

## Long-term Isothermal Stability of Deep Eutectic Solvents

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Deep eutectic solvents play an important role in the clean production of chemicals and the fractionation of renewable sources. When dissolving lignin or cellulose at elevated temperatures, the thermal stability of deep eutectic solvents is of great importance. However, studies concerning the long-term isothermal stability of deep eutectic solvents are scarce. In this study, the thermal stability of deep eutectic solvents, namely, choline chloride with oxalic acid dihydrate, glycerol, glycolic, malic acid, and citric acid monohydrate were investigated using thermogravimetric analysis (TGA). The isothermal decomposition experiments were conducted at a constant temperature (60, 80, 100, and 120 °C) for 10 h. These long-term isothermal thermogravimetric studies of the deep eutectic solvents showed a non-linear weight loss as a function of time at each temperature. According to these studies it is recommended to perform fractionation or dissolution of biomass below 80 °C.

*Keywords:* Deep eutectic solvents; Long-term stability; Clean production; Green chemistry

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### INTRODUCTION

Biomass can undergo traditional treatment methods or be transformed into other raw materials, biofuels, and biochemicals. The upgrading of existing technologies and the development of new biorefinery procedures are support for the transformation of biomass. Valorisation is a key factor for an economic lignocellulosic biorefinery (Jablonský *et al.* 2015; Šurina *et al.* 2015). A simple, clean fractionation of the biomass' main components represents an important step in the renewable, "clean" carbon economy. One of the promising technologies is the use of ionic liquids. Ionic liquids can be applied in obtaining new products from biomass, where they are used as solvents when recycling polymeric materials and electrochemical plating; as a portable media in solar systems; as a transport medium for reactive gases; and, most recently, in biotechnology, *e.g.* for enzymatic hydrolysis (Abbott *et al.* 2003, 2004). A relatively new generation of ionic liquids, known as deep eutectic solvents (DESs), is another important group of advanced solvents used to dissolve lignocellulosic biomass and enable its processing (Carriazo *et al.* 2012; Francisco *et al.* 2012; Zhang *et al.* 2012). Generally, DESs are obtained by mixing two substances, a hydrogen donor and a hydrogen acceptor that can be mutually connected through hydrogen bonding (Zhang *et al.* 2012).

Developments in this area have been sharply expanding, as indicated by recent publications and patented applications that use DESs for dissolving the individual components of biomass (Jablonsky *et al.* 2018). Some papers focus on the extraction of valuable compounds from biomass using a deep eutectic solvent. DESs were used to extract flavonoids from the plants *Camaecyparis obtusa*, *Carthamus tinctorius*, and *Flos sophorae* as well as from model oil (Bi *et al.* 2013; Dai *et al.* 2013a,b; Gu *et al.* 2014; Nam *et al.* 2015; Tang *et al.* 2015). Especially promising is current research into obtaining flavonoids through a NADESs. Such work (De Dios 2013; Kroon *et al.* 2013; Jablonský *et al.* 2015; Kumar *et al.* 2016a) has focused on the use of DESs in the fractionation process or the separation process of the biomass components. As new types of ionic liquids, DESs can be used in fractionation processes or extraction of different types of substances from various agricultural and silvicultural vegetation. Extraction and fractionation methods as well as a solvent should be chosen considering the sample matrix properties, the chemical properties of the analytes, the matrix-analyte interactions, efficiency and speed, environmental friendliness, and cost (Co *et al.* 2011; Zheljzkov *et al.* 2012, 2013; Nađalin *et al.* 2014).

