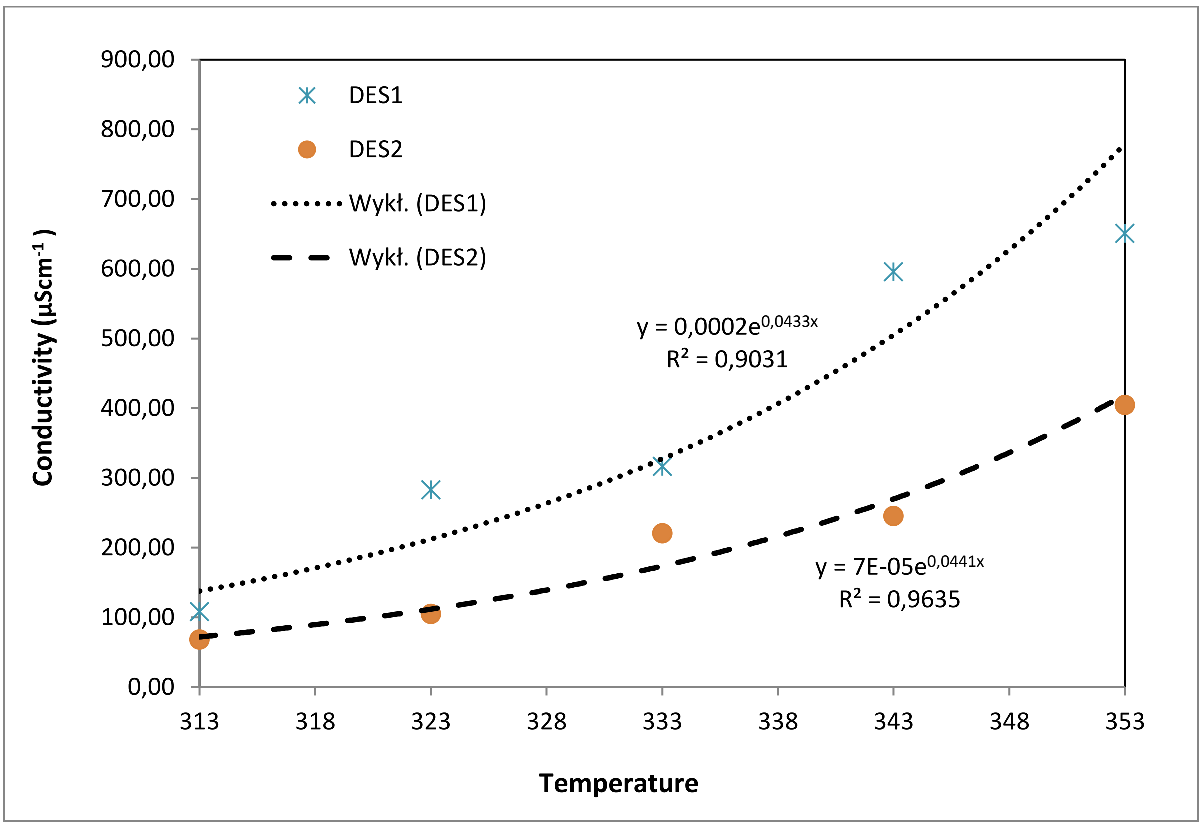

Figure 3. Conductivity of castor oil based deep eutectic solvents as a function of temperature

The conductivity-temperature relationship is described by Arrhenius like expression (Eq. 4):

$$K = K_o e^{\frac{-E_K}{RT}} \tag{4}$$

where K is the conductivity in μScm^{-1}, K_o is the pre-exponential factor, E_k is the activation energy of conductivity, R is the universal gas constant, and T is the temperature in Kelvin. The value of R^2, as shown in Figure 3, is greater 0.9 for both DES1 and DES2, validating the functional relation in Equation 4.

3. 5. Surface tension

Surface tension is an important property for such industrial operations as mixing, fluid flow, and separations. **Figure 4** show the variation of surface tension with temperature for DES1 and DES2. It is observed that surface tension decrease with increase in temperature. Similar trend have been reported for other DESs (Zhang et al., 2012; Smith et al., 2014; Aroso et al., 2017; AlOmar et al., 2016; Ibrahim et al., 2019). This has been attributed to break up of the intermolecular forces (hydrogen bond network) between the HBA and HBD as temperature increases (Abbott et al., 2011). The surface tension of DES1 is higher than that of DES2. The highest value of surface tension is that of DES1 at 313 K (35.8 dyn/cm or mN/m), this value is markedly low when compared with other choline chloride-based DES. For example, the surface tension of ChCl:glycerol is 56.04 mN/m at 313 K while that of ChCl:ethylene glycol is 48.95 mN/m at 313 K.
The linear relation between surface tension (γ) and temperature (T) is given by equation 5:

$$\gamma = a + bT \quad (5)$$

where a and b are constants. The values of these constants for DES1 and DES2 are shown in **Figure 4**.

