Properties of sugar-based low-melting mixtures

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Physico-chemical properties of ternary sugar-based low-melting mixtures were determined. Choline chloride, urea and glucose or sorbitol, serving as sugars, were blended in various compositions. The refractive index, density, viscosity, decomposition temperatures and glass transition temperatures were measured. Further, the influence of temperature and water content was investigated. The results show that the mixtures are liquid below room temperature and the viscosity and density are dependent on the temperature and composition. Moreover, the viscosity decreases with increasing water content. These mixtures are biodegradable, low toxic, non-volatile, non-reactive with water and can be accomplished with low-cost materials. In consideration of these advantages and a melting point below room temperature, these low-melting mixtures can be a good alternative to ionic liquids as well as environmentally unfriendly and toxic solvents.

Keywords: low-melting mixtures; carbohydrate; deep eutectic solvent

Introduction

A eutectic system is the mixture of chemical compounds or elements which exhibits a single chemical composition at which it solidifies at a lower temperature than at any other composition. The depression of the freezing point is related to the strength of interaction between the components [1,2]. Eutectic systems with a very large depression of the melting point, which can be up to 200 °C, are called deep eutectic solvents (DESs). About 10 years ago, Abbott et al. reported for the first time on such systems [3]. The very significant melting temperature lowering at the eutectic point results from the strong interaction of the anion with the hydrogen bond donor. Hence, the lattice energy is decreased which leads to a depression of the melting point [3,4]. One type of DES is the blend of an organic salt and hydrogen bond donor [5,6], the most prominent being probably the mixture of choline chloride (ChCl) and urea (U) [3].

Not only the easy production, low costs, non-volatility and non-inflammability are considerable advantages of these new systems, but also their easy biodegradability [4,7]. Further, and also very important, typical DES derive from renewable resources, whereas most solvents used in industrial processes and chemistry still stem from petrol. For some applications, for example its use in biocatalysis, ‘green’ DES can be a promising alternative [8–17].

To create new systems, carbohydrates were discovered as mixing partners [18]. The largest part of all biomass is carbohydrates with a percentage of 75 and, hence, they are the most important and widespread renewable feedstocks on earth [8]. Carbohydrates are poorly soluble in almost all solvents except water, which is a major drawback concerning their use [19]. Since a few years, it is reported that carbohydrates can be incorporated in ionic liquids (ILs) [19–21]. However, from an environmental point of view, creating green fluids by combining carbohydrates and ILs is not the best idea, since ILs tend to be toxic and have moderate biodegradability [22–24].

Therefore, it is tempting to combine carbohydrates with DES. In this line, Imperator et al. reported the utilisation of low-melting mixtures (LMMs) of sugars or sugar alcohols, urea and inorganic salts as solvents for Diels–Alder reactions [18,22]. In a carbohydrate–urea–salt melt, a [4+2] cycloaddition between cyclopentadiene and different acrylates yielded the respective products with good yields [18]. In a continuation of their work, the authors used these LMMs as a solvent medium for further reactions, in which both sugar and urea were used as reaction partners. For example, β-D-glucosyl urea was prepared from a D-glucose/urea/NH4Cl melt (3:7:1 wt/wt/wt) in a condensation reaction using different catalysts [22,25].

The melting points of the used mixtures are in the range from 65 to 85 °C, as summarised in Table 1 [18,26]. Until now, to the best of our knowledge, there are no such sugar-based LMMs reported in the literature with melting points lower than 50 °C. In the present paper, we introduce ternary mixtures of urea with choline chloride as salt and glucose or sorbitol as sugar, all showing melting points below room temperature. We present some basic properties of them, such as temperature-dependent densities, viscosities and glass transition temperatures.

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Table 1. Melting points of mixtures of carbohydrates, urea and inorganic salts in different composition.

| Carbohydrate | Urea  | Salt  | Ratio (weight%) | Melting points in °C | Ref. |
|--------------|-------|-------|-----------------|----------------------|------|
| Glucose      | Urea  | NH₄Cl | 5:2.5:2.5       | 84                   | [13] |
| Glucose      | Urea  | NH₄Cl | 6:3:1           | 78                   | [13] |
| Glucose      | Urea  | NaCl  | 6:3:1           | 78                   | [21] |
| Glucose      | Urea  | CaCl₂ | 5:4:1           | 75                   | [13] |
| Sorbitol     | DMU⁴  | NH₄Cl | 7:2:1           | 67                   | [21] |

⁴DMU: 1,3-dimethylurea.