Thermodynamic properties of DESs, such as glass transition temperature, melting temperature, thermal decomposition temperature, heat capacity, enthalpy, and entropy of phase transitions are important data for the understanding of these liquids and their application in different sectors. Adiabatic calorimetry and techniques of thermal analysis can be used to determine thermodynamic properties of DESs (Tan *et al.* 2011). Studies dealing with DESs have been based on the assumption that DESs will exhibit negligible vapor pressure. Any evaluation of DESs thermal properties is, due to their volatile nature, critical for their intended application (Kamavaram and Reddy 2008). Vapor pressure is influenced mainly by the hydrogen-bond acceptor (HBA) and donor (HBD) combination that is inherent in forming a DES. Thermogravimetric analysis (TGA) is one of the commonly used methods to determine the thermal stability of materials and substances (Cao and Mu 2014; Chemat *et al.* 2016; Deferm *et al.* 2018). Numerous DESs have been reported to be stable in their liquid form up to temperatures of 150 °C or higher (Chen *et al.* 2018). The obtained results were duly evaluated, taking various experimental conditions into account. In the case of the used TGA technique they referred mainly to the carrier gas, the sample purity, the heating rate, and the sample mass (Chen *et al.* 2018). Especially, it was pointed out that dynamic TGA studies with a fast heating rate ( $\geq 10$  °C min<sup>-1</sup>) lead to gross overestimations of the thermal stability (Cao and Mu 2014; Deferm *et al.* 2018; Maton *et al.* 2013; Villanueva *et al.* 2013). The temperature limit of ionic liquids stability is not precisely defined by the onset decomposition temperature (Dai *et al.* 2013a; Kamavaram and Reddy 2008). Studies on long-term stability are limited, and most investigations focus on conventional ionic liquids (Cao and Mu 2014; Clough *et al.* 2013; Peng *et al.* 2010). However, a few works on the thermal stability of DESs have been published too (Deferm *et al.* 2018; Ghaedi *et al.* 2018; Morrison *et al.* 2009; Skulcova *et al.* 2017; Chen *et al.* 2018). It was shown that dynamic TGA is no longer reliable for estimating the thermal stability even at low heating rates, and the method often leads to overestimations of the long-term thermal stabilities (Deferm *et al.* 2018; Maton *et al.* 2013). Static TGA provides more reliable thermal stability data and should be preferentially used. Investigation of the long-term stability of DESs is very important for industrial applications, in which DESs must endure certain high temperature for a period of time (Chen *et al.* 2018).

The main objective of this study was to characterize long-term thermal stability of DESs. The term “thermal stability” means that the composition of DES components and their products does not change in a certain operational temperature range. Moreover, no turbidity is formed within the time of the DES application. These requirements are met even in the case of evaporation of a small portion of water. In our work, isothermal TGA at different temperature intervals were used to determine the long-term stability of mixtures based on choline chloride in combination with oxalic acid dehydrate (molar ratio 1:1); glycerol (1:2); glycolic acid (1:3); malic acid (1:1); and citric acid monohydrate (1:1). Long-term stability of these DESs was evaluated because choline chloride-based eutectic solvent with carboxylic acids and glycerol were used as extractants for the extracting of polyphenolic compounds from spruce bark. The results obtained were recently published by Skulcova *et al.* (2018). Extractions were performed for 1 h at 60 °C under continuous stirring. The work focused on investigation of thermal stability describing behaviour of the prepared DESs exposed to various temperatures at isothermal conditions. The stability of these mixtures were characterized from the viewpoint of the loss of mass (supposed bound and/or unbound water loss), the loss of DESs components, and thermal decomposition of DESs components. In addition, long-term thermal stability was followed by determination of water content not taken into account at the stability evaluation. This is the stability informing on mass loss due to isothermal impact of heat and involving evaporation of DES components and their decomposition.

## EXPERIMENTAL

### Materials

Glycerol (99%) and citric acid monohydrate ( $\geq 98\%$ ) were obtained from Centralchem, s.r.o. (Bratislava, Slovakia). Choline chloride ( $\geq 98\%$ ), malic acid ( $\geq 98\%$ ), glycolic acid (99%), and oxalic acid dihydrate ( $\geq 99\%$ ) were purchased from Sigma-Aldrich (Bratislava, Slovakia).

The deep eutectic solvents were prepared according to the procedure previously reported (Jablonský *et al.* 2015). The solvents were prepared with choline chloride and oxalic acid dihydrate; glycerol; glycolic; malic acid; and citric acid monohydrate. Choline chloride was dried in a vacuum oven at 40 °C prior to its use to eliminate moisture contamination, the chemicals were used as received.

### *Determination of water content*

The water contents were determined with a TITRINO 702 SM from Metrohm Ltd. (Herisau, Switzerland), and coulometric Karl-Fischer titration.

### *Density*

Densities were determined with a pycnometer. The samples density was measured at different temperatures (23 °C to 75 °C). All measurements were performed three times with individual samples.

### *Viscosity*

The viscoelastic properties were characterized on a Brookfield DV- II + Pro rotating viscometer from Ecotest, s.r.o. (Bratislava, Slovakia). The samples viscosity was

measured at different temperatures (28 °C to 60 °C) at different revolutions (5, 10, 20, 50, and 100 RPM) using a spindle 18 with an adapter. All measurements were performed three times with individual samples.

#### *pH measurement*

The pH was measured in aqueous solutions of DES at a concentration of 0.5 mol/L. The pH was determined using a digital pH meter from Hanna Instruments (Bratislava, Slovakia). The samples were heated to the desired temperature at 23 °C to 60 °C.

#### *Conductivity measurement*

Conductivity was measured using a DiST4 conductivity meter from Hanna Instruments (Bratislava, Slovakia) at ambient temperature. All measurements were performed three times with individual samples.

