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Novel “acid tuned” deep eutectic solvents based on protonated L-proline

Patrycja Janicka [a], Andrzej Przyjazny [b], Grzegorz Boczkaj [a,c,*]

[a] Gdansk University of Technology, Faculty of Chemistry, Department of Process Engineering and Chemical Technology, 80 – 233 Gdansk, G. Narutowicza St. 11/12, Poland
[b] Kettering University, 1700 University Avenue, Flint, MI 48504, USA
[c] EkoTech Center, Gdansk University of Technology, G. Narutowicza St. 11/12, 80-233 Gdansk, Poland

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The paper presents new types of deep eutectic solvents (DESs) based on L-proline protonated using three different acids (hydrochloric, sulfuric and phosphoric)and playing the role of a hydrogen bond acceptor (HBA). Glucose and xylitol were used as hydrogen bond donors (HBD). A series of deep eutectic solvents with various mole ratios were obtained for the systems L-proline: glucose and L-proline: xylitol. Density, melting point, pH and viscosity of the synthesized DESs were determined along with the effect of water content, mole fraction of the HBA in DES and temperature on properties of the DESs. A wide range of densities (1343–1606 kg/m^3), viscosities at 20 °C (699.6–48,590 mPa·s) and pH of 0.1 M DES solutions (1.578–2.456) make the obtained deep eutectic solvents potentially applicable in numerous technological processes, extractions as well as in analytical techniques, including microextraction. Components of these DESs are of natural origin and non-toxic, thus environmentally friendly and suitable for food as well as pharmaceutical industry.

1. Introduction

The continuous development of the industry requires new technological solutions. The material, energy and ecological barriers have a significant impact on the direction of development of the chemical industry [1]. Organic solvents used in many processes, including extraction, electroplating or chemical synthesis, have a detrimental effect on the environment and health of living organisms. Therefore, more ecological substances capable of dissolving selected chemical compounds are sought. Organic solvents commonly used in various industries show high toxicity and, furthermore, most often high volatility, which leads to their evaporation into the atmosphere, adversely affecting air quality. According to the principles of green chemistry, at the level of process design, more ecological solutions are sought, one of which is the use of biodegradable and non-volatile solvents [2].

Deep eutectic solvents (DESs) are an alternative to commonly used organic solvents. DES is a mixture of at least two chemical compounds, characterized by a lower melting point than the melting points of the components included in the deep eutectic solvent. These solvents contain chemical compounds capable of donating and accepting protons and electrons, which makes them capable of hydrogen bonding and at the same time makes them capable of dissolving many substances [3]. Most of the DESs described so far in the literature consist of components that do not have a harmful effect on the environment and health of living organisms, which is their advantage over traditional organic solvents in the context of the existing ecological barrier. This property, combined with low production costs and the simplicity of the synthesis process, make DESs enjoy increasing interest in the scientific community. In 1994, Gill et al. [4] proved that deep eutectic solvents can be used as substrates for enzymatic reactions. Enzymes have been found to be able to retain their activity when dissolved in eutectic mixtures that provide a better reaction medium than traditional organic solvents. Four years later further scientific advances were made in the field of applications of deep eutectic solvents. Erbeldinger et al. [5] included in their works the use of heterogenous eutectic mixtures for enzymatic synthesis. These discoveries have a huge impact on innovative industrial processes. In 2010, Gutierrez described in one of his works the possibility of keeping alive bacteria in nonaqueous solvents [6], while Clouthier analyzed the processes of enzymatic catalysis and whole-cell biocatalysis [7]. In 2014, studies have been carried out [8] that proved that phenolic compounds derived from green coffee beans or other natural sources could be extracted with high efficiency using DESs. So far, these solvents have found numerous applications. The potential of using DESs has been confirmed, among others, in fuel desul-

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* Corresponding author at: Gdansk University of Technology, Faculty of Chemistry, Department of Process Engineering and Chemical Technology, 80 – 233 Gdansk, G. Narutowicza St. 11/12, Poland.

E-mail address: grzegorz.boczkaj@pg.edu.pl (G. Boczkaj).

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furization [9], biorefineries [10], electroplating [11], absorption of carbon dioxide [12] and as effective and selective extractants [13].

The possibility of varying the properties of DESs by selecting the components used for their synthesis, or by the addition of water (which affects, among others, the viscosity, density and conductivity of DESs) or acid (which additionally affects the pH of the eutectic liquid) makes it possible to design a solvent with specific properties, strictly meeting the requirements.

