The pH Behavior of Seventeen Deep Eutectic Solvents

Andrea Skulcova,[a,]* Albert Russ,[b] Michal Jablonsky,[a] and Jozef Sima [c]

Deep eutectic solvents (DESs) are a unique category of green solvents that have gained attention in biomass processing due to their distinctive properties not offered by traditional solvents. The pH behavior of 17 selected DESs along with their temperature dependence on pH were evaluated in this study. For all investigated DESs, a temperature increase caused a decrease in pH value.

Keywords: Deep eutectic solvents; pH; Properties; Choline chloride

Contact information: a: Slovak University of Technology in Bratislava, Faculty of Chemical and Food Technology, Institute of Natural and Synthetic Polymers, Department of Wood, Pulp and Paper; b: Radlinského 9, Bratislava, 812 37, Slovak Republic; b: Pulp and Paper Research Institute, Dúbravská cesta 14, Bratislava, 84104, Slovak republic; c: Institute of Inorganic Chemistry, Technology and Materials, Department of Inorganic Chemistry, Radlinského 9, Bratislava, 812 37, Slovak Republic;
** Corresponding author: andrea.skulcova@stuba.sk*

INTRODUCTION

Deep eutectic solvents (DESs) are a specific category of solvents that are defined as a mixture of a hydrogen bond donor and hydrogen bond acceptor. Interaction of these two substances results in a liquid (at 23 ± 2 °C) with significantly different properties than those of their constituents. The main characteristic of a DES is its melting point, which is usually lower than each of its components. Thus in many cases, a DES is typically a viscous liquid at 23 ± 2 °C, whereas its components are crystalline solids. Most DESs are liquids under 70 °C, and some remain liquid at ambient temperature (Zhang *et al.* 2012). DESs do not degrade in water, and they are biodegradable and non-toxic, compared with other groups of ionic liquids. Their preparation is also relatively easy and less expensive (Francisco *et al.* 2013). Unlike traditional ionic liquids, DESs are easy to prepare in a pure form (Popescu *et al.* 2014). The DESs are also referred to as green solvents because of their negligible vapour pressure, non-flammability, non-explosiveness, low toxicity, and electrochemical as well as thermal stabilities. Chemical and thermal stabilities are necessary during chemical processes such as extraction or hydrolysis.

DESs and other ionic liquids tend to be more viscous than molecular liquids, for example, common organic solvents and water. An extensive hydrogen bonding network as well as van der Waals interactions result in high viscosity of DESs and, in turn, in lower mobility of free species in such media (Fischer 2015). Viscosity is a key characteristic of DESs when they are primarily used for mixing and dissolving various compounds such as cellulose from lignocellulosic material on a potentially industrial scale. In practice, viscosity has influence on transporting, mixing, extraction, removal, and/or recycling of DESs. DESs exhibit higher densities than water and common organic solvents. They are comparable to ionic liquids and normally range between 1.1 to 2.4 g.cm^{-3} (Zhang *et al.* 2012).

Because of their favourable properties, DESs are used in many industrial applications as an alternative to conventional organic solvents. DESs have been introduced in many sectors and applications, such as extraction (Bi *et al.* 2013; Dai *et al.* 2013a; Gu *et al.* 2014; Nam *et al.* 2015; Tang *et al.* 2015), fractionation (de Dio 2013; Jablonský *et al.* 2015; Kumar *et al.* 2016a; Škulcová *et al.* 2016a), catalysis (Hu *et al.* 2009), preparation of biofuels (Shahbaz *et al.* 2011; Fang *et al.* 2012), and separation of azeotropic mixtures (Oliveira *et al.* 2013). DESs have been used for solubilizing biopolymers from lignocellulosic biomass (Jablonský *et al.* 2015; Loow *et al.* 2018). Two recent reviews focused on DESs usage in the chemical industry (Škulcová *et al*. 2016b) and biomass conversion (Loow *et al.* 2017). For every application, it is very important to identify the relevant properties of available solvent.