**Table 1.** Compositions and Abbreviations of Prepared DESs

Abbreviation	DES	Molar Ratio	Water Content** (%)
DES1	ChCl*:Oxalic acid dihydrate	1:1	14.27
DES2	ChCl:Glycerol	1:2	0.31
DES3	ChCl:Glycolic acid	1:3	5.25
DES4	ChCl:Malic acid	1:1	2.86
DES5	ChCl:Citric acid monohydrate	1:1	6.82
*Choline chloride			
**Karl Fisher method			

## Methods

### *Long-term isothermal stability*

A thermogravimetric analyser/Differential scanning calorimeter 1 (TGA/DSC) instrument from Mettler Toledo (Bratislava, Slovakia) was used to perform the thermogravimetric analysis of DESs. The analysis was performed in a reduction atmosphere (nitrogen, 50 mL/min). The long-term stability was conducted at isothermal mode. Isothermal thermogravimetry was performed at a constant temperature for 10 h. Measurements were taken in the temperature range from 60 °C to 120 °C at 20 °C intervals.

## RESULTS AND DISCUSSION

The long-term thermal behaviour of DESs was investigated using isothermal studies for 10 h with a nitrogen purge at 50 mL/min. The results obtained at different temperatures are shown in Figs. 1 through 5. Nonlinear weight vs. time dependences were observed in the range 60 °C to 120 °C at intervals of 10 °C. Table 2 illustrates the comparison of weight change of the deep eutectic solvents as a function of temperature after 10 h of isothermal thermogravimetry. Weight differences between 3.1% and 5.9% were recorded at 60 °C, a difference mainly due to air humidity. At 120 °C these differences were between 11.7% and 34.6%.

The greatest weight loss was confirmed when the eutectic solvent was prepared from choline chloride and citric acid monohydrate. Citric acid monohydrate has bound

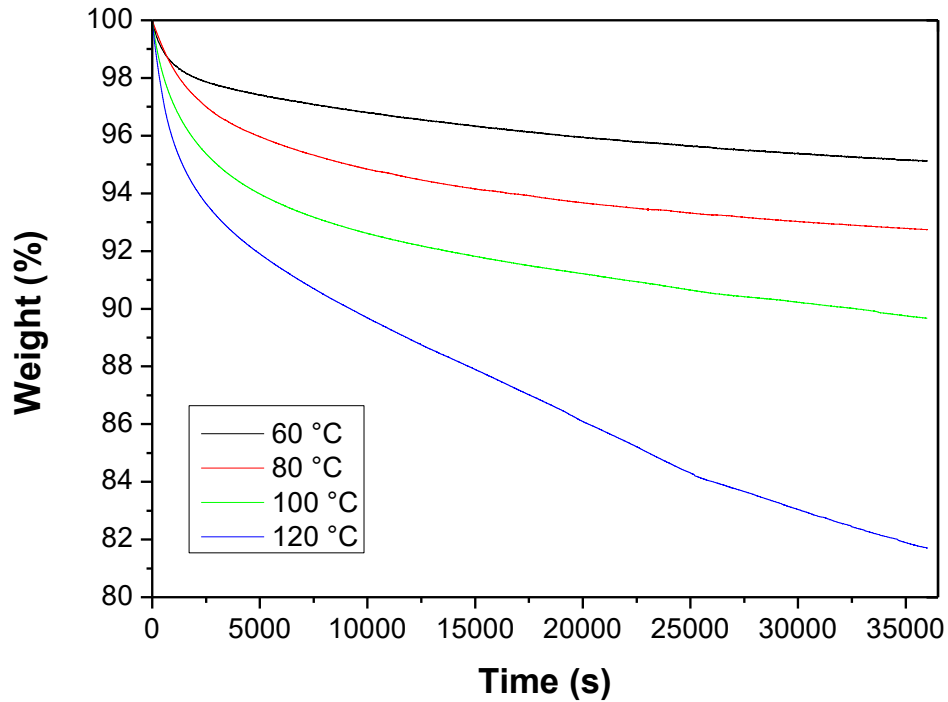
water that is released between 70 °C and 100 °C. Faster heating increases the temperature at which the water evaporates, and heating at lower temperatures results in a slower evaporation of the bound water. A weight loss of 34.58% was observed at 120 °C, which was a remarkable difference from the 7.3% experienced at 100 °C. Based on the evaluation of the thermal stability of DESs, it was concluded that these solvents have different stabilities.