This paper describes a new type of deep eutectic solvents consisting of protonated L-proline as HBA and glucose/xylitol as HBD. For the synthesized DESs the physicochemical characteristics were determined and the effect of the type of acid used in the protonation of L-proline on their final properties was examined.

2. Experimental

2.1. Materials

L-Proline (purity 99%, Sigma Aldrich), glucose and xylitol (pure., WarChem) as well as hydrochloric, sulfuric and phosphoric acids (analytical reagent, POCH S.A.) were used in the investigations. Reagents were used as received / purchased.

2.2. Apparatus

Chemicals were weighed on a AS.310.R2 analytical balance (Radwag). A 06-MSH-PRO-T magnetic stirrer with heating (Chemland) with a PT 1000 temperature sensor were used for stirring with simultaneous heating. A Rotavapor R-300 rotary evaporator with a V-300 vacuum pump (BUCHI) were used to evaporate the solvent from samples. A CC-505 pH-meter with a CT2B-121 temperature sensor, a Pt-1000B resistor and a standard EPS-1 pH combination electrode (Elmetron) were used to measure the pH of the obtained DESs. In order to measure DES viscosity, a programmable DV- II+ viscometer with a built-in temperature sensor (Brookfield) was used. The viscometer was connected to a LTD-6 thermostat (Grant) with the operating temperature range from −20 °C to 100 °C. A Karl-Fisher 652 KF titrator (Metrohm) was used to measure the water content. A type MM4 magnetic stirrer (ATM) was also used at this stage. The melting point of DESs was measured using a CC 906 cryostat (Huber).

2.3. Procedure

2.3.1. Preparation of DES

The required amounts of both chemical compounds (HBA and HBD) were determined in order to prepare a mixture with the desired mole ratio (ranging from 1:1.5 to 10:1). Next, the required amounts of HBA and HBD were weighed using an analytical balance (AS.310.R2). The compound serving as HBA (proline, Prol) was placed in a vial, and the appropriate amount of 1 M acid solution was added. The mixture was stirred until a clear solution was obtained. Then, HBD (glucose, Gluc; xylitol, Xyl) was added to the resulting solution. The mixture was stirred again to obtain a clear solution. The solvent (water) was evaporated from the mixture using a rotary evaporator (Rotavapor R-300) until removal was determined to be complete, and then its content was equilibrated with the atmosphere for 24 h.

2.3.2. DES density measurement

The density of DESs was measured by drawing 1 mL of the analyzed liquid using a graduated pipet. After 1 mL DES was collected, the pipet was weighed using an analytical balance (AS.310.R2). Relative standard deviation (RSD) for the method was calculated in order to assess its precision. The difference in the mass of the pipet after sampling the liquid and before sampling the liquid was the mass of 1 mL of the analyzed liquid. All the measurements were carried out in triplicate.

2.3.3. Measurement of DES melting point

The melting point of DESs was determined using a cryostat. A thermometer sensor was inserted into the vial with the DES and the vial was placed in a chamber cooled by the cryostat. After cooling the sample to a temperature at which the liquid behaved like a solid (no motion inside the liquid was observed), its temperature was gradually increased and the temperature at which the thermometer sensor could be moved was recorded. The test was performed at 0.1 °C intervals.

2.3.4. Measurement of DES viscosity

The viscosity of the prepared DESs was determined using a programmable DV- II+ viscometer with an integrated temperature sensor (Brookfield). The viscometer was connected with a Grant LTD-6 thermostat which allowed the measurement of DES viscosities at various temperatures. Each measurement was carried out in triplicate.

2.3.5. Measurement of DES water content

The percent water content in the prepared DESs was determined using a 652 KF coulometer (Metrohm). A known mass of the sample was placed in the anolyte chamber with a syringe and the titration was commenced. The percent water content in the DES sample was calculated using the data obtained from the coulometric titration. Each measurement was carried out in triplicate.

2.3.6. Measurement of DES pH

In order to measure the pH of the synthesized deep eutectic solvents, DES solutions with a concentration of 0.1 M in deionized water (Millipore) were prepared.

The solution in the vial was tested at room temperature as well as at 30 °C and 40 °C by immersing the pH combination electrode in the investigated solution. The solution was heated to higher temperatures (i.e. 30 °C and 40 °C) by placing the sample vial in a water bath on a hot plate. Each measurement was performed in triplicate.