Experimental section

General

Prior to use, choline chloride (Alfa Aesar >98%), urea (Merck, p.A.), D(−)-sorbitol (Sor) (Merck, extra pure for microbiology) and D(+)−glucose (Glu) (Merck, anhydrous for biochemistry) were dried under vacuum for several days. The density was measured as a function of temperature with an Anton Paar DSA 5000 M. The viscosity was determined with a Bohlin CVO 120 rheometer. All samples were measured at different temperatures with a CP4°/4 mm cone under argon atmosphere. The differential scanning calorimetry (DSC) measurements were performed with a Perkin Elmer DSC 8000 under nitrogen atmosphere. The thermogravimetric analysis was carried out by a Perkin Elmer TGA 7 under air atmosphere. The water content was determined with coulometric Karl-Fischer titrations, using an Abimed MCI analyser (Model CA-02). The refractive index was measured with a Krüss Abbe refractometer at 25 °C with a wavelength of 589 nm.

Preparation of the low-melting mixtures

Choline chloride, urea, glucose and sorbitol were mixed under nitrogen atmosphere and stirred at 75 °C until a homogeneous colourless liquid was formed. The mixtures were stored in sealed flasks. The compositions, water content, their abbreviations as used further on in the text and refractive indices of the four prepared mixtures are shown in Table 2. Figure 1 shows a sample of Glu–U–ChCl1 at room temperature.

Table 2. Molar ratios and refractive indices as well as the water content of the four prepared low-melting mixtures.

| Mixture                   | Molar ratio | Refractive index | Water content (weight%) | Abbreviation |
|---------------------------|-------------|------------------|-------------------------|--------------|
| Glucose–Urea–ChCl         | 1:1:1       | 1.5166           | 0.39                    | Glu–U–ChCl1 |
| Glucose–Urea–ChCl         | 1:2:1       | 1.5150           | 0.10                    | Glu–U–ChCl2 |
| Glucose–Urea–ChCl         | 1:1:1       | 1.5108           | 0.19                    | Sor–U–ChCl1 |
| Glucose–Urea–ChCl         | 1:2:1       | 1.5111           | 0.13                    | Sor–U–ChCl2 |

Results and discussion

Density

The densities of different mixtures were measured within temperatures ranging from 15 to 65 °C. The results are depicted in Figure 2. Obviously, there is a linear dependence between density and temperature. The densities of the glucose systems vary between 1.315 g/cm³ at 15 °C and 1.290 g/cm³ at 65 °C and those of the sorbitol systems between 1.290 g/cm³ at 15 °C and 1.261 g/cm³ at 65 °C.
mixtures with higher urea content show a slightly higher density.

**Viscosity**

The viscosity of a LMM is an important issue, since high viscosities can decrease the reaction rate in the case of diffusion-controlled chemical reactions. As shown in Figures 3 and 4, the viscosities of the mixtures listed in Table 2 vary significantly as a function of temperature with a more pronounced temperature dependence of the glucose systems. The viscosities were measured in a temperature range from 15 to 75 °C. Since the LMMs are very hygroscopic, humidity should be avoided. Note that for these glucose-containing systems, the higher fraction of urea decreases the viscosity at all temperatures. Nevertheless and as expected [27], the viscosities are all very high around room temperatures (up to 1520 Pa·s), whereas they significantly drop down at higher temperatures to values as low as 0.04 Pa·s. One may speculate that the extensive hydrogen bond network between the components is responsible both for the high viscosities at low temperatures and for the strong temperature dependence. Further, electrostatic and van der Waals interactions or the large sizes of the species, which cause a small void volume and, therefore, a lower mobility of these species, may also contribute to the high viscosities [27]. Note that all four mixtures show a Newtonian behaviour over the whole temperature range studied [28].

As the amount of water in such systems is an important parameter, we measured the viscosity as a function of the water content for one of the mixtures. Figure 4 shows the results for the system Glu–U–ChClI. With a water content of 7.8 wt%, the viscosity drops by a factor of 50 compared to the mixture with only 0.4 wt% of water.

**Thermogravimetric analysis**

The thermal stability and decomposition temperatures were measured with a thermogravimetric analyser in a temperature range of 30–900 °C with heating rate of 10 °C min⁻¹. The decomposition temperatures were determined from the onset of mass loss, derived from the intersection of the baseline before the thermal decomposition with the tangent during mass loss. Figure 5 depicts the mass loss in percentage as a function of temperature for each mixture.
The decomposition temperatures range around 175 °C. No appreciable difference in thermal stability between the different mixtures was detected. However, the further degradation of the LMM containing glucose differs from the ones containing sorbitol. In the latter case, the mixtures degrade in one step, whereas the glucose mixtures decompose in several steps. The single-step degradation of the sorbitol mixtures is consistent with previous studies \[9,29\] and own measurements of urea, choline chloride and sorbitol which are included in the electronic supplementary information (ESI). The first step in the thermogram of the Glu–U–ChCl mixtures results from the degradation of urea. The further steps arise from the degradation of glucose which decomposes in two steps (ESI) \[30\].