The stability of the solvents proceeded in the following order: DES choline chloride with, respectively, malic acid (11.7%), glycerol (12.9%), glycolic acid (15.6%), oxalic acid dehydrate (18.3%), and citric acid monohydrate (34.6%), at 120 °C and 10 h. Provided that the temperature while applying isothermal methods was 80 °C, the most stable was DES choline chloride with malic acid (weight loss of 4.4%) > glycerol (5.0%) > citric acid monohydrate (5.2%) > oxalic acid dihydrate (7.3%) > glycolic acid (11.7%). Conversely, the stability at 60 °C ascended in the following order: DES choline chloride with, respectively, citric acid monohydrate (3.1%), malic acid (4.2%), glycerol (4.7%), oxalic acid dehydrate (4.9%), and glycolic acid (5.9%).

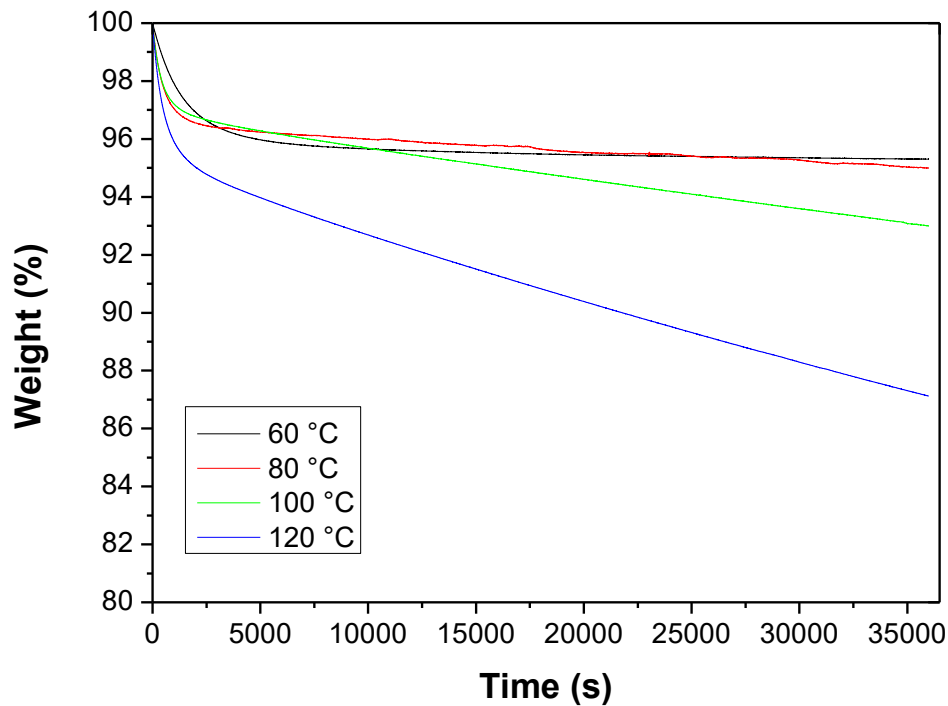
The above results describe the actual thermal stability of the prepared samples that also contained water (Table 1). The phenomena related to water content changes were described and explained by van Osch *et al.* (2015), Sheldon (2016), and Zhekenov *et al.* (2017). NMR investigation of aqueous systems with various concentrations of DESs showed that the DESs chemical properties are invariable in a relatively large concentration range span. DESs are frequently applied mixed with water. Their components can react with water, producing new compounds which themselves do not form the DESs. However, usually the components are weak acids and bases. The equilibrium constants of their protolytic reaction with water are therefore low, which means that even in the presence of water the components in practice should not change their composition and structure. On the other hand, it is known that the presence of water in a DES system and its effect on the efficiency of extraction strongly depends on the water content. It is well known, that the presence of water can have a strong influence mainly on dynamic TGA results. Comparison of the thermal stability of DESs at 120 °C without water content was as follows: DES choline chloride with, respectively, oxalic acid dihydrate (4.0%), malic acid (8.8%), glycolic acid (10.4%), glycerol (12.6%), and citric acid monohydrate (27.8%) at 120 °C and 10 h. The long-term stability of the examined DES choline chloride with, respectively, oxalic acid dehydrate, glycerol, glycolic, malic acid, and citric acid monohydrate indicated that these types of fluids could have practical potential use in many industrial applications and as a solvent in fractionation and extraction processes.

