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PROPERTIES AND THERMAL BEHAVIOR OF DEEP EUTECTIC SOLVENTS BASED LACTIC ACID

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Abstract

Deep eutectic solvents seem to be a very promising alternative to conventional organic solvents. Their wide range of applications helps to find new technology based on green aspects with high efficiency of recycling. In every application is very important to know: temperature behaviors, acidity, thermal stability, conductive properties and relationship to water. This paper discusses laboratory applications of deep eutectic solvents with promising future application in industry.

Investigated deep eutectic solvents are based on lactic acid - natural organic compound. Preparation of deep eutectic solvents comprises of mixing two compounds at 60 - 80 ^{0}C until homogenous liquid is made. Second compound in prepared deep eutectic solvents was amino acid such as alanine, glycine; and betaine, one of the B group vitamins; and choline chloride, food additive for farm animals. Prepared deep eutectic solvents were cooled down at room temperature and observed due to recrystallization. Studied deep eutectic solvents can be stable in liquid state at room temperature. Depending on their composition, thermal stability is changing. Thermal characterization was measured using Mettler Toledo TGA/DSC 1 Stare System, under the nitrogen atmosphere. The samples were heated at a constant heating rate of 10 °C/min from 30 - 400 °C. Viscosities were measured using rotational viscometer Brookfield DV 2+ and densities were measured pycnometrically. pH and conductivity values were determined using digital pH meter and conductivity meter from Hanna Instrument.

Results show that pH values vary from 1.66 to 2.54, conductivities vary between 0.12 and 1.33 mS/cm and density at ambient temperature vary from 1230.44 to 1168.30 kg/m3. Dynamic viscosities were changed with increasing temperature from 28 to 90 ^{0}C. Viscosity increased in the following order of hydrogen bond acceptor: glycine < choline chloride < alanine < betaine. Evaluation of thermal stability showed one or more degradation peaks for each sample.

These properties belong to important characteristic of any liquid. Based on results, we can suitably choose the solvent for further use such as: extraction of dyes, antioxidants or natural biopolymers, lignin, cellulose or sugars. Very similar deep eutectic solvents were used in our previous paper for bark and straw extraction.

***Key words**: Deep eutectic solvents, Thermal analysis, Physical properties, Lactic acid.*

1. Introduction

Nowadays, there is a wider public interest in renewables sources, materials, energy and more environmentally friendly industrial processes and applications. Plant biomass or lignocellulose is currently processed on wide range of materials, biofuels and chemicals, especially for the purpose of obtaining: pulp, paper, furniture, food supplements or fuel. By modernizing the current biorefineries new ecological processes can be applied, which would use "green" chemicals and had lower energy costs. Many scientific publications aim to optimize the processing of lignocellulosic biomass by introducing new technology based on deep eutectic solvents (DESs). Deep eutectic solvents are considered as "green" solvents due to their: biocompatibility, biodegradability, non-flammability, low toxicity and natural origin. They are composed of two or more compounds, which form hydrogen bonds between each other. Melting point of deep eutectic solvent is considerably lower than melting points of original compounds. Prepared DESs are usually liquid at ambient temperature

(23 ± 2 ^{0}C). Even the many publications, DESs are often compared with ionic liquids or even called a new generation of ionic liquids. DESs are an alternative to ionic liquid. Many of DESs have advantages against ionic liquids which are flammable, toxic, synthesized from fossil sources and really expensive [1]. The use of DESs in the lignocellulosic industry opens to door new ecological and breakthrough processes.

DESs have different properties depending on the initial compounds from which are prepared. Usually, following properties are examined: melting point, thermal stability, pH, viscosity, density, conductivity, surface tension, refractive index and effect of water. This paper has been dealt with DESs based on lactic acid as hydrogen bond donor. Lactic acid is natural non-toxic acid. It can be biodegradable and can be use in liquid form what facilitates the preparation of the DES. DESs also obtained as hydrogen bond acceptor alanine, glycine, betaine and choline chloride. Betaine and choline chloride belong to B vitamin group and choline chloride is often used as food additive for farm animals. Prepared DESs were characterized (density, viscosity, pH, thermal stability and refractive index) and discussed due to their possibility of application in plant biomass industry.

