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Research Article

THERMAL STABILITY OF SELECTEDDEEP EUTECTIC SOLVENTS

Haz, A*., Strizincova, P., Majova, V., Skulcova, A and Jablonsky M

Slovak University of Technology, Faculty of Chemical and Food Technology, Institute of Natural and Synthetic Polymers, Department of Wood, Pulp and Paper, Radlinského 9, 831 07 Bratislava, Slovak Republic

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ABSTRACT

In this study, a new type of "green solvents" named deep eutectic solvents (DESs) has been synthesized combining hydrogen bond acceptors (HBAs) and hydrogen bond donors (HBDs). Choline chloride (ChCl) was chosen as typical HBA, and lactic acid, tartaric acid, citric acid and oxalic acid were chosen as HBDs. The thermal stability of deep eutectic solvents is an important parameter for their application and limits the maximum operation temperature. The thermal stability of DESs such as lactic, tartaric, citric and oxalic acid with choline chloride showed wide range of application (134.8 – 197.8°C). All DESs were observed in temperature range 25 – 400°C.

INTRODUCTION

Lot of works during the last two decades has been focused on the applications of ionic liquids (ILs). One of the drawbacks of ILs is their questionable "green" character. This feature depends to their poor biodegradability, biocompatibility, and sustainability (Zhang *et al*, 2012). In recent years, a new kind of intermediary deep eutectic solvents (DESs) has been exploited. A DES is generally composed of a mixture consisting of a hydrogen bond acceptor (HBA), such as a quaternary salt, with a hydrogen bond donor (HBD), such as amines, carboxylic acids, a lcohol, and carbohydrates (Abbott *et al*, 2003).Abbot *et al*. introduced deep eutectic solvents (DESs), as an analogue of ILs, in 2003 (Abbott *et al*, 2003). To simplify and to better understanding the behaviour of DESs, Abbott *et al*. categorized DESs into four types: Type I (quaternary salt and metal halide), Type II (quaternary salt and hydrated metal halide), Type III (quaternary salt and hydrogen bond donor) and Type IV (metal halide and hydrogen bond donor) (Abbott *et al*, 2004).

It was firstly reported by (Abbott *et al*, 2004) which can be formed by naturally mixing two or more compounds named hydrogen bond donor (HBD) and hydrogen bond acceptor (HBA) in a certain molar ratio. These compounds can be associated with each other depending on hydrogen bond interactions (Pena-Pereira and Namiesnik, 2014). DESs have the physicochemical characteristics similar to ILs, such as a melting point close to room temperature, similar starting materials, undetectable vapour pressure, non-volatility, non-flammability, wide liquid temperature range and special solubility for many compounds (van Osch *et al*, 2015; Bubalo *et al*, 2015).Thermal characterization of DESs can lead to further scientific developments. Valorisation is a key factor for an economic lignocellulosic biorefinery (Jablonsky *et al*, 2015; Surina *et al*. 2015).Some papers are focused on the extraction of valuable compounds from biomass using eutectic mixtures. The works (Jablonsky *et al*, 2015; de Dio *et al*, 2013; Kroon *et al*, 2013; Kumar *et al*, 2016; Skulcova *et al*, 2016a; Skulcova *et al*, 2016b) were focused on the usage of DESs in the fractionation process or separation process of the biomass components.

In the work of (Craveiro *et al*. 2016) was used polarized optical microscopy measurements coupled with differential scanning calorimetry analysis to better understand the thermal behaviour of natural deep eutectic solvents, e.g., the influence of water on the glass transition and melting temperature. Rengstl and co-workers have recently reported on the thermal behavior of DES based on different choline ILs (Rengstl *et al*, 2014). Dai and co-workers determined the thermal characteristics of some of NADES with water in its composition (Dai *et al*, 2013).