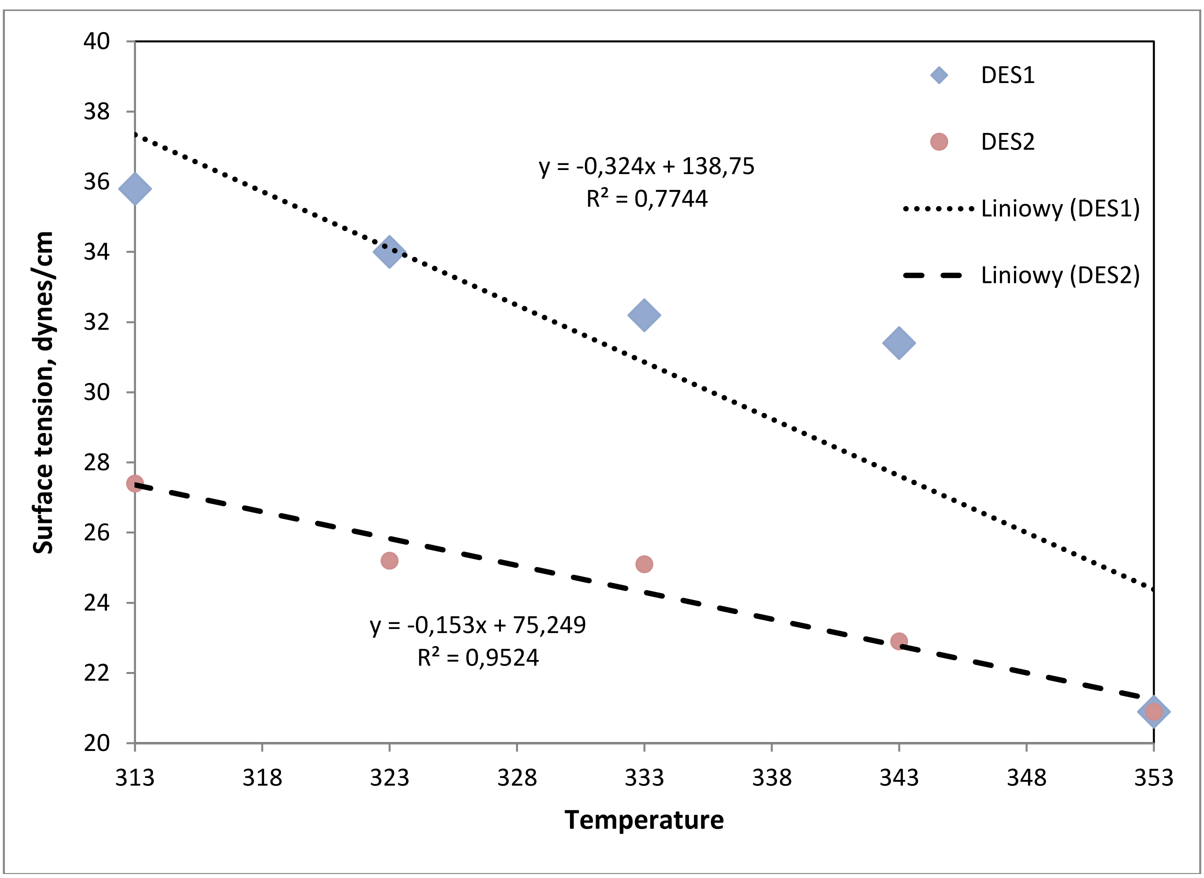

Figure 4. Surface tension of castor oil based DES as a function of temperature

3. 6. Refractive index

Refractive index is an important physical property of solvents, being a metric for measuring solvation capacity as encapsulated in solvatochromic parameters. It is a measure of the bending of light ray when passing from one medium to another. In this study, the refractive index of DES1 and DES2 were measured as a function of temperature (313 K to 353 K), and plotted in **Figure 5**. There is only a slight decrease in refractive index for the both DES, 1.4894 to 1.4474 for DES1 and 1.4780 to 1.4515 for DES2, as temperature increase from 313 K to 353 K. Shahbaz et al. (2013) reported a value of 1.4852 for ChCl:glycerol (1:2) and 1.4678 for ChCl:ethylene glycol (1:2) at 298 K. The values obtained for DES1 and DES2 are comparable with these two choline chloride-based DES. There is paucity of data on effect of temperature on refractive index of DES, prompting Shahbaz and co-workers to use Lorentz-Lorenz equation for predicting