**Table 2.** Weight Loss of the Deep Eutectic Solvents as a Function of Temperature After 10 h

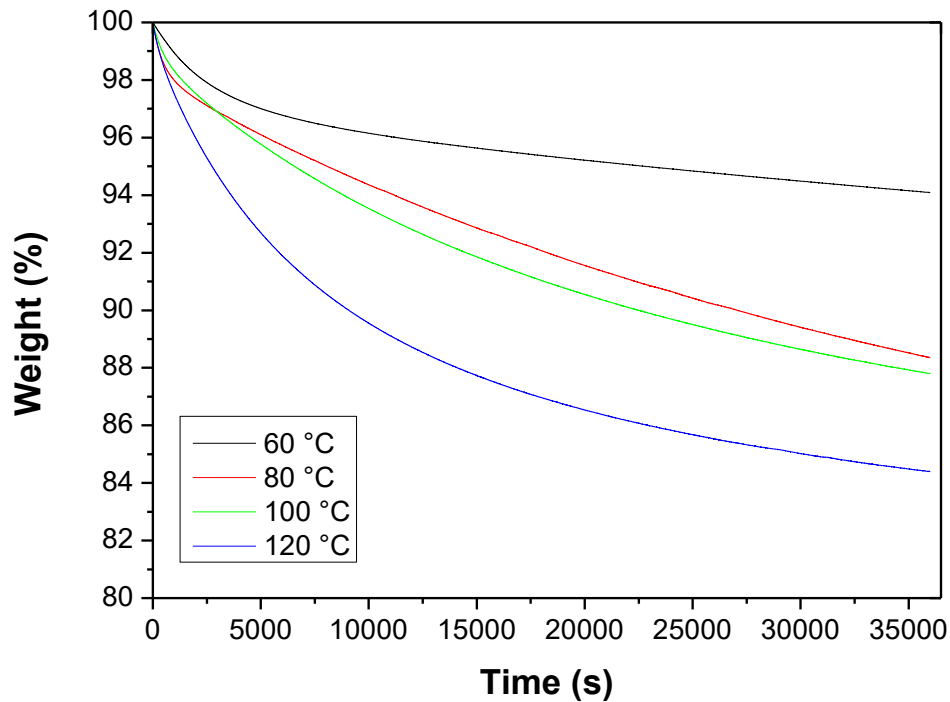
DES	60 °C	80 °C	100 °C	120 °C
	Weight Loss After 10 h (%)			
ChCl*:Oxalic acid × 2H <sub>2</sub> O	4.9	7.3	10.3	18.3
ChCl:Glycerol	4.7	5.0	6.7	12.9
ChCl:Glycolic acid	5.9	11.7	12.2	15.6
ChCl:Malic acid	4.2	4.4	6.6	11.7
ChCl:Citric acid × H <sub>2</sub> O	3.1	5.2	7.3	34.6
*Choline chloride				



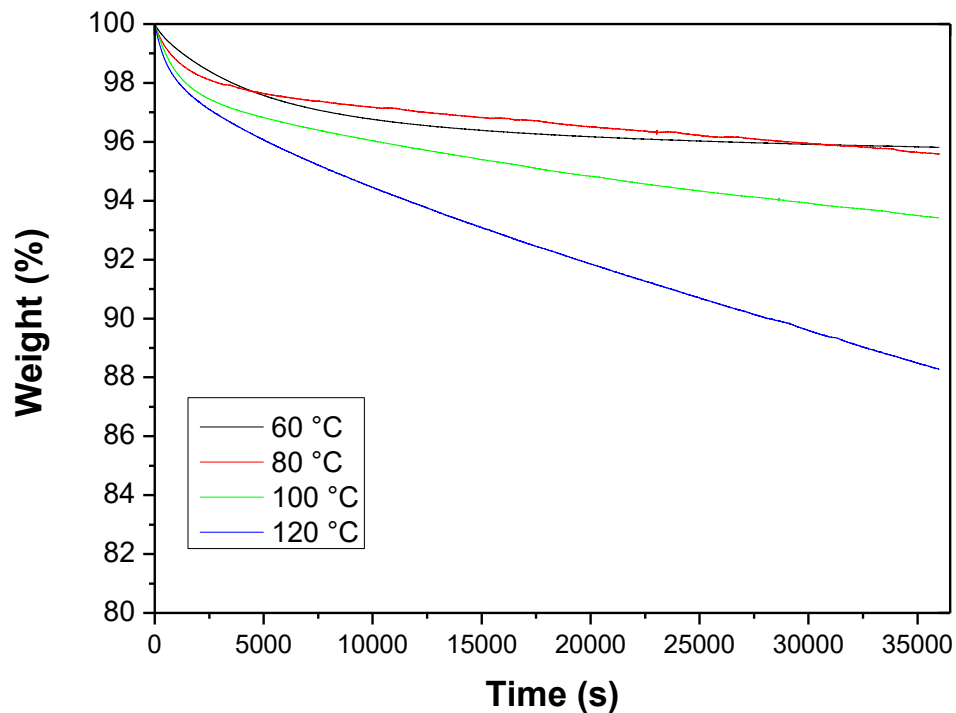
**Fig. 1.** Isothermal thermogravimetry of DES1, choline chloride and oxalic acid  $\times$  2H<sub>2</sub>O, molar ratio 1:1, at different temperatures under nitrogen purge (50 mL/min)