Corresponding author:* **Haz, A
Slovak University of Technology, Faculty of Chemical and Food Technology, Institute of Natural and Synthetic Polymers, Department of Wood, Pulp and Paper, Radlinského 9, 831 07 Bratislava, Slovak Republic

(Florindo *et al*, 2014)and they also reported on the strong influence of water on the properties of ChCl: carboxylic acid-based DES. It is known that hydrogen bonds between the organic salt and the hydrogen bond donor cause charge delocalization and depression of the melting point (Abbott *et al*, 2003; Abbott *et al*, 2004). Charge is delocalized and results in a decrease of the melting point of the mixture compared to the pure substances (Rengstl *et al*, 2014).The thermal stability of deep eutectic solvents is an important parameter and limits the maximum operation temperature. (Seeberger *et al.* 2009)The thermal stability of ionic liquids is often determined by thermogravimetric analysis (TGA) in nitrogen atmosphere and with a constant heating rate, typically 5 to 20 K/min (Ohtani*et al*. 2008; Seeberger *et al*. 2009)

MATERIALS AND METHODS

Materials

Choline chloride (≥98%, Sigma Aldrich), tartaric acid (99.5 %), citric acid× H_2O(p.a.), lactic acid (90 %, VWR®)and oxalic acid × $2H_2O$ (p.a.)were used as received without further purification except drying for 24 h at 50°C under vacuum to reduce the moisture content to minimum. The details of molecular formula and molecular weight of all components are shown in Table 1.

Table 1 Details of molecular formula and molecular weight of choline chloride (ChCl), lactic acid, oxalic acid and tartaric acid used in the present work.

Compound	Molecular formula	Molecular weight (g·mol⁻¹)
Choline chloride	$C_5H_{14}ClNO$	139.62
Lactic acid	$C_3H_6O_3$	90.08
Oxalic acid	$C_2H_2O_4$. $2H_2O$	126.06
Tartaric acid	$C_4H_6O_6$	150.09
Citric acid	$C_6H_8O_7$. H_2O	210.13

The mixtures (DESs) were prepared with molar ratio 1:1 and stirred in an oil bath to form a homogeneous liquid at 60 – 80 °C (according to carboxylic acid).

All synthesized DESs were left overnight in glass erlenmeyer flasks and sealed with parafilm to ensure stability (i.e., humidity, recrystallization/precipitation of salt) of resultant DESs.

Methods

Thermal analysis

A Mettler Toledo TGA/DSC 1 instrument was used to perform thermo gravimetric analysis of deep eutectic solvents and their pure components. The analysis was performed under nitrogen atmosphere (flow rate 50 mL/min). The measurements were performed in the temperature interval of 25 - 400°C in three segments. At the beginning, the sample was conditioned at 25°C for 3 min. Subsequently, thermodynamic segment occurs increasing the temperature by 10 °C/min. After reaching 400°C, the measurement was finalised at 400°C for 3 min. The accuracy of the temperature is better than ±1 °C.

RESULT AND DISCUSSION

TGA is the most common used technique to investigate the thermal stability. Ramped temperature analysis and isothermal temperature analysis could be used to measure short-term and long-term stability of DESs. Both of the mare important for comprehensive understanding of the stability. For any new solvents it is important to characterize the thermal and physical properties, to establish their potential for any further applications. The thermal decomposition temperatures of pure components (i.e., ChCl, lactic, oxalic, tartaric and citric acid) were measured (Table 2).The differences in thermal decomposition temperature as a function of temperature/time is shown in Fig. 1,2.

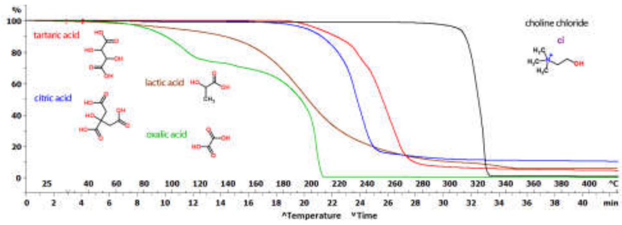

Fig.1 Thermogravimetric analysis of pure components of all DESs

Thermal decomposition temperatures are in the following order, oxalic acid, lactic acid, citric acid, tartaric acid and choline chloride. For oxalic acid dihydrate as compound with lowest thermal stability (Fig. 1 green line), the weight loss percentages were 25.21% and 28.5% at about 120°C, respectively, indicating that the complete dehydration temperature for oxalic acid dehydrate was about 120 °C. The completed composition temperatures of these two components were 200 °C and 324°C, respectively.