same eventhough at 298 K only. A recent study on ionic liquids shows a similar decrease in refractive index with temperature and also affirmed the reliability of Lorentz-Lorenz equation for predicting refractive index (Wu et al., 2020).

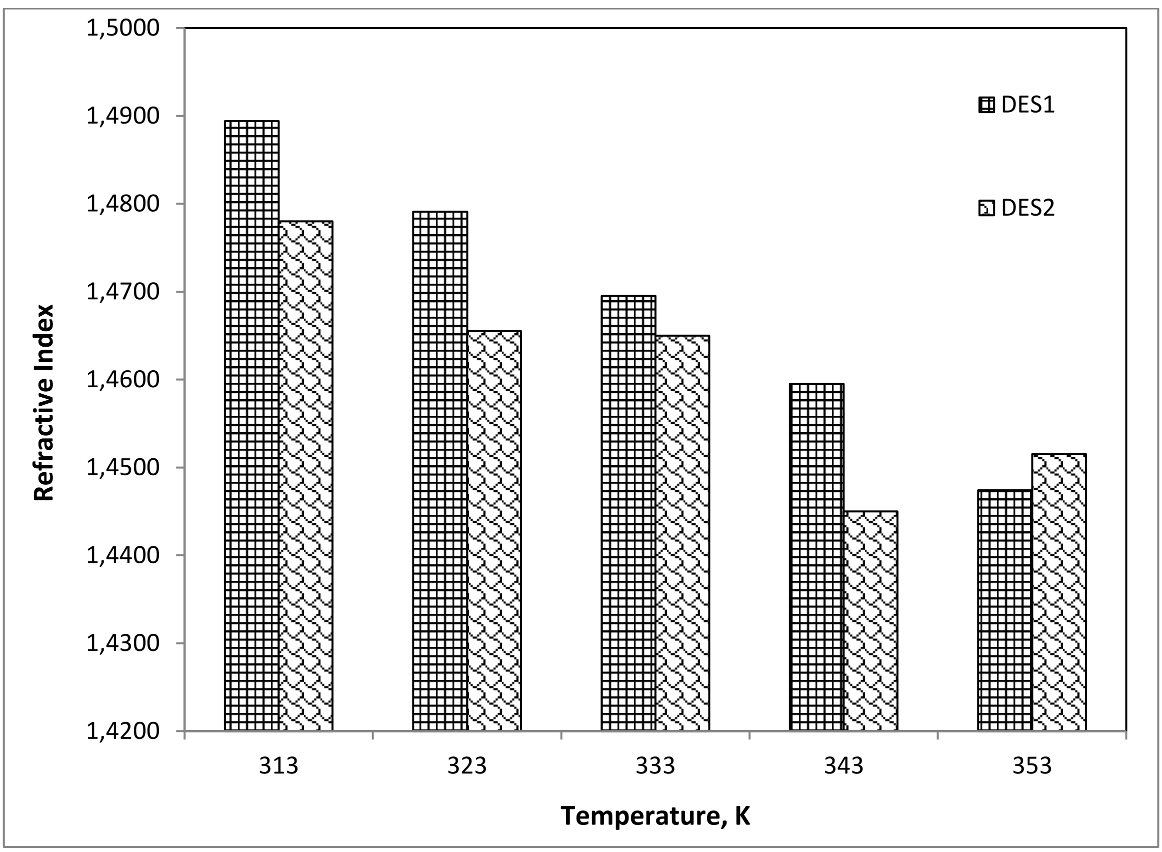

Figure 5. Refractive index of castor oil based DES as a function temperature

3. 7. pH

pH is a measure of the Bronsted acidity or basicity of a substance. **Figure 6** present the pH of DES1 and DES2 as a function of temperature. It is observed that the pH deceases with increase in temperature and are all below 7. This indicates that DES1 and DES2 are acidic, and the strength of the acidity increase with increase in temperature. Castor oil-based DES can therefore be classified as Bronsted acidic deep eutectic solvent (BADES) and would be suitable to mediate reactions that require acidic medium such as esterification and transesterification. Qin et al. (2020) showed that pH of acidic DES respond weakly to change in temperature. This is somewhat in agreement with our finding in this study.