The pH is an important physical property and it has essential impact on chemical reactions. The pH effect is important for DESs applications in catalysis, biochemical reactions, or in metal treatment. Hayyan *et al.* (2012) studied various types of DESs based on fructose and choline chloride in different molar ratios. The results showed that with the decreasing of hydrogen bond donor content, the pH value was decreased. However, a higher content of fructose in the mixtures leads to a higher acidity. In addition, pH values decreased with increasing temperature as follows: fructose:choline chloride in molar ratio 1:1 and 2:1 substantially, and fructose:choline chloride in molar ratio 1.5:1 and 2.5:1 slightly. Every combination of molar ratios shows a negative slope as the pH decreased with increasing temperature in intervals of 25 to 85 °C from 6.1 to 4.4 (molar ratio 1:1), from 6.8 to 6.3 (molar ratio 1.5:1), from 6.6 to 4.9 (molar ratio 2:1), and from 7.1 to 6.5 (molar ratio 2.5:1) (Hayyan *et al.* 2012). The obtained pH values were fitted linearly, and the parameters are summarized in Table 1. Kareem *et al.* (2010) supported conclusions of Hayyan *et al.* (2012) concerning the temperature dependence on pH evolution of DESs. The DESs from their study were based on triphenylphosphonium salt derivatives such as methyltriphenylphosphonium bromide ($(CH_3)Ph_3PBr$) and benzyltriphenylphosphonium chloride ($(PhCH_2)Ph_3PCl$). These results showed that the pH in some cases (*e.g.*, $(PhCH_2)Ph_3PCl$:glycerol) slightly increased with increasing temperature or it became significantly increased with increasing temperature (*e.g.*, $(CH_3)Ph_3PBr$:2,2,2-trifluoracetamide). The two DESs $(CH_3)Ph_3PBr$:glycerol and $(CH_3)Ph_3PBr$:ethylene glycol showed decreased pH with increasing of temperature. The pH values of DES based on $(PhCH_2)Ph_3PCl$:ethylene glycol appear to be stable within the temperature range 5 °C to 95 °C. It was found that the type of hydrogen bond donor used has a significant influence on the pH. The results are summarized in Table 1. Hayyan *et al.* (2013) studied pH values as function of temperature for the DESs based on choline chloride and glucose, and found that pH varied from 6.03 to 7.11. All DESs studied had pH around 7, which indicates neutral mixtures. Table 1 summarizes molar ratios of prepared DESs and model parameters after linear fitting (Hayyan *et al.* 2013). From the measured data, it is clear that the nature of the hydrogen bond donor has an impact on acidity generated – glucose based DESs are less acidic than fructose based DESs in combination with choline chloride.

Naser *et al.* (2013) have published that the pH values of DESs based on potassium carbonate and glycerol varied, along with the content of potassium carbonate, and also with temperature in the range of 11.5 to 13.5. The DESs studied were basic, which makes them suitable for application as basic medium. Generally, the acidity and basicity of DESs were governed by the acidity/basicity constants of donor and acceptor materials used and their combination. This fact was demonstrated also by Kareem *et al.* (2013). The type of hydrogen bond donor had a strong effect on determining the acidity of DES (Kareem *et al.* 2013).

Table 1. pH-Temperature Model Parameters and Equations for Some DESs

DES	Molar Ratio	Equation	a	b	Reference
ChCl: D-fructose	1:1	pH = *a* + *b*×*T* *T* <25, 85> °C	6.9568	–0.0309	Hayyan *et al.* (2012)
	1.5:1		7.1757	–0.0100	
	2:1		7.5120	–0.0306	
	2.5:1		7.3893	–0.0116	
ChCl: D-glucose	1:1	pH = *a* + *b*×*T* *T* <298.15, 358.15> K	9.994	–106.1	Hayyan *et al.* (2013)
	1.5:1		13.120	–201.8	
	2:1		9.957	–99.3	
	2.5:1		10.560	–115.7	
$(CH_3)Ph_3PBr$: glycerol	1:1.75	pH = *a* + *b*×*T* *T* <5, 95> °C	7.0887	$–49 \times 10^4$	Kareem *et al.* (2010)
$(CH_3)Ph_3PBr$:ethylene glycol	1:4		6.5710	$–89 \times 10^4$	
$(CH_3)Ph_3PBr$:2,2,2-trifluor-acetamide	1:8		2.4267	114×10^4	
$(PhCH_2)Ph_3PCl$: glycerol	1:5		6.8470	22×10^4	
$(PhCH_2)Ph_3PCl$:ethylene glycol	1:3		5.7630	$–22 \times 10^4$	