3. Results and discussion

3.1. Preparation of DES

DESs were obtained by protonation of HBA by acid solution (dissolving HBA in a specific volume of aqueous solution of appropriate, 67 RPM, 50 °C) under atmospheric pressure conditions - using a BUCHI rotary evaporator until a clear solution was obtained), followed by addition of HBD (everything was again stirred on the BUCHI rotary evaporator until a clear solution was obtained). Then the solvent (water) was evaporated at 50 °C under reduced pressure (10 mbar) for 2 h. Colorless, clear liquids without solid particles were obtained. The purpose of the acid addition was to subject HBA to protonation, which has a positive effect on the formation of hydrogen bonds between the hydrogen bond acceptor and donor. The chemical compounds used were solid at room temperature; their melting points are 221 °C [Prol] [14], 146 °C [Gluc] [15], 92 °C[Xyl] [16] (Fig. 1).

From the point of view of formation of hydrogen bond, proline in its protonated form acquires properties analogous to choline chloride – a positively charged quaternary amine group is formed with a counter-ion, which is the anion of the mineral acid used for protonation. The decision to protonate proline was made after

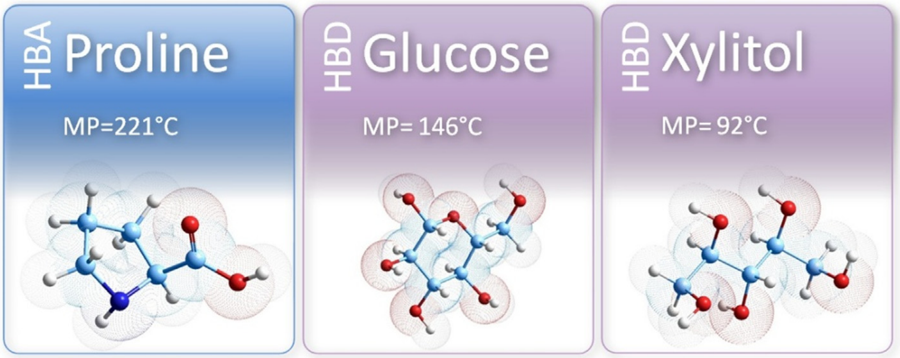

Fig. 1. Structural formulas of L-proline, glucose and xylitol.

unsuccessful preliminary attempts to obtain DES using native L-proline. Contrary to literature reports [17,18], it was not possible to synthesize DES by mixing HBA with HBD at elevated temperature, nor with the addition of water. Most likely, the use of an ineffective classic approach was the reason for a small number of papers on the synthesis of proline-based DESs. Only when the approach described in this paper was used, it was possible to obtain the expected DESs in a repeatable manner. Due to its non-toxicity and biological compatibility, proline has a great potential in the synthesis of DESs and their potential applications, especially in so-called natural deep eutectic solvents (NDESs).

3.2. Physicochemical properties of DESs

The density, viscosity and melting point of the obtained DESs were measured, then the water content in each of the samples was determined in order to assess its effect on the measured properties of each of the DESs. The obtained results of water content measurement were taken into account during analysis of the results of individual physicochemical properties.

3.2.1. Density and melting point

The values of density, melting point and water content of individual DESs are listed in Table S1.

The obtained DESs, despite the use of three different mineral acids in order to protonate proline, had the same mole ratio of HBA to HBD of 5:1 (in one case 6:1). At the same time, the same mole ratio was obtained for both glucose and xylitol as HBD. The possibility of using alternatively three counterions in the quaternary ammonium salt (chloride, orthophosphate and sulfate, respectively) to synthesize DES allowed the modification of DES according to the purpose of their synthesis. For example, in the case of industrial processes, there is a strong tendency to eliminate chemical agents containing chlorine, due to the possibility of formation under unfavorable conditions of hydrogen chloride, showing a strong corrosive effect on industrial fittings. On the other hand, in extraction systems, the use of anions with a significantly different structure and properties may enable the adjustment of DES selectivity as an extractant.