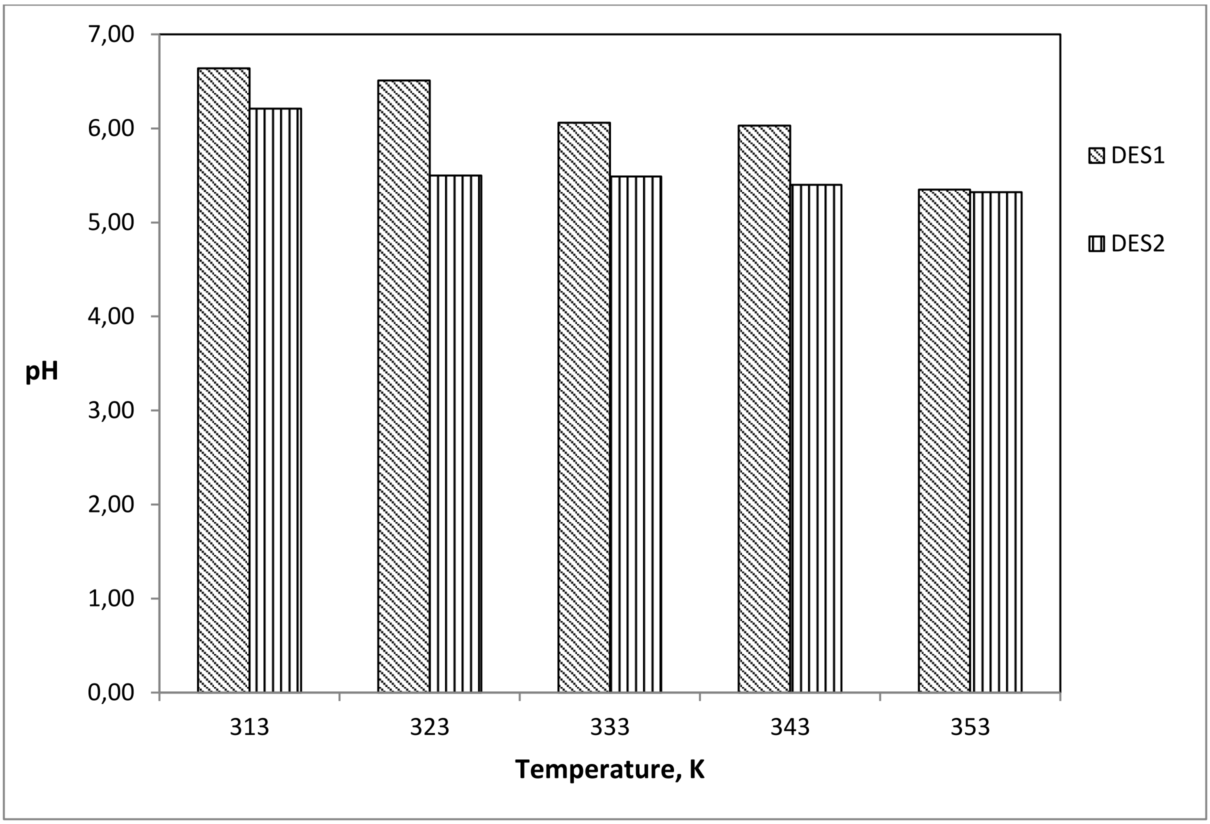

Figure 6. pH of castor oil based DES as a function of temperature.

4. CONCLUSION

Castor oil was evaluated as hydrogen bond donor in a mixture with choline chloride. Deep eutectic solvents were formed at ChCl:castor oil molar ratio of 1:3 and 1:4. Their physicochemical properties generally follow the trend known for other DES, in terms of temperature variations.

However, the density of castor oil based DES is uniquely low in comparison with other DES and ionic liquids. The viscosity, conductivity, surface tension and refractive index of castor oil based-based DES all fall within the known range for other choline chloride DESs.

Based on its pH values, castor oil based DES is a Bronsted acidic deep eutectic solvent. This discovery offers significant potential to expand the possible combinations of salts and HBDs and further increase the areas of application of this solvent.

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