**Glass transition temperature**

A lot of ILs are already known as good glass formers, i.e. they can be cooled from the equilibrium state down to low temperatures without crystallising \[31–33\]. They enter the metastable supercooled liquid state and undergo a glass transition which leads to an out-of-equilibrium glassy state \[32\]. The DSC signature of the glass transition is a sigmoidal change in heat flux reflecting a characteristic change in heat capacity, $\Delta C_p$, when the sample is heated from the glassy state to the liquid state \[33\]. For all four mixtures, glass transition temperatures were found.

The measurements were performed with a heating rate of 15 °C min$^{-1}$ from −80 to 50 °C. The glass transition temperatures of the mixtures vary from −37.3 to −28.6 °C. The LMM containing sorbitol exhibits a lower transition temperature than those containing glucose. Further, the compositions with higher carbohydrate content show a lower transition temperature.

ILs can have a strong jump in the molar heat capacity, $\Delta C_{pm}$, because each molecule unit is in fact composed of two sub-units (the cation and the anion). Therefore, they have an appreciable relative mobility in the supercooled liquid state \[32\]. For example, the values of a series of $[\text{C}_n\text{O}_m\text{mim}]\text{X}$ of imidazolium cation-based room temperature ILs (RTILs) are in the region of 92–177 J mol$^{-1}$ K$^{-1}$ \[32\]. Compared to the RTILs, the measured LMMs have slightly lower $\Delta C_{pm}$ values, ranging from 57 to 93 J mol$^{-1}$K$^{-1}$. However, these values are still very high compared to polymeric systems $\Delta C_{pm} = 10$ J mol$^{-1}$K$^{-1}$ for polyethylene ($T_g = −133$ °C) and $\Delta C_{pm} = 36$ J mol$^{-1}$K$^{-1}$ for poly(vinyl acetate) ($T_g = −269$ °C) \[32,34\], and typical solvents such as glycerol ($T_g = −88$ °C) and toluene ($T_g = 116$ °C) with values of $\Delta C_{pm} = 23$ J mol$^{-1}$K$^{-1}$ and 53 J mol$^{-1}$K$^{-1}$, respectively \[32,35\].

Compared to these substances, the higher values for $\Delta C_{pm}$ at $T_g$ indicate that more degrees of freedom are released on heating above $T_g$, probably because the LMMs consist of three components. As shown in Table 3, the sorbitol systems exhibit higher $\Delta C_{pm}$ values than the corresponding glucose mixtures. Further, the melts with the

| Mixture      | $T_g$ (°C) | $\Delta C_p$ (J g$^{-1}$K$^{-1}$) | $\Delta C_{pm}$ (J mol$^{-1}$K$^{-1}$) |
|--------------|------------|----------------------------------|---------------------------------------|
| Glu–U–ChCl1  | −28.6      | 0.546                            | 69                                    |
| Glu–U–ChCl2  | −25.9      | 0.520                            | 57                                    |
| Sor–U–ChCl1  | −37.3      | 0.733                            | 93                                    |
| Sor–U–ChCl2  | −35.2      | 0.606                            | 67                                    |
higher carbohydrate content have a larger jump in heat capacity $\Delta C_p$. 

Conclusion
New very low melting mixtures were obtained by mixing ChCl with urea and a carbohydrate (glucose or sorbitol). Their density measurements show a linear correlation between density and temperature. The densities of the LMM containing glucose have higher values than those containing sorbitol. Further, the mixtures with a higher urea content show increased densities. The viscosities of the melts are quite high, especially at low temperatures, i.e. around room temperature. We measured how the viscosities of the mixtures depend on the chemical nature of the LMM components (type of carbohydrate and molar ratios of the components), on the temperature and on the water content. As in the case of other known DES, the viscosity is obviously governed by an extensive hydrogen bond network between the components, which results in a lower mobility of free species within the DES and, therefore, a higher viscosity [27]. The thermogravimetric analysis showed a stability until 175 °C which is a decent result for LMMs [9].

Another typical feature of the LMMs is the absence of a crystal structure. While cooling, the mixtures stay in a metastable supercooled liquid state down to at least $-28.6$ °C. At lower temperatures, they undergo a glass transition.

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Supplemental data
Supplemental data for this article can be accessed here.