ChCl, choline chloride; $(CH_3)Ph_3PBr$, methyltriphenylphosphonium bromide; $PhCH_2)Ph_3PCl$, benzyltriphenylphosphonium chloride

DESs are used in practice diluted with a small amount of water (Dai *et al.* 2013b; Kumar *et al.* 2016a; Florindo *et al.* 2017). This is because of the influence of water on hydrogen bondings and thereby on the physical properties of DESs. Osch *et al.* (2015) examined NMR spectra of pure DESs and water-diluted DESs. It was found that the NMR spectra of both systems were nearly identical. It was thus established that water had no substantial effect on DESs behaviour from the viewpoint of their eutectic nature (Sheldon 2016; Zhekenov *et al.* 2017)

In the present study, the focus is on the pH of the selected water-diluted DESs based on organic acids, amino acids, alcohols, or ammonium salts. The purpose of this study was to determine the pH dependence on temperature and to compare these results with previous works.

The DESs prepared in this study are potentially usable for biomass fractionation. In this case it is really important to set suitable temperature and acidity conditions in order to preserve the valuable biomass-component properties.

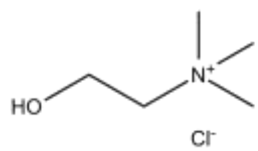
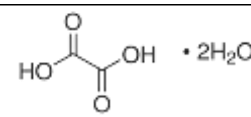
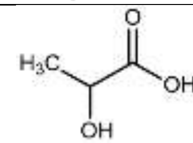
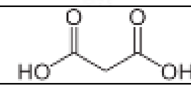
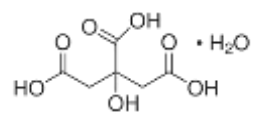
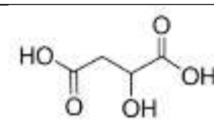
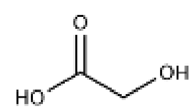
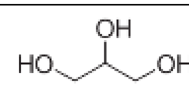
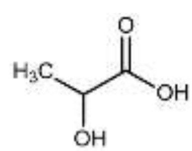
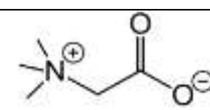
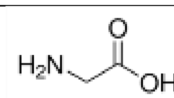
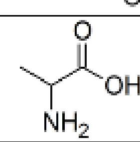
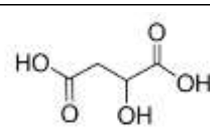
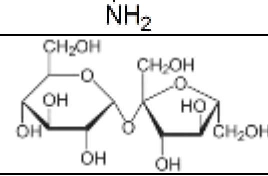
EXPERIMENTAL

Materials

The DESs samples were prepared at various molar ratios as given in Table 2, within the temperature range of 60 °C to 80 °C in order to minimize operating costs. Due to its hygroscopic nature, choline chloride was dried under vacuum before treating. The DESs were stirred thoroughly until it becomes a homogenous liquid. The stirring speed was 60 rpm.

Glycerol (86%) was obtained from Penta s.r.o., Praha, Czech Republic. All other chemicals were purchased from Sigma Aldrich (Bratislava, Slovakia): choline chloride (≥ 98%), lactic acid (90%), malonic acid (99%), malic acid (≥ 99%), glycolic acid (99%), oxalic acid × $2H_2O$ (≥ 99%), citric acid × H_2O (≥ 99%), ethylene glycol (≥ 99%), betaine (≥ 98%), glycine (≥ 99%), alanine (≥ 99%), and sucrose (≥ 99%).