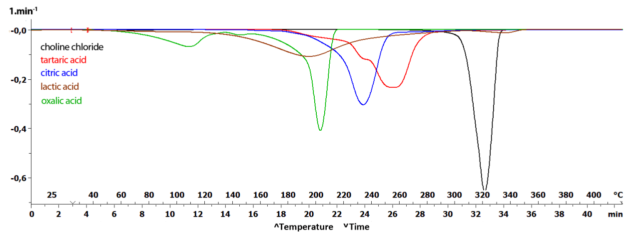

Fig.2 First derivative of TG curves of pure components of all DESs

Table 2 Measured parameters during thermal and multi-step decomposition of DES's with formation of volatile reaction products

DES	Onset temperature [°C]	1st peak - rate of change of mass [°C]	2nd peak - rate of change of mass [°C]
Choline chloride	309.13	-	316.90
Citric acid	212.73	-	229.95
Lactic acid	155.46	-	193.46
Oxalic acid	74.47/192.92*	105.2	197.03
Tartaric acid	228.61	-	256.52

*in a second step

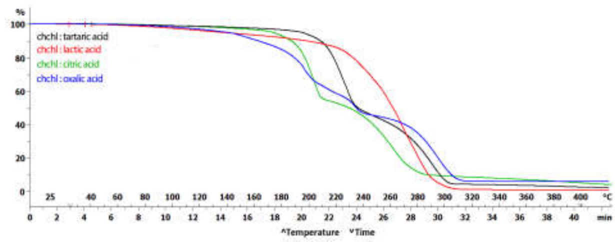

Fig.3 Thermogravimetric analysis of all prepared DESsin temperature interval 25 – 400°C

All these deep eutectic solvents have shown a wide variation in their thermal degradation phenomena. DESs decomposition is a process involving several competing reactions. The degradation of DESs takes place in a narrow temperature range of 150-300°C but the major degradation takes place between 190-280°C.The effect of the four organic acids in DES mixtures resulted in increasing thermal decomposition temperatures. Stability of prepared mixtures with choline chloride rises with following the order oxalic acid, citric acid, lactic acid, tartaric acid. Increase in thermal decomposition temperatures might be related to the intermolecular interaction and coordinating nature of theions in mixtures (Chemat*et al*, 2016).

The highest thermal stability was measured at choline chloride: tartaric acid (197.84°C) which was similar to choline chloride: lactic acid (196.83°C).

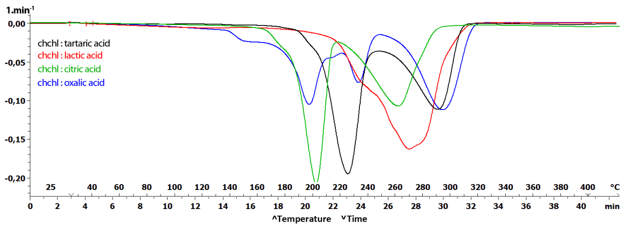

Fig.4 First derivative of TG curves of all prepared DESsin temperature interval 25 – 400°C

In work (Skulcova *et al*, 2016c)long-term isothermal stabilities of three deep eutectic solvents were analysed. It has been found out that the use of DES at a higher temperature has limitations. Based on the results it can be recommended to use DESs such as choline chloride with lactic and tartaric acid at temperatures below 80°C. In the temperature range 60-120°C it has been found out that ChCl:tartaric acid has the best thermal stability(Skulcova *et al*, 2016c).This result was also confirmed in this paper.

Table 3 Measured parameters during thermal and multi-step decomposition of DESs with formation of volatile reaction products

DES	Onset temperature [°C]	1st peak - rate of change of mass [°C]	2nd peak - rate of change of mass [°C]	3th peak - rate of change of mass [°C]
Citric acid: ChCl	154.49	193.00	254.78	-
Lactic acid: ChCl	196.83	-	272.97	-
Oxalic acid: ChCl	134.81	196.86	234.77	294.95
Tartaric acid: ChCl	197.84	226.52	292.04	-

CONCLUSION

Prepared binary deep eutectic solvents were studied in temperature range 25 – 400°C. Citric acid: choline chloride has from all measured DES the lowest temperature of degradation 154.49°C. For all studied DESs is important to know this property for the possibility of their targeted applications (stability during regeneration). As most thermal stabile DES from this paper we can considered choline chloride combination with tartaric acid (197.84°C) and lactic acid (196.83°C). These organic acids have in pure state temperature of thermal degradation determined for 228.61 and 155.46°C. Determined temperatures of thermal degradation of DESs can be useful in many of their possible applications.

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