2. Materials and Methods

All chemicals were purchased from Sigma Aldrich s.r.o.: choline chloride (≥ 98%), lactic acid (90 %), betaine (≥ 98%), glycine (≥ 99%), and alanine (≥ 99%). DESs were prepared by mixing two initial compounds (Table 1) at 60 - 80 ^{0}C until homogenous liquid was made.

Thermal characterization was measured using Mettler Toledo TGA/DSC 1 Stare System, under the nitrogen atmosphere. The samples were heated from 30 to 400 ^{0}C. Viscosities were measured using rotational viscometer Brookfield DV 2+ and densities were measured pycnometrically. pH and conductivity values were determined using digital pH meter and conductivity meter from Hanna Instrument. Refractive index was measured using digital refractometer KERN ORD 92 HM.

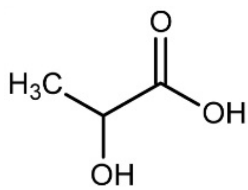
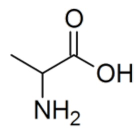
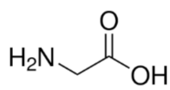
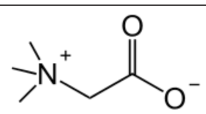
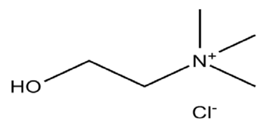
3. Results and Discussion

Novel DESs based on: lactic acid and choline chloride, alanine, glycine and betaine were synthetized. Hydrogen bond acceptor has an influence on physical properties.

The viscosity is a parameter influencing the hydrodynamic processes in all applications of deep eutectic solvents. Low viscosity makes solvents easy to handle more applicable and helps to decrease energy costs [2]. The general trend is decreasing viscosity with increasing temperature. The change of viscosity with increasing temperature can be described with Arrhenius or Vogel-Fulcher-Tammann model [3]. The viscosities of tested DESs were fitted using Arrhenius model (Table 2). Hydrogen bonding plays a large role in the viscosity of the ionic systems. The strength of van der Waals interactions and tendency to form hydrogen bonds are the major factors which contribute to the viscosity of an ionic liquid [4].

For every DES η_0, E_η and R are viscosity constant, the activation energy and the gas constant.

Table 1. Prepared deep eutectic solvents, molar ratios of lactic acid and hydrogen bond acceptors and their structures

Hydrogen bond donor	Hydrogen bond acceptor	Molar ratio	Structure of HBD	Structure of HBA
Lactic acid	Alanine	9:1		
	Glycine	9:1		
	Betaine	2:1		
	Choline chloride	9:1		 choline chloride

Legend: HBA - hydrogen bond donor.
HBD - hydrogen bond acceptor.

Table 2. Viscosity - temperature model parameters from equation $\eta = \eta_0 \times \exp(E_\eta/(R \times T))$

DES	$\eta_0 \times 10^6$ (mPas)	E_η/R (K^{-1})	Adj. R^2
Lactic acid: alanine	6.103	5133.21	0.9932
Lactic acid: glycine	95.174	3924.80	0.9933
Lactic acid: betaine	4.853	5613.28	0.9940
Lactic acid: choline chloride	53.503	4219.71	0.9892

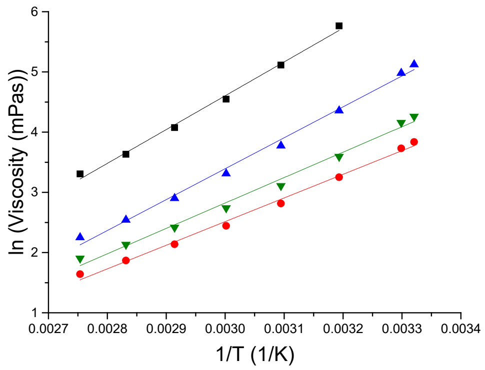


Figure 1. Arrhenius plot of the natural logarithm of viscosity of the four DESs as a function of reciprocal temperature (▲lactic acid: alanine, ●lactic acid: glycine, ■lactic acid: betaine, ▼lactic acid: choline chloride)