Table 2. Compositions and Structures of Prepared Deep Eutectic Solvents

DES Reagents	Molar Ratio	Structures	
Choline chloride: Ethylene glycol	1:2		
Choline chloride: Oxalic acid × $2H_2O$	1:1		
Choline chloride: Lactic acid	1:5		
	1:9		
	1:10		
Choline chloride: Malonic acid	1:1		
Choline chloride: Citric acid × H_2O	1:1		
	2:1		
Choline chloride: Malic acid	1:1		
	2:1		
Choline chloride: Glycolic acid	1:3		
Choline chloride: Glycerol	1:2		
Lactic acid: Betaine	2:1		
Lactic acid: Glycine	2:1		
	9:1		
Lactic acid: Alanine	9:1		
Malic acid: Sucrose	1:1		

Methods

For pH measurements, the DESs concentration used was 0.5 mol/L. The DESs samples were weighed and dissolved in a corresponding volume of deionized water. The freshly prepared solutions were kept at 23 ± 2 °C for a period of 30 min. After pH was measured at this temperature, each solution was placed in a water bath and heated gradually up to 60 °C. The pH was determined using digital pH meter from Hanna Instruments® (Bratislava, Slovakia).

RESULTS AND DISCUSSION

The DESs were prepared using varying amounts of hydrogen-bond donors with a fixed hydrogen-bond acceptor – choline chloride. Three DESs were prepared based on lactic acid with amino acids – glycine, alanine, and betaine. One DES was prepared by mixing malic acid and sucrose. The pH values decreased steadily with increasing temperature for of all DESs. Graphical evaluation of the dependence of pH on temperature is shown in Fig. 1, and the data were fitted by linear regression.