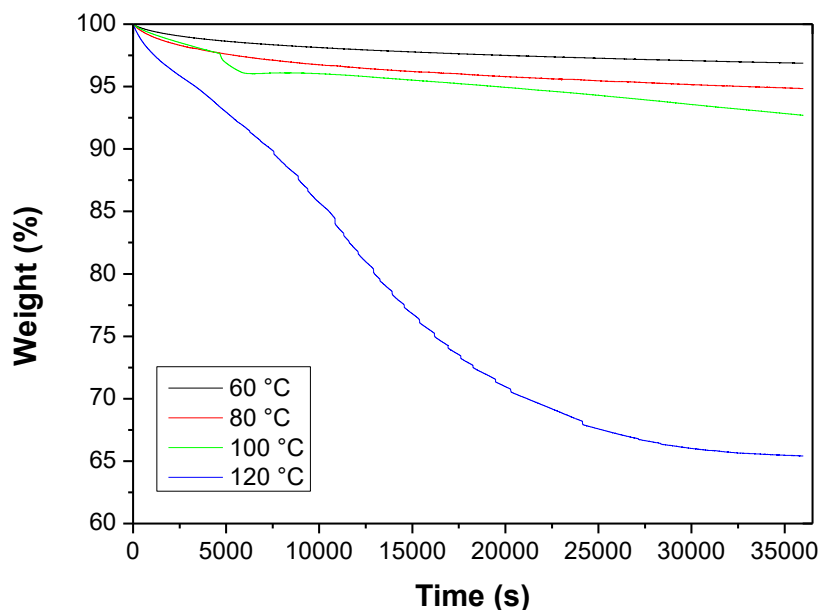
**Fig. 2.** Isothermal thermogravimetry of DES2, choline chloride and glycerol, molar ratio 1:2, at different temperatures under nitrogen purge (50 mL/min)



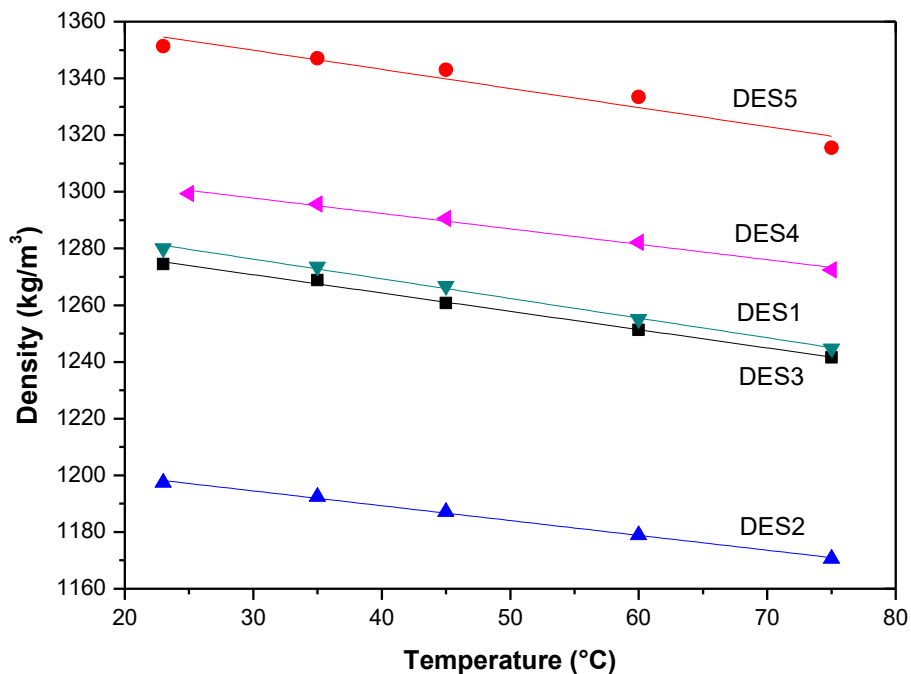
**Fig. 3.** Isothermal thermogravimetry of DES3, choline chloride and glycolic acid, molar ratio 1:3, at different temperatures under nitrogen purge (50 mL/min)



**Fig. 4.** Isothermal thermogravimetry of DES4, choline chloride and malic acid, molar ratio 1:1, at different temperatures under nitrogen purge (50 mL/min)



**Fig. 5.** Isothermal thermogravimetry of DES5, choline chloride and citric acid x H<sub>2</sub>O, molar ratio 1:1, at different temperatures under nitrogen purge (50 mL/min)



**Fig. 6.** Densities of DESs as a function of temperature

Density is an important property for chemical materials and their processing. In general, the densities of DESs exhibit higher values than that of water. For many applications it is important to know how temperature affects density (Hayyan *et al.* 2012). The density is dependent upon the packing and molecular organisation of the DES (Abbott *et al.* 2007) and on the water content, as it decreases with an increased percentage of water (Yadav and Pandey 2014; Yadav *et al.* 2014).