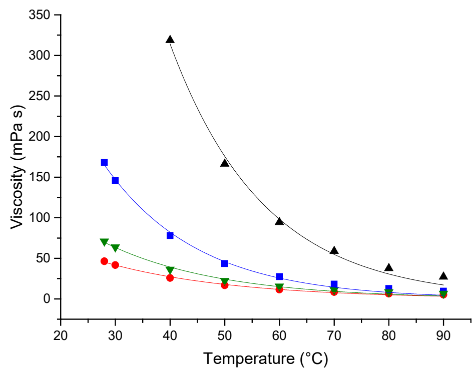


Figure 2. Dependence of viscosity of the four DESs as a function of temperature (■lactic acid: betaine, ▲lactic acid: alanine, ▼lactic acid: choline chloride, ●lactic acid: glycine)

It has been observed, that natural logarithm of viscosity vary from 1.90 to 5.76. DES lactic acid: betaine had significantly higher viscosity than others measured DES. Lactic acid: betaine DES was measured from 40 to 90 ^{0}C because there was a problem with high viscosity and rotating viscometer at lower temperatures. DESs contained alanine, glycine and choline chloride were measured from 28 to 90 ^{0}C. Dynamic viscosity decreases with increasing temperature. Viscosities of DESs increase in following order of hydrogen bond acceptor: glycine < choline chloride < alanine < betaine. It is possible, that this trend is caused by molar mass of hydrogen bond acceptors. Molar mass of hydrogen bond acceptors increase in following order: glycine < alanine < betaine < choline chloride. Choline chloride has a similar chemical structure as aminoacids, but COO^- group is replaced by OH^- group. There is a hypothesis that this group has an effect on viscosity due to hydrogen bonds between compounds.

The viscosity of these systems shows a decrease exponentially as the temperature is increased due to increased kinetic energy (Figure 2).

All measured DESs possess densities higher than water. In general, temperature dependent has a linear character with decreasing tendency. The molecules are moving at higher speed at increasing temperature, so the molar volume of solvent increases [3]. The correlation with temperature was expressed by linear equation (Table 3). Parameters a and b expressed intercept and slope. Negative slopes confirm decreasing density and correlation was very good for every measured DES. As has been described previously part, as the viscosity of the system decreases, the density of the system decreases as well.

Densities of examined solvents vary from 1127 to 1230 kg/m^3 (Figure 3). Results correspond with previous work Lynam *et al.*, [5]. This work studied DESs based on formic acid: choline chloride, lactic acid: choline chloride, acetic acid: choline chloride, lactic acid: betaine and lactic acid: proline at 24 and 155 ^{0}C. DES lactic acid: choline chloride (10 : 1) showed density 1190 kg/m^3 at 24 ^{0}C [5], while DES lactic acid: choline chloride (9 : 1) (measured in this work) showed density 1217 kg/m^3 at the same temperature. These results are very similar and it looks like the small change in hydrogen bond acceptor amount has no significant effect on the density. DES lactic acid: betaine showed density at 24 ^{0}C 1200 kg/m^3 [5], and 1195 kg/m^3 (this work). This fact proved, that DESs are not sensitive on preparation and on the origin of chemicals.

pH is one of the physical property that is important in many industrial applications to ensure acidity property of medium. Table 4 shows pH values from linear regression. pH values decreased with increasing temperature (Figure 4).

All DESs showed very low pH, between 0.79 and 2.45. In industry application is important to ensure pH with minimal corrosion effect. Low pH (approximately 1 - 2) is good for fractionation, because acidic medium helps in acidic hydrolysis process.