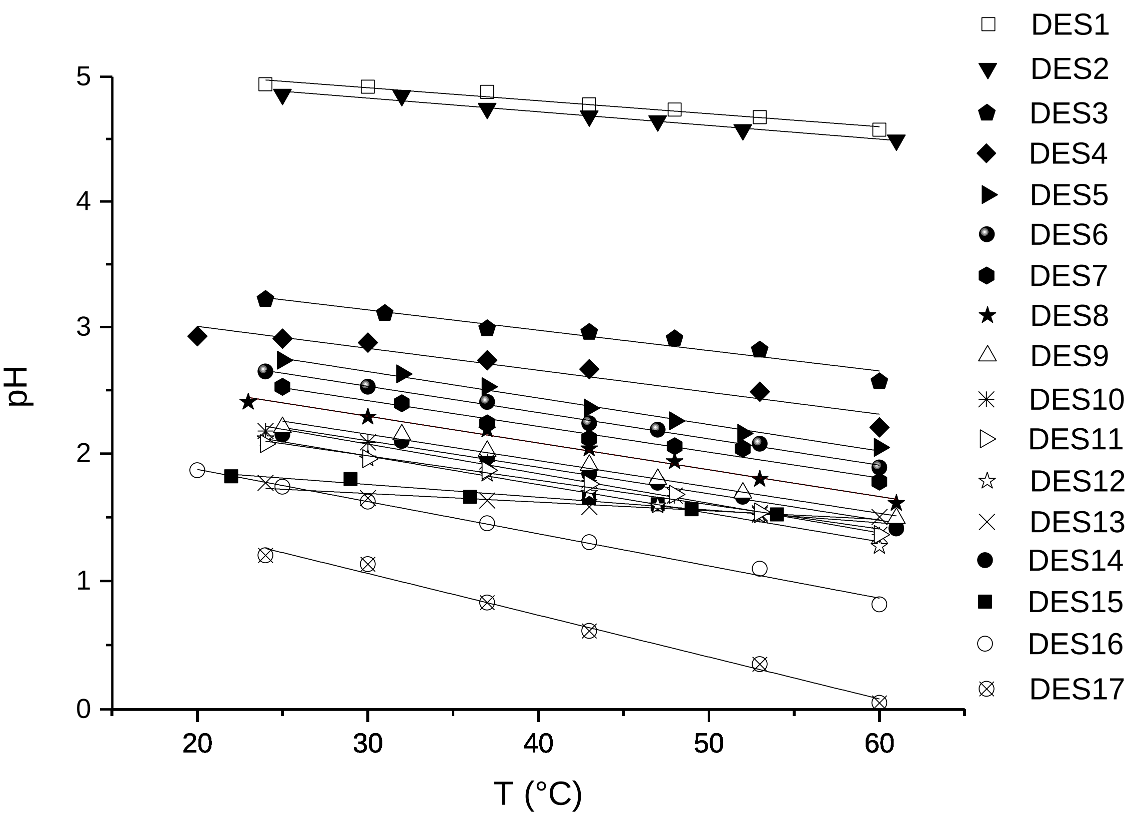


Fig. 1. Dependence of DESs pH on temperature

Aqueous solutions of DESs prepared from choline chloride:glycerol (1:2) and choline chloride:ethylene glycol (1:2) showed the highest pH values of approximately between 4.40 to 4.00, and 4.36 to 4.08 of all the measured DESs solutions. These values are probably caused by the presence of alcohol in DESs structures. Ethylene glycol and glycerol have acidic hydrogens in their structures and, therefore the pH is lower than 7 for these compounds. Figure 1 indicated a larger difference between the pH values of the DESs, which contained ethylene glycol or glycerol. Alcohol based DESs form a separate group. The pH values of alcohol based DESs were decreased slowly with increasing temperature.

The second group comprised DESs based on organic acid. Acid in the DES structure has its impact on pH ranging from 1.2 to 2.74 at ambient temperature (23 ± 2 °C) and from 0.05 to 2.09 at 60 °C. The pH values of DESs based on oxalic acid and malonic acid decreased steeply with increasing temperature as documented by Fig. 1. This study of pH behaviors proved that hydrogen-bond donor has a strong effect on the resultant pH. Nature of hydrogen bond donor dictates the acidity of mixture obtained.

Table 3. pH-Temperature Model Parameters for Studied DESs

	DES Type	Molar ratio	a	b (°C^{-1})	R^2	T (°C)
DES1	ChCl: Glycerol	1:2	4.721	–0.010	0.960	25 – 60
DES2	ChCl: Ethylene glycol	1:2	4.656	–0.011	0.972	25 – 60
DES3	Lactic acid: Glycine	2:1	3.140	–0.016	0.925	24 – 60
DES4	Betaine: Lactic acid	1:2	2.874	–0.017	0.923	20 – 60
DES5	Lactic acid: Glycin	9:1	2.798	–0.021	0.989	25 – 60
DES6	Lactic acid: Alanine	9:1	2.676	–0.021	0.994	24 – 60
DES7	Malic acid: Sucrose*	1:1	2.551	–0.020	0.972	25 – 60
DES8	ChCl: Malic acid	1:1	2.083	–0.019	0.980	24 – 60
DES9	ChCl: Lactic acid	1:10	2.299	–0.021	0.985	25 – 60
DES10	ChCl: Citric acid[a]	1:1	2.299	–0.023	0.992	24 – 60
DES11	ChCl: Malic acid	2:1	2.452	–0.021	0.988	23 – 61
DES12	Lactic acid: ChCl	9:1	2.180	–0.023	0.990	24 – 60
DES13	ChCl: Glycolic acid	1:3	1.410	–0.007	0.897	23 – 61
DES14	ChCl: Lactic acid	1:5	2.252	–0.021	0.977	25 – 61
DES15	ChCl: Citric acid[a]	2:1	1.580	–0.010	0.965	22 – 61
DES16	ChCl: Malonic acid	1:1	1.905	–0.025	0.992	20 – 60
DES17	ChCl: Oxalic acid[b]	1:1	2.037	–0.033	0.990	23 – 60

Note: The concentration of DES was 0.5 mol/L. The fundamental equation for the general linear model was pH = $a + b \times T$ (°C). ChCl, choline chloride. *10 wt.% of water; [a] monohydrate; [b] dihydrate

The negative values of slope (b) reflect the rate of pH decrease with increasing temperature. The highest rate of pH decrease was associated with 1:1 choline chloride:oxalic acid mixture with a value of -0.033, whereas most rates of pH decrease were found to range between −0.025 and −0.007. The DES choline chloride:citric acid (2:1) is the least temperature dependent DES with the rate of pH decrease only −0.010. The average slope was calculated as −0.019. It should be pointed out that the above-mentioned rates differ from that calculated for pure water (a = 7.32382, b = −0.01344) which supports the idea that DESs preserve their individual characters in aqueous solutions.