References
[1] W.F. Smith and J. Hashemi, Foundations of Materials Science and Engineering (McGraw-Hill, New York, 2003).
[2] P. Atkins and J. de Paula, Physical Chemistry (W. H. Freeman, Oxford, 2006).
[3] A.P. Abbott, G. Capper, D.L. Davies, R.K. Rasheed, and V. Tambyrajah, Chem. Commun. (1), 70–71 (2003).
[4] A.P. Abbott, D. Boothby, G. Capper, D.L. Davies, and R.K. Rasheed, J. Am. Chem. Soc. 126 (29), 9142–9147 (2004).
[5] A.P. Abbott, J.C. Barron, K.S. Ryder, and D. Wilson, Chem. Eur. J. 13 (22), 6495–6501 (2007).
[6] D. Carriazo, M.C. Serrano, M.C. Gutierrez, M.L. Ferrer, and F. del Monte, Chem. Soc. Rev. 41 (14), 4996–5014 (2012).
[7] International Programme on Chemical Safety’s INCHEM service, http://www.inchem.org/
[8] D. Peters, Chem. Ing. Tech. 78 (3), 229–238 (2006).
[9] M. Sharma, C. Mukesh, D. Mondal, and K. Prasad, RSC Adv. 3 (39), 18149–18155 (2013).
[10] M. Francisco, A. van den Bruinhorst, and M.C. Kroon, Angew. Chem. Int. Ed. 52 (11), 3074–3085 (2013).
[11] M. Francisco, A. van den Bruinhorst, and M.C. Kroon, Green Chem. 14 (8), 2153–2157 (2012).
[12] B. Tang and K. Row, Monatsh. Chem. 144 (10), 1427–1454 (2013).
[13] M.C. Gutiérrez, M.L. Ferrer, L. Yuste, F. Rojo, and F. del Monte, Angew. Chem. Int. Ed. 49 (12), 2158–2162 (2010).
[14] E. Durand, J. Lecontec, B. Bará, and P. Villeneuve, Eur. J. Lipid Sci. Technol. 116, 16–23 (2013).
[15] E. Durand, J. Lecontec, B. Barea, E. Dubreucq, R. Lortie, and P. Villeneuve, Green Chem. 15 (8), 2275–2282 (2013).
[16] E. Durand, J. Lecontec, and P. Villeneuve, Eur. J. Lipid Sci. Technol. 115 (4), 379–385 (2013).
[17] J.T. Gorka, F. Sriend, and R.J. Kazlauskas, Chem. Commun. (10), 1235–1237 (2008).
[18] G. Imperato, E. Eibler, J. Niedermaier, and B. Konig, Chem. Commun. (9), 1170–1172 (2005).
[19] M.E. Zakrzewska, E. Bogel-Lukasik, and R. Bogel-Lukasik, Energy Fuels 24 (2), 737–745 (2010).
[20] M.E. Zakrzewska, E. Bogel-Lukasik, and R. Bogel-Lukasik, Chem. Rev. 111 (2), 397–417 (2010).
[21] L. Poletti, C. Chiappe, L. Lay, D. Pieraccini, L. Polito, and G. Russo, Green Chem. 9 (4), 337–341 (2007).
[22] C. Russ and B. Konig, Green Chem. 14 (11), 2969–2982 (2012).
[23] M. Deetlefs and K.R. Seddon, Green Chem. 12 (1), 17–30 (2010).
[24] M.T. Garcia, N. Gathergood, and P.J. Scammells, Green Chem. 7 (1), 9–14 (2005).
[25] C. Russ, F. Ilgen, C. Reil, C. Luff, A. Haji Begli, and B. Konig, Green Chem. 13 (1), 156–161 (2011).
[26] G. Imperato, S. Hoger, D. Lenoir, and B. Konig, Green Chem. 52 (39), 18149–18155 (2013).
[27] Q. Zhang, K. De Oliveira Vigier, S. Royer, and F. Jerome, Chem. Soc. Rev. 41 (21), 7108–7146 (2012).
[28] D.F. Evans and H. Wenerström, The Colloidal Domain: Where Physics, Chemistry, Biology, and Technology Meet. (Wiley-VCH, New York, 1999).
[29] D. Rengstl, Ph. D. Thesis, University of Regensburg, 2013.
[30] A. Magoni and M. Pyda, Carbohydr. Res. 346 (16), 2558–2566 (2011).
[31] J.D. Holbrey and K.R. Seddon, J. Chem. Soc., Dalton Trans. (13), 2133–2140 (1999).
[32] L.C. Branco, J.N. Rosa, J.J. Moura Ramos, and C.A.M. Afonso, Chem. Eur. J. 18 (16), 3671–3677 (2002).
[33] J.J. Moura Ramos, C.A.M. Afonso, and L.C. Branco, J. Therm. Anal. Calorim. 71 (2), 659–666 (2003).
[34] P.G. De Benedetti, Metastable Liquids: Concepts and Principles (Princeton University Press, Princeton, NJ, 1996).
[35] L.H. Sperling, Introduction to Physical Polymer Science (Wiley, New York, 2005).