Table 3. Density - temperature model parameters from equation ρ = a + b×T

DES	a (kg/m³)	b× 10² (⁰C⁻¹)	Adj. R²
Lactic acid: alanine	1249.64	-79.57	0.9954
Lactic acid: glycine	1186.15	-79.18	0.9967
Lactic acid: betaine	1210.56	-63.89	0.9985
Lactic acid: choline chloride	1236.05	-75.21	0.9990

Table 4. pH - temperature model parameters from equation pH = a + b×T

DES	a	b × 10³ (⁰C⁻¹)	Adj. R²
Lactic acid: alanine	2.68	-20.77	0.9937
Lactic acid: glycine	2.80	-20.92	0.9890
Lactic acid: betaine	2.87	-17.35	0.9234
Lactic acid: choline chloride	2.18	-22.58	0.9897

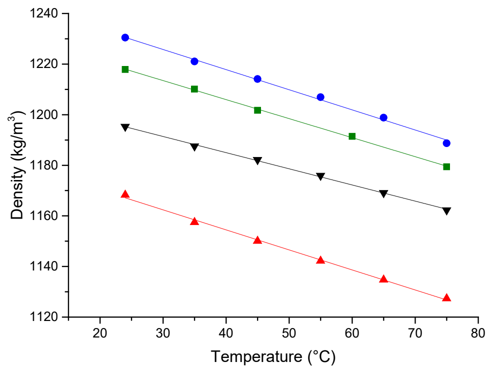


Figure 3. Temperature dependent densities of the four DESs (▲lactic acid: alanine, ●lactic acid: glycine, ■lactic acid: betaine, ▼lactic acid: choline chloride)

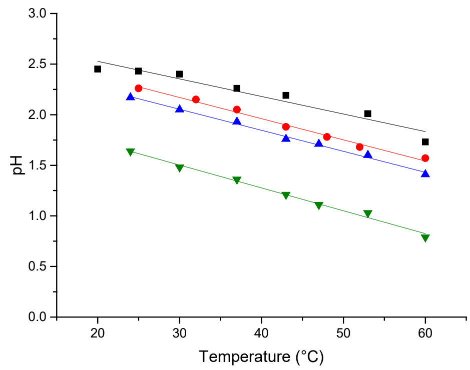


Figure 4. Temperature dependent densities of the four DESs (▲lactic acid: alanine, ●lactic acid: glycine, ■lactic acid: betaine, ▼lactic acid: choline chloride)

Refractive index is material property that expresses how the light propagates through the medium. It is property that helps to check the purity of materials [6]. For transparent liquids refractive index is between 1 - 2. At room temperature (23 ± 2 ⁰C), refractive indices for studied DESs were 1.4397, 1.4422, 1.4432 and 1.4620. The measured values of refractive indices differ on the second decimal place (Table 5).

Table 5. Refractive index of measured DESs

DES	Refractive index
Lactic acid: alanine	1.4397
Lactic acid: glycine	1.4422
Lactic acid: betaine	1.4620
Lactic acid: choline chloride	1.4432

A more detailed characterization of DESs is thermogravimetric analysis. The thermal properties of DESs were also presented in previous works [5, 7, 8, 9, and 10]. It is important to know degradation temperature of DESs or upper limit of their usability. The behavior of prepared DES by mixing chemicals that contained water was described. The aim was to monitor the behavior of these systems during thermal stress. These systems contained water are directly used for extraction or fractionation of biomass. In work [11] was determined T_{dcp}, i.e. the temperature at which 10% of mass was removed.

Three DESs present a single degradation peak in temperature range 30 - 400 ⁰C, one DES presents two peaks. Thermal stability is a significant factor in the usefulness of DESs. The influence of elevated tempera-

Table 6. Thermal properties for four measured DESs

DES	T_{dcp} (⁰C)	T_{max} (⁰C)	Mass decrease at T_{max} (%)
Lactic acid: alanine	157.52	200.56	22.35
		303.25	78.28
Lactic acid: glycine	124.59	189.53	38.43
Lactic acid: betaine	193.57	261.57	62.20
Lactic acid: choline chloride	130.02	261.65	70.11

Legend: T_{dcp} – decomposition temperature determined at 10 % mass decrease.
T_{max} – temperature at which the rate of sample lost was maximal.