Biomass pretreatment at pH < 7 using hydrochloric acid or sulfuric acid often results in solubilisation of the hemicellulose fraction (Hendriks and Zeeman 2009). In contrast, Kumar *et al.* (2016b) showed that DESs-pretreatment at low pH value (≤ 2) had no severe effect on hemicellulose solubility. These authors categorized green solvents into two groups: acidic (pH values from 2.0 to 3.0) and neutral (pH values from 6.0 to 7.0). The DESs investigated in this work could also be classified into two groups: acidic (pH range

0 to 3.0) and slightly acidic (pH range 4.0 to 4.5). The DESs in the former group contained an acid; the latter DESs group contained an alcohol as hydrogen bond donor. Lignin extracted from acidic DESs showed only one maximum of absorbance at 280 nm in its UV-Visible absorption spectrum, while with neutral DESs an additional peak around 305 to 315 nm was observed. These results indicated that pH value has a significant effect on the extracted lignin composition and properties, which should be taken into account at biomass treatment using DESs. According to the Vivekanand *et al.* (2014), p-coumaryl alcohol has a characteristic absorption maximum at 280 nm and branched chain aromatic ring structure components such as coniferyl alcohol and sinapyl alcohol absorbs at higher wavelengths around 300 to 315 nm. Therefore it is shown that acidity may affect the extraction of various structures of lignin compounds.

The pH plays the following role in biomass pretreatment: pH < 7 values result in hydrolysis of the hemicelluloses to monomeric sugars and minimize the need for hemicellulases. The neutral conditions (pH ~ 7) lead to solubilisation of most of hemicelluloses but do not usually result in total conversion into monomeric sugars, and hence hemicellulases are required. In alkaline pH, part of hemicelluloses are in solid fraction, and hemicellulases are needed for both solid and dissolved fraction of hemicelluloses (Galbe 2011). Trajano and Wyman (2013) have shown that the advantage of low pH reactions lies in the ability to achieve high product yields. On the contrary, the capital costs of reactors and equipment are high due to the need for expensive corrosion resistant materials. In addition, the pretreated biomass often requires washing or neutralization. DESs are specific mixtures, because some metal oxides are soluble in them. Therefore, it is recommended to work with non-metal equipment and hence the problem with corrosion becomes irrelevant. Very low pH facilitates the solubilisation of cellulose similarly as high temperature and extended time of pretreatment (Trajano and Wyman 2013).

The possibilities of application investigated DESs were studied in the papers of Majová *et al.* (2017) and Škulcová *et al.* (2017). Majová *et al.* (2017) used DESs based on choline chloride: glycerol (1:2), betaine lactic: acid (1:2), lactic acid: alanine (9:1), choline chloride: malic acid (1:1), choline chloride: lactic acid (1:10, 1:9, 1:5), choline chloride: glycolic acid (1:3), choline chloride: malonic acid (1:1), and choline chloride: oxalic acid dihydrate (1:1). The dissolution of cellulose and delignification of pulps with different lignin contents were studied for all prepared DESs.

CONCLUSIONS

1. Aqueous solutions of the selected DESs showed pH 2.74 or less with two exceptions: choline chloride: ethylene glycol (1:2) and choline chloride:glycerol (1:2), where the pH varied between 4 to 4.44.
2. The DESs examined in this study were acidic with slight increasing acidity with increasing temperature.
3. The average values of slope with increased temperature was about −0.019 which corresponded to average pH decrease by 0.69 parting from 20 °C to 60 °C.

4. These facts make DESs suitable for some applications than which involve acidic media, for chemical, biological, and environmental applications or as solvents in extraction processes.

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