The experiments revealed that for all but one DES, the eutectic point was at a 5:1 ratio of HBA to HBD. The comparison of DES densities at the eutectic point revealed significant differences, depending on the type of acid used. The lowest density (ca. 1355 kg/m^3) was obtained when hydrochloric acid was used for the synthesis of DES. For sulfuric acid, the DES density was about 1493 kg/m^3, and for orthophosphoric acid a high value of ca.1602 kg/m^3 was obtained. Comparing the obtained results with the literature, for example DESs obtained by mixing L-proline as HBD and malic/glycolic acids as acceptors had densities in the range of 1245.1–1467.2 kg/m^3 [19]. In each case, the obtained density values prove the ease of phase separation when using DESs as extractants compared to most organic solvents. At the same time, the kind of acid used allowed density adjustment depending on the specific application. The differences in the density of DESs followed the type of acid used for their synthesis, as each acid had a different density. Sulfuric and phosphoric acid have a higher density than proline (1380 kg/m^3) [14], glucose (1560 kg/m^3) [15] or xylitol (1520 kg/m^3) [16], while the density of hydrochloric acid is lower.

The larger-scale production of the DESs described in the publication has an additional cost due to acid consumption and energy costs for water evaporation. However, the fact that DES were obtained from readily biodegradable components, may balance these costs from the Life Cycle Assessment point of view of DESs, as the disposal costs would be much lower than for classic solvents. Another advantage of DESs disposal compared to traditional solvents was the lower disposal fees of DESs so the process of using them could be more economical.

Moreover, the density of the prepared DESs depends on the mole fraction of proline as well as the water content. The density of the samples decreased with increasing water content (Fig. 2). At the same time, no significant effect of the HBD used on the density of the obtained DES was observed.

In order to eliminate the effect of water content on the density of the obtained DESs, the density of pure DES (ρ_{DES}') was calculated from the measured values, taking into account the water content in the samples:

$$\rho_{pureDES} = \frac{a_{pureDES}}{\left(\frac{1}{\rho_{DES(with\quad water\quad content)}} - \frac{a_{water \in DES}}{\rho_{water}}\right)}$$

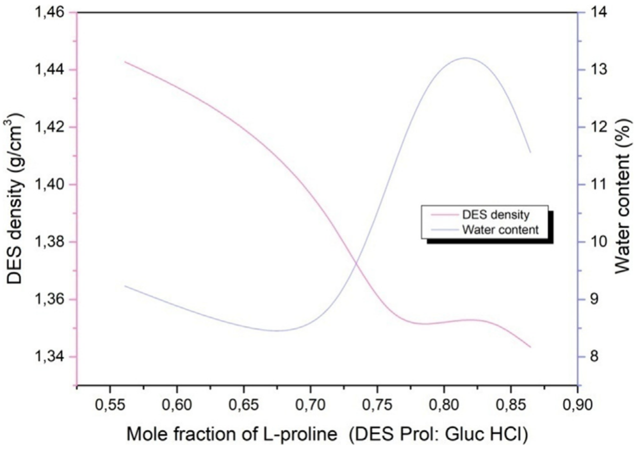

Fig. 2. Density dependence for the Proline: Glucose system (for DES obtained using aqueous HCl solution.

where $\rho_{DES\ (with\ water\ content)}$ - density of DES containing water, $a_{pureDES}$ - mass fraction of DES, ρ_{water} at 22 °C = 997.8 kg/m^3.

The calculated DES densities range from 1394.4 kg/m^3 to 1733.9 kg/m^3 (Table S1).

The lowest melting point values were obtained for liquids prepared using phosphoric acid: Prol: Gluc (mole fraction of proline 0.83, mole ratio HBA:HBD 5:1) −51.1 °C and liquids prepared using phosphoric acid: Prol: Xyl (mole fraction of proline 0.83) −44.8 °C, and the highest ones for liquids obtained using sulfuric acid: Prol: Gluc (mole fraction of proline 0.83) −29.4 °C, and Prol:Xyl (mole fraction of proline 0.83) −31.4 °C. The eutectic point was obtained for proline mole fraction of 0.83 (Fig. 3.). For comparison, for DESs composed of choline chloride and glucose (mole ratios 1:1, 1.5:1, 2:1, 2.5:1), the melting points were 31 °C, 24 °C, 15 °C and 44 °C, respectively [20]. Comparatively, the glass transition temperatures of the DES composed of proline and malic and glycolic acids ranged from −47.0 °C to −1.7 °C [19]. Thus, it can be concluded that the obtained DESs have a comparable range of melting point values to other DESs based on proline despite different function (as HBD) with malic/ glycolic acids as HBAs [19]. The melting points of the obtained DESs are very low, which is a significant advantage of solvents that can be used, for example, in the extraction process. DESs with melting points below room temperature are solvents that are easy to use. As a result, they are used in numerous chemical processes. In the case of using the developed DESs as solvents for drugs, their storage at a reduced temperature, e.g. in a freezer in the form of capsules, would not change their physical state.

