Long-term isothermal stability of deep eutectic solvents based on choline chloride with malonic or lactic or tartaric acid

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Abstract— The increasing amount of papers published on ionic liquids generates an extensive quantity of data. Deep eutectic solvents (DESs) have recently been developed as a new and attractive alternative to traditional ionic liquids. The thermal stability of a deep eutectic solvent is an important parameter and limits the maximum operating temperature. The long-term thermogravimetric studies of DESs such as malonic, lactic and tartaric acid with choline chloride showed non-linear weight loss as a function of time at each temperature of 20 °C interval in the range 60–120 °C over a period of 10 hours.

Index Terms— deep eutectic solvents, long-term stability, stability, green solvents

1 Introduction

A new generation of interesting compounds that enter in recent years to focus on science and technology, derived from renewable sources are deep eutectic solvents as an attractive alternative to traditional ionic liquids. DESs are usually regarded as eutectic mixtures formed by mixing hydrogen bond donor (HBD) and hydrogen bond acceptor (HBA) [1]. Generally, DESs were eutectic mixtures of a quaternary ammonium salt and a metal salt or hydrogen bond donor such as glycerol and urea [2]. The excellent properties of DESs indicate their potential as promising green solvents for the extraction of phenolic compounds with favourable prospects for wide use in the field of green technology [3-9] or fractionation of biomass [10-15]. Thermal stability is a significant factor that determines the applicability of deep eutectic solvents for high-temperature applications. The thermal properties such as melting point, glass transition temperature, thermal decomposition temperature and molar heat capacity will be helpful in the setting of process operation conditions [16]. The thermal stability of ionic liquids is often determined by thermogravimetric analysis (TGA) in the nitrogen atmosphere and with a constant heating rate, typically 5 to 20 K / min [17-18]. The stable temperature limit of ionic liquids is not precisely defined by the onset decomposition temperature [19]. Studies on long-term stability are limited, and most investigations focus on conventional ionic liquids [20-22]. Lack of reliable long-term thermal stabilities of deep eutectic solvent leads to the current research. In the present study, three DESs were prepared by mixing malonic, lactic and tartaric acid as hydrogen bond donor (HBD) with choline chloride as a salt at a molar ratio 1:1. The thermogravimetric method was performed for each DES to compare the long-term isothermal stability.

2 Experimental

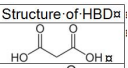
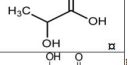
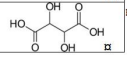
2.1 Deep eutectic solvents

Choline chloride (≥ 98% mass fraction purity) was purchased from SIGMA Life Science. Malonic, tartaric acid (all ≥ 99%) were purchased from RAECHIM and lactic acid (90% wt solution) from VWR CHEMICALS. Deep eutectic solvents such as choline chloride with malonic, lactic and tartaric acid were prepared according to the procedure reported elsewhere [11]. This method gave DES with 100% atom economy since it completely forms a eutectic mixture with no by-product formation. Choline chloride was dried in a vacuum oven prior to use to eliminate moisture contamination.

2.2 Thermal characterization

Thermogravimetric analysis (TGA) of DESs was carried out using Mettler Toledo TGA / DSC 1 instruments. The measurements were performed in the temperature interval of 25-400°C, using nitrogen at a flow rate of 50 mL / min by heating (10k / min). At the beginning, the sample was conditioned at 25°C for 3 min. After reaching 400°C, the measurement was concluded at 400°C for 3 min. The temperature of decomposition (Tdcp) was taken as the onset temperature at which 10% of the initial mass had been lost during the TGA scanning experiment.

TABLE 1
Compositions and Abbreviations of Prepared DESs

Abbreviation¤	DES¤	Molar·ratio¤	Structure·of·HBD¤
DES1¤	ChCl:·malonic·acid¤	1:1¤	
DES2¤	ChCl:·lactic·acid¤	1:1¤	
DES3¤	ChCl:·tartaric·acid¤	1:1¤	

2.3 Long-term thermal stability

Mettler Toledo TGA / DSC 1 instruments were used to perform thermogravimetric analysis of deep eutectic solvents. The analysis was performed in the reduction atmosphere (nitrogen). Isothermal thermogravimetry was performed at a constant temperature for 10 hours. Measurements were carried out at each temperature of 20°C interval in the range 60 – 120°C.