ture was observed in weight changes of DESs. From Table 6 is clear that investigated DESs are stable to the 193.57 ^{0}C. If we compare thermal behavior of DESs based on decomposition temperature, the most stable DES was lactic acid: betaine and the least stable DES was lactic acid: glycine. Lactic acid is normally unstable at temperature above 122 ^{0}C, but hydrogen bonds ensure stability and prevent the formation of lactide. This information suggests that application of DESs up to temperature 124.59 ^{0}C for glycine based DES, 157.52 ^{0}C for alanine based DES, 193.57 ^{0}C for betaine based DES and 130.02 ^{0}C for choline chloride based DES should be possible.

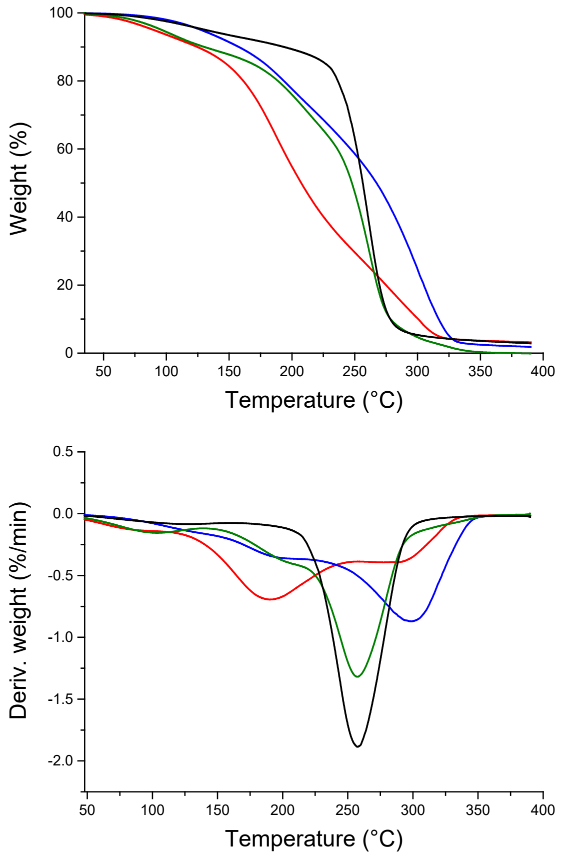


Figure 5. Thermogravimetric analysis of the four DESs (▲lactic acid: alanine, ●lactic acid: glycine, ■lactic acid: betaine, ▼lactic acid: choline chloride)

Thermogravimetric analysis indicates that studied DESs are stable at typical lignocellulosic processing temperatures. DESs unlike conventional organic solvents, offer many advantages, so they can be a promising alternative in modern biorefinery. Since 2009, the use of DESs in the lignocellulosic industry has been actively investigated [12]. They were used as catalyst [13], solvent for organic syntheses [14], separation agent [15, 16], reaction medium, extracting agent [17, 18, 19, and 20], solvent [21]. Valorization of lignocellulosic materials using eco-solvents is a key factor for economic processes on the field of chemistry industry.

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4. Conclusions

- Lactic acid based DESs has been prepared and tested. The physical properties including viscosity, density, pH, refractive index and thermal stability were measured and reported. It was found that physical properties depend on structure of hydrogen bond acceptor.

- Results proved, that DESs have higher viscosity than water or conventional organic solvents, so they must be used at higher temperature.

- Thermogravimetric analysis showed, that they are stable up to 124.59 °C (lactic acid: glycine (9:1)), 130.02 °C (lactic acid: choline chloride (9:1)), 157.52 °C (lactic acid: alanine (9:1)) and 193.57 °C (lactic acid: betaine (2:1)).

- The pH of studied DES was lower than 2.5, so they are acid due to the lactic acid contained in DES. Refractive index values were in the range 1.4397 – 1.4620.

- Most of studied DESs properties were fitted linearly as a function of temperature, or according to Arrhenius model (viscosity). Results from this study will be used for next processes based on extraction or fractionation of lignocellulosic materials or for the development of DES applications in biorefinery concept.

5. References

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