The increase in temperature results in more molecular activity and mobility (Kareem *et al.* 2010). The studied DESs density measurements were conducted as a function of temperature in the range of 23 °C to 75 °C. The effect of temperature on the densities of different DES is depicted in Fig. 6. The measured densities of the DESs were less than 1352 kg/m<sup>3</sup>. The reduction in density was linear for all studied DESs. The highest density was that of DES5 with the molar ratio 1:3, which reached a maximum of 1352 kg/m<sup>3</sup> at 23 °C and a minimum of 1315.5 kg/m<sup>3</sup> at 75 °C. In contrast, DES2 had the lowest density (1170.6 kg/m<sup>3</sup> at the highest temperature of 75 °C). One way to achieve a lower extraction cost is to run the process at lower temperatures. The disadvantage of lower temperatures is the resulting higher density and viscosity of the deep eutectic solvent, which influences the penetration into the matrix, while extending the extraction time and influencing the process's efficiency. The results of this work showed that an increased temperature resulted in a reduction in the density and facilitated the penetration of the DESs into the matrix. These results suggested that, in terms of thermal stability, it was more beneficial to use lower extraction temperatures, but that viscosity and density of the deep eutectic solvent at low temperature prevented the extraction process. Therefore, it could be appropriate to optimize the process parameters to work at higher temperatures while also preventing remarkable thermal degradation of the DES at these temperatures. According to the results of this paper, it is advisable to apply temperatures lower than 80 °C during the extraction and fractionation processes.

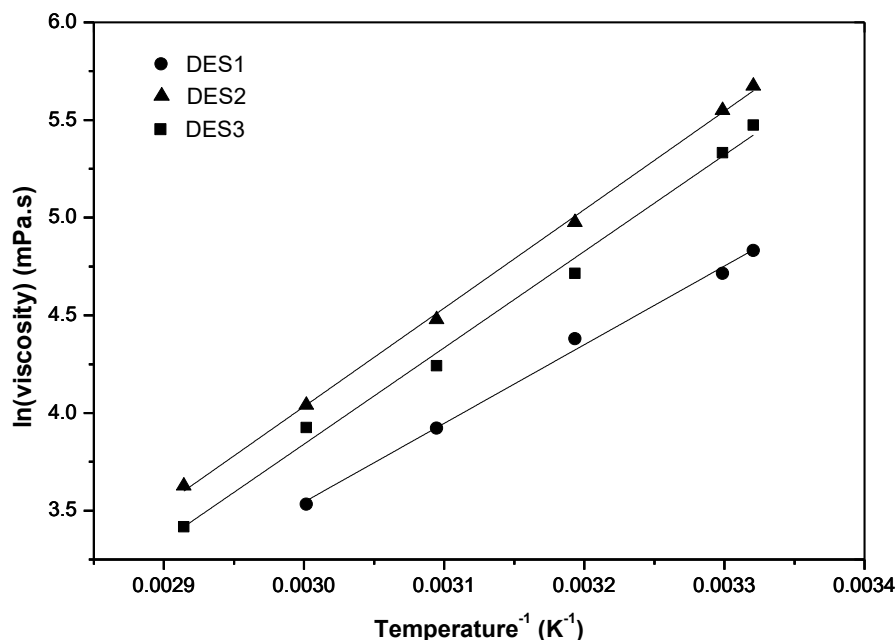
Conductivity as a summation parameter measures the concentration level of ions in the solution. The measured values varied from 0.00 mS/cm to 4.95 mS/cm. It has been observed that dicarboxylic acid-containing DESs exhibited higher conductivity compared with other DESs investigated (Abbott *et al.* 2004). The work of Smith *et al.* (2014) has shown the conductivity of DES choline chloride:ethylene glycol (1:2) is 7.61 mS/cm, which is considerably more than chlorine:oxalic acid (1:1). The conductivity of DES choline chloride:glycerol is close to the conductivity interval for natural drinking and surface water, which is 0.1 mS/cm to 1 mS/cm. The work of Zhang *et al.* (2012) measured the conductivity of selected DESs, with the choline chloride:glycerol conductivity at 1.05 mS/cm, which corresponds to the results of the present study.