3 Results and Discussion

The thermogravimetric analysis is mostly usable method for studying thermal stability of ionic liquids, either in dynamic or isothermal mode [18], [20-25]. The authors as [18], [23-24] also underline that the strongly heating-rate dependent onset temperatures should not be used to evaluate the thermal stability and maximum operating temperatures of ionic liquids. However, the definition of stability and of the maximum operating temperature is still not quite clear [18].The representation of the thermogravimetric data and also the experimental conditions itself are important and unfortunately often only poorly documented [25]. The onset decomposition temperature determined for ionic liquids using the fast-scan TGA method is used to serve as the limiting value for their practical applications [19]. Decomposition temperatures are one the remarkable properties of deep eutectic solvents. The thermal stabilities of different DESs were quantified by the decomposition temperature (Tdcp), which denotes the temperature at which 10% of the initial mass had been lost during the TGA scanning experiment. As summarized in Table 2, different combinations of the choline salts with various H-bond donors exerted greater influence on Tdcp. Tmax, the maximum value on the derivative weight curve, is the temperature at which the degradation rate is fastest. The Tmax of solvents studied in this work is summarized in Tab. 2. In the case of DES2: ChCl:lactic acid it appears only one peak at 273.14°C and weight loss is 62.9%. The DES1: ChCl: malonic acid and DES3: ChCl: tartaric acid is present by two thermogram peaks.

TABLE 2
THERMAL PROPERTIES OF STUDIED DESS.

DES	T_{dcp} (°C)	T_{max} (°C)	Weight loss (%)
DES1: ChCl: malonic acid	126	151.94	27.32
		300.07	77.58
DES2: ChCl: lactic acid	212	273.14	62.90
DES3: ChCl: tartaric acid	194	226.52	35.38
		291.25	84.18

ChCl – choline chloride

From the industrial application point of view, DESs must endure certain temperature for a period of time. In that case, Tonset is no longer applicable for judging the thermal stability. Therefore, long-term thermal stability is needed, which is measured isothermally at different temperature interval [20]. Long-term thermogravimetric studies of DESs at different temperatures are shown in Fig. 1-3. The comparison of weight change of the deep eutectic solvents as a function of temperature after 10 hours of isothermal thermogravimetry is illustrated in Tab. 3. Weight loss increased gradually in the temperature range 60-120°C.The experimental results showed that the long-term thermal stability of deep eutectic solvents decreased with increasing temperature and was significantly lower than the onset temperature of decomposition of DESs. In addition, there is less weight loss when all the DESs were heated for 10 hours at 60°C, which indicates that this DES is stable under 60°C.The maximum applicable temperatures of these DESs depend on the duration of the applications and the tolerance to the changes of quantity and quality. Tolerable stability could be up to 80°C. At higher temperatures, mass loss of ionic liquids over time is not only caused by decomposition. According to work of Shirota et al. [26], the chain length of the ionic liquids seems to have no influence on their thermal stability. This result is also supported by data given by Götz et al. [27]. In our work, it is not possible to confirm this effect. Mass loss is also caused by evaporation [18] and [24].

Long-term stabilities of investigated DESs are summarized below (rank stability):
For 60°C, DES1:ChCl: malonic acid < DES2: ChCl: lactic acid < DES3: ChCl: tartaric acid
For 80°C, DES2: ChCl: lactic acid < DES1:ChCl: malonic acid < DES3: ChCl: tartaric acid
For 100°C, DES1:ChCl: malonic acid < DES2: ChCl: lactic acid < DES3: ChCl: tartaric acid
For 120°C, DES1:ChCl: malonic acid < DES2: ChCl: lactic acid < DES3: ChCl: tartaric acid

In the temperature range 60-120°C, the results show that DES3: ChCl: tartaric acid has the best thermal stability.