3.2.2. Viscosity

Most ionic liquids and deep eutectic solvents have a higher viscosity than conventional organic solvents. The high viscosity of these substances is related to their low fluidity, which results from the presence of many hydrogen bonds in their structure and, to a lesser extent, the presence of van der Waals forces and electrostatic interactions [8]. This study demonstrated a significant effect of proline content in DES on the viscosity of the obtained DESs. The expected influence of temperature on DES viscosity was also confirmed (Table S2). A particularly large difference in viscosity values was observed for the measurements made at 20 °C and 30 °C. For DES Prol:Xyl (using sulfuric acid) with a mole ratio of 4:1 (HBA: HBD), the difference in viscosity values between the measurements performed at 20 °C (26,094 mPa·s) and 30 °C (7123 mPa·s) was 18971 mPa·s, thereby accounting for 72.7% of the DES viscosity at 20 °C (Fig. 4). For the measurements carried out at higher temperatures (40 °C and 50 °C), the viscosity drop was smaller. In some cases, similar viscosity values were obtained for both temperatures (Prol:Gluc 3:1 (using hydrochloric acid) 403.2 mPa·s (40 °C) and 372.8 mPa·s (50 °C)).

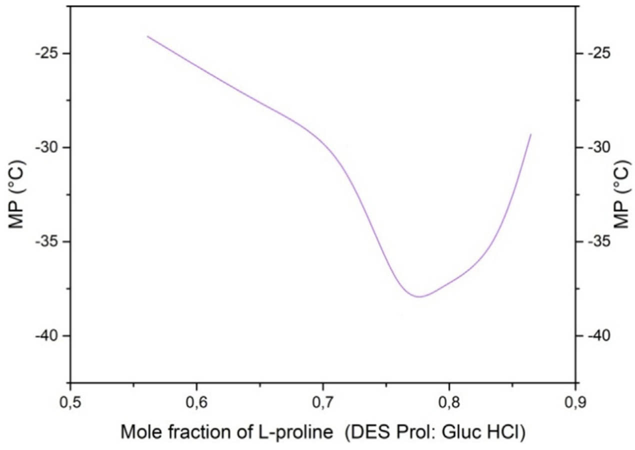

Fig. 3. Phase diagram for the Proline: Glucose system (for DES obtained using aqueous HCl solution).

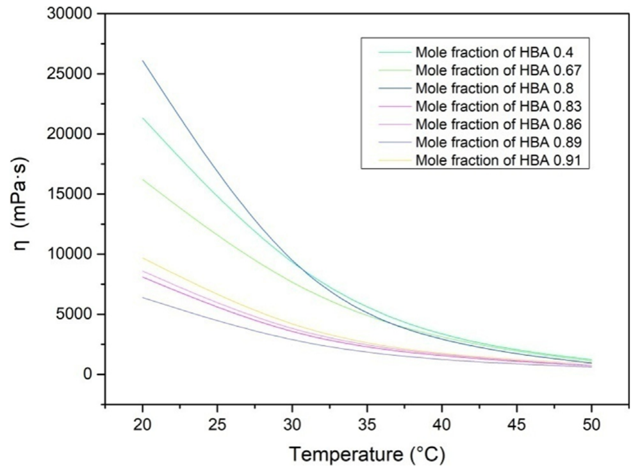

Fig. 4. The dependence of DES viscosity on temperature (Prol:XylH$_2$SO$_4$).

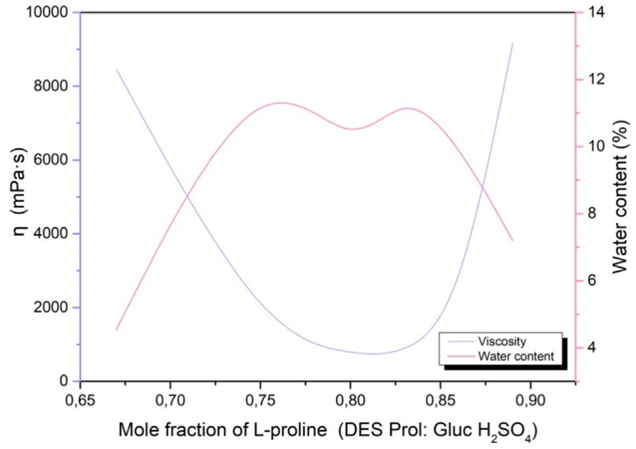

Fig. 5. The dependence of DES (Prol:Gluc H$_2$SO$_4$) viscosity on the mole fraction of proline.