The conductivity of DES choline chloride:citric acid was not measurable under the given conditions. Its high density did not allow the immersion of the electrode.

The DES choline chloride:malic acid has proven to be non-conductive. The work of Kumar *et al.* (2016b) measured the conductivity of DES choline chloride:malic acid as 0.197 mS/cm (at ambient temperature). Kumar *et al.* (2016b) also observed the effect of water on the conductivity of DES and found that an increase in the content of DES water resulted in increased conductivity to a maximum point after which it decreased. This property may have been the reason for the different conductivities of the same DES.

**Table 3.** Conductivities of DESs at Ambient Temperature

Abbreviation	DES	Conductivity mS/cm
DES1	ChCl:Oxalic acid dihydrate	4.95
DES2	ChCl:Glycerol	1.05
DES3	ChCl:Glycolic acid	1.24
DES4	ChCl:Malic acid	0.00
DES5	ChCl:Citric acid monohydrate	ND*
*Not detected		



**Fig. 7.** Temperature dependence of dynamic viscosity measured for DESs

The temperature dependence of dynamic viscosity measured for DESs is shown in Fig. 7. Due to device limitations and high density, it was not possible to measure the dynamic viscosity of choline chloride:malic acid and choline chloride: citric acid. As with many liquids, the viscosity was also a noticeable physical quantity for DESs. Deep eutectic solvents have a relatively high viscosity compared with water, due to the hydrogen bonds between components. The presence of Van der Waals interactions, electrostatic interactions, and the size of ions forming the DES can also contribute to high viscosity (Zhang *et al.* 2012). Because DESs are considered a new group of solvents, it is desirable to find DESs with low viscosity to ensure the functionality of the solvent. The viscosity of the resulting solvent is strongly dependent upon the temperature and water content of the starting materials (Zhang *et al.* 2012). At room temperature, the highest dynamic viscosity value was DES2 choline chloride:glycerol, and the lowest was DES1 choline chloride:oxalic acid. At 60 °C, the highest value was also DES2 and the lowest was DES1, and so the trend was maintained. Zhang *et al.* (2012) examined the viscosity of DESs from various works. The DES choline chloride:glycerol (1:2) had a viscosity of 376 cP (20 °C) and 259 cP (25 °C). The DES was measured at 28 °C and 291.2 mPa.s, corresponding to 291.2 cP.

The viscosities of most DESs vary considerably with temperature changes. The dependence of viscosity on temperature has an Arrhenian character. The dependence of natural logarithm from  $T^{-1}$  was linear and its slope and intercept were evaluated (Table 4).

**Table 4.** Values of Parameters Slope and Intercept for Equation  $\ln(\eta) = a + b(T^{-1})$  for Viscosity (mPa.s) in the Temperature Range 301.15 to 343.15 K

Abbreviation	Slope (a)	Intercept (b)×10 <sup>-3</sup>
DES1	-10.961	4.934
DES2	-11.090	5.041
DES3	-8.536	4.027

The chemical nature of hydrogen bond donor (HBD) had a strong effect on the acidity or alkalinity of the resulting DES. The prepared DES in this study had a distinct acidic character because HBD are organic acids and tri-alcoholic glycerol. The pH of the DES with glycerol was higher than the pH of the DES containing an organic acid. With increasing temperature, the pH decreases, while the DES choline chloride:oxalic acid was 0.05 at 60 °C. The pH change with increasing temperature for DES choline chloride:glycolic acid and glycerol had a slight downward tendency. The pH of both DESs choline chloride:malic acid and choline chloride: citric acid decreased remarkably with rising temperatures. Similarly, the pH also decreased for choline chloride:oxalic acid.

**Table 5.** Values of Parameters Slope and Intercept for Equation  $\text{pH} = a + b(T)$  for pH in the Temperature Range 24 to 60 °C

Abbreviation	Slope (a)	Intercept (b)×10 <sup>3</sup>
DES1	2.037	-32.60
DES2	4.721	-10.27
DES3	1.409	-6.79
DES4	2.082	-19.28
DES5	2.298	-23.39

## CONCLUSIONS

1. Long-term isothermal thermogravimetry studies of the deep eutectic solvents showed non-linear weight loss as a function of time at each recorded temperature. Preferably, the fractionation or dissolution of biomass should be conducted below 80 °C.
2. The density of the investigated DESs decreased with increased temperature.
3. The pH of the DES with glycerol was noticeably higher than the pH of the DES containing an organic acid; these pHs were below 2.3. The DES containing glycerol had a pH of up to approximately 4.7. As the temperature increased, the pH decreased.

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