TABLE 3
THE WEIGHT OF LOSS OF THE DEEP EUTECTIC SOLVENTS AS A FUNCTION OF TEMPERATURE AFTER 10 HOURS

DES	60°C	80°C	100°C	120°C
	Weight of loss after 10 hours, (%)			
DES1: ChCl: malonic acid	5.98±0.82	6.44±0.33	37.67±1.5	35.48±0.93
DES2: ChCl: lactic acid	4.83±0.51	7.85±0.34	12.50±0.15	17.47±0.42
DES3: ChCl: tartaric acid	3.48±0.07	4.77±0.28	4.82±0.32	9.39±0.37

ChCl – choline chloride

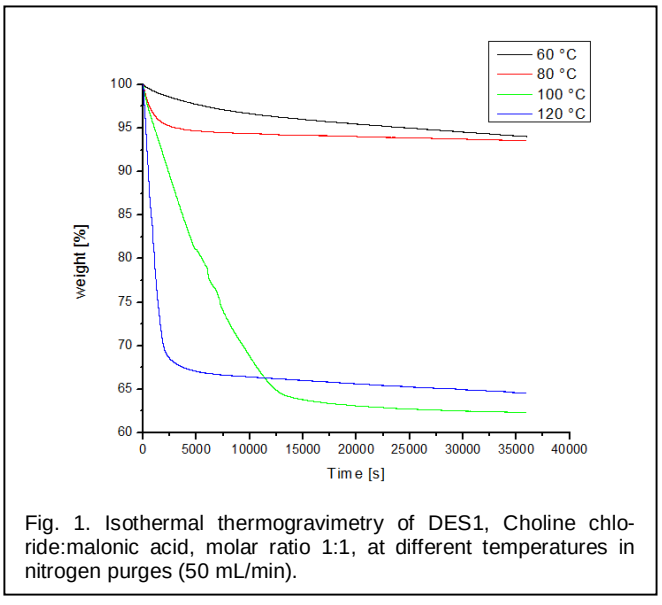


Fig. 1. Isothermal thermogravimetry of DES1, Choline chloride:malonic acid, molar ratio 1:1, at different temperatures in nitrogen purges (50 mL/min).

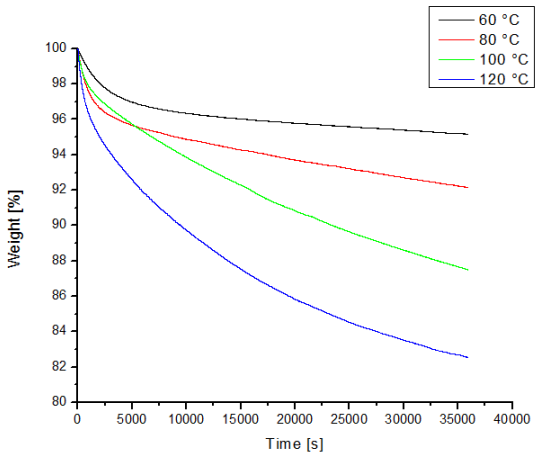


Fig. 2. Isothermal thermogravimetry of DES2, Choline chloride: lactic acid, molar ratio 1:1, at different temperatures in nitrogen purges (50 mL/min).

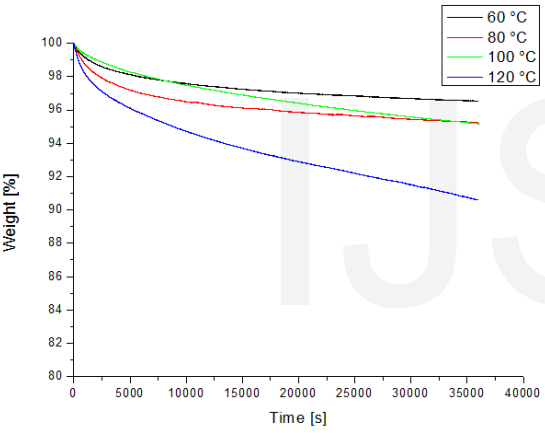


Fig. 3. Isothermal thermogravimetry of DES3, Choline chloride: tartaric acid, molar ratio 1:1, at different temperatures in nitrogen purges (50 mL/min).

4 Conclusion

In this thermal investigation, long-term isothermal stabilities of three deep eutectic solvents were analyzed. It has been found 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 malonic, lactic and tartaric acid at temperatures below 80°C. In the temperature range 60-120°C the results show that ChCl: tartaric acid has the best thermal stability.

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