The equilibrium water content in DES samples was taken into account (Fig. 5). The obtained results reveal that the DES viscosity, apart from the mole fraction of proline, is also affected by the water content in the samples. The dynamic viscosity of water at 20 °C is 1.002 mPa·s, being a small fraction of the viscosity values obtained for DESs (at the same temperature 20 °C). Moreover, the addition of water to DES significantly reduces the hydrogen bonds between HBA and HBD, which also reduces the viscosity [21].

The DES viscosity was measured at 50 °C for various shear rates. The results were consistent, an example plot for Prol: Xyl (10:1 H$_3$PO$_4$) is shown in Fig. 6.

The viscosity of the tested DES varies significantly with increasing shear rate. The tested liquid showed a plastic-viscous nature [22]; it is a non-Newtonian fluid for which the stress in its volume decreases with the increase in the shear rate.

3.2.3. pH of 0.1 M DES solutions

The pH of 0.1 M aqueous DES solutions was also determined (Table S3). It is one of the factors determining the efficiency of

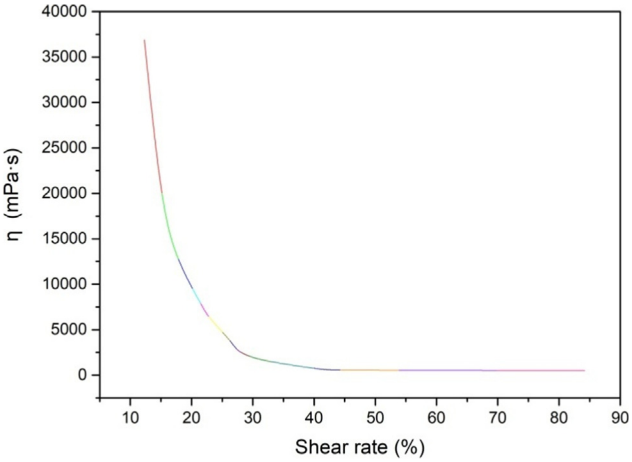

Fig. 6. The dependence of DES (Prol: Xyl 10:1 H_3PO_4) viscosity on the shear rate.

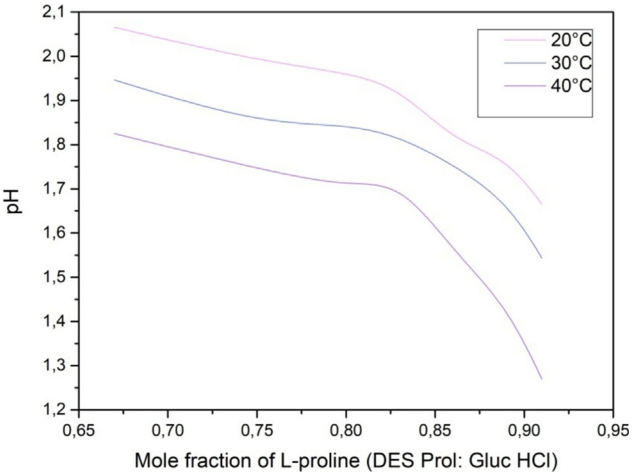

Fig. 7. The dependence of pH of a solution on the mole fraction of proline in DES Prol:Gluc (HCl).

the extraction process or the reactions taking place in the DES medium (which is especially important, for example, in metal processing or for reactants capable of dissociation or undergoing protonation).

In order to measure the pH of the obtained eutectic liquids, 0.1 M aqueous DES solutions were prepared. The measurements were carried out at room temperature and at 30 °C and 40 °C, by immersing the combination electrode in the DES solution.

An example of the dependence of the pH value on the mole fraction of proline in DES Prol: Gluc HCl is shown in Fig. 7. The experiments revealed that with an increase in the mole fraction of proline in DES, a decrease in pH was observed for each of the studied cases (Supporting Information: Table S1). The proline molecule contains a proton from the inorganic acid, hence with an increase in the amount of proline in the HBA:HBD mole ratio, the concentration of bound acid in DES increased. The amount of acid in DES was equimolar to the L-proline content used for DES synthesis.

In each of the cases, a decrease in pH was observed as the temperature of the DES solution increased. This effect is typical and known for aqueous solution. At the same time, the results of studies carried out for DESs demonstrated that with an increase in the mole fraction of proline in DES, a decrease in pH took place regardless of the temperature at which the measurements were performed.

4. Conclusions

This work describes new types of DESs based on proline (as HBA) and glucose or xylitol (as HBD), for which the density, melting point, pH and viscosity were measured. The effect of the sugar used as HBD and the acid used to protonate proline on the properties of the deep eutectic solvent was investigated. The present studies confirmed the possibility of obtaining DES by protonation of proline regardless of the acid used. At the same time, the significance of the type of counterion (in this case an inorganic acid anion) in HBA for the properties of the obtained DES was demonstrated. Depending on the mineral acid used and the resulting presence of chloride, sulfate or orthophosphate anion, the properties of DES can be modified. The solvents obtained with the use of phosphoric acid were found to have the lowest melting point, with the eutectic point determined from the melting point measurements being the HBA:HBD ratio of 1:5. For Proline:Xylitol eutectic liquid (using 1 M phosphoric acid solution) the melting point at this point was −44.8 °C, and for Proline:Glucose (using 1 M phosphoric acid solution) the melting point was −51.1 °C. The melting points of the DES obtained were close to the melting point of DES consisting of L-proline and DL-lactic acid (−49.15 °C), described in the literature. The authors of the study [23] obtained DES directly – without the need to add a mineral acid, most likely due to the acidic nature of the chemical compound used as HBD. In this case, protonation of L-proline occurred as a result of ionization of DL-lactic acid. Another approach [19] presented a synthesis of DES using proline as a hydrogen bond donor (the carboxyl group of proline is responsible for its ability to create eutectic systems also as a hydrogen bond donor). On the other hand, this paper demonstrated that regardless of the nature of the HBD used, it is possible to initiate the formation of hydrogen bonds between the components of the mixture of an HBD and an acceptor capable of attaching a proton introduced into the system by adding any acid from the three tested inorganic acids - H_2SO_4, HCl or H_3PO_4. In each of the cases, a decrease in pH for each of the investigated liquids was observed with an increase in the mole fraction of proline in DES. This is due to the change in concentration of the protonated HBA (proline). The viscosity of the synthesized DESs significantly decreased with increasing temperature, and was also closely related to the water content of the deep eutectic solvent.

Due to the non-Newtonian nature of the obtained fluids, it should be taken into account that at high shear rates (e.g. by stirring in the reactor), a significant reduction in the viscosity of DES can be obtained. With an increase in the mixing speed, the resulting decrease in viscosity will bring about an increase in mass exchange between the two phases of the extraction system, leading to more efficient isolation of the extracted component from the matrix, as well as reducing mixing resistance, translating into lower energy costs of the process.

The need to use an acid addition to obtain deep eutectic solvents based on proline as HBA demonstrated in this paper, opens up new possibilities for a wide range of novel DESs based on this substance, as well as other types of DESs using an analogous approach to the synthesis of deep eutectic solvents. The synthesized new DESs are nontoxic – they were obtained from nontoxic and biodegradable compounds, which are also relatively in expensive. The properties of the obtained DESs (low melting points, significant temperature sensitivity on DESs viscosity, non-volatile character) makes them attractive for numerous applications e.g among others – as extractants of chemical compounds and solvents for chemical synthesis and in numerous other applications – this aspects will be addressed in future papers on these DESs. Particularly interesting is their low pH which can be advantageous in many processes performed under acidic pH conditions. The demonstrated possibility of modification of properties of the obtained DESs allows the adjustment of their properties for the intended use.

CRediT authorship contribution statement

Patrycja Janicka: Investigation, Formal analysis, Writing - original draft, Conceptualization, Methodology, Validation, Data curation. **Andrzej Przyjazny:** Formal analysis, Writing - review & editing. **Grzegorz Boczkaj:** Conceptualization, Methodology, Validation, Investigation, Formal analysis, Writing - original draft, Writing - review & editing, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.molliq.2021.115965.

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