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Thermophysical Properties and Solubility of Different Sugar-Derived Molecules in Deep Eutectic Solvents

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S Supporting Information

ABSTRACT: Deep eutectic solvents (DESs) are designer solvents analogous to ionic liquids but with lower preparation cost. Most known DESs are water-miscible, but recently water-immiscible DESs have also been presented, which are a combination of hydrogen bond donors and acceptors with long hydrophobic alkyl chains (e.g., decanoic acid + quaternary ammonium salts). These hydrophobic DESs are very interesting as solvents for recovering molecules from aqueous solutions. In this study the solubility of the sugar derived molecules furfural (FF), hydroxymethylfurfural (HMF), dimethyladipate, glucose, fructose, cyclopentanediol, cyclopentanone, and tetrahydrofurfuryl alcohol was experimentally screened in six different DESs (five hydrophilic and one hydrophobic) at 30–50–80 °C, for the first time. The Kamlet–Taft parameters of the DESs were also determined, and correlations with the solubility data were established. Moreover, the thermophysical properties (viscosity, decomposition temperature) of the six DESs were measured. All DESs showed Newtonian viscosity behavior. Their thermal stability was good but decreased when sugars were added to the DES phase. The hydrophobic DES had the most interesting solubility properties (highest solubility for FF and HMF, and lowest solubility for the monosaccharides glucose and fructose) and is water-immiscible. Moreover, the hydrophobic DES has the highest Kamlet–Taft π parameter (measure of dipolarity/polarizability ratio) that can be related to the high selectivity for HMF and FF over glucose. Thus, especially the hydrophobic DES is a promising extractant that can be used for selective removal of FF and HMF by liquid–liquid extraction from aqueous biomass solutions, e.g. in biorefineries.

1. INTRODUCTION

Recently, biomass has received considerable attention, both as an energy source and as renewable raw material.¹ The macro sugar polymers in biomass are cellulose and hemicellulose. By hydrolysis, they depolymerize into free sugar monomers (e.g., glucose and fructose), which can be further transformed into different platform chemicals. For example, furfural (FF) and hydroxymethylfurfural (HMF) can be obtained by acid hydrolysis of these sugar monomers. C₆ sugar monomers can also be converted to methyl glucosides,² and HMF into dimethyl sulfoxides (DMSO)³ or levulinic acid.⁴ These sugar conversions generally occur in different solvents (such as water or methanol), which interact with sugars, reaction intermediates, sugar derivatives, and acid catalysts in very different ways, resulting in low yields, especially in aqueous solvents.

The most interesting sugar-derived platform chemicals are FF and HMF, which can be manufactured from renewable agricultural resources and residues from forest products. Moreover, they are versatile intermediates from which other products can be made, including monomers for bioplastics, e.g., dimethyladipate, cyclopentanediol, cyclopentanone, and tetrahydrofurfuryl alcohol. The main challenge in the production of these sugar-derived platform chemicals is their isolation. Separation is needed to prevent further conversion to undesired side products (e.g., humins).

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Table 1. Chemicals, Source, CAS Number, Melting Point (T_m), and Purity

name	purity	source	CAS nr	T_m (°C)
Acetic Acid	99.7%	Sigma-Aldrich	64-19-7	16.2
2,6-diphenyl-4-(2,4,6-Triphenylpyridio)phenolate (Reichardt's dye)	90%	Sigma-Aldrich	10081-39-7	271-275
4-Nitroaniline	>99%	Sigma-Aldrich	100-01-6	146-149
Betaine	>99%	Sigma-Aldrich	107-43-7	310
Choline Chloride	>99%	Sigma-Aldrich	67-48-1	302-305
1,3 Cyclopentanediol mixture cis and trans	95%	Sigma-Aldrich	59719-74-3	40
Cyclopentanone	99%	Sigma-Aldrich	120-92-3	-51
Decanoic acid	>98%	Sigma-Aldrich	334-48-5	27-32
Dimethyladipate	>99%	Sigma-Aldrich	627-93-0	8
Ethylene Glycol	>99%	Sigma-Aldrich	107-21-1	-13
D-Fructose	>99%	Sigma-Aldrich	57-48-7	100-104
Furfural	>99%	Sigma-Aldrich	98-01-1	-36
Glucose	>99.5%	Sigma-Aldrich	50-99-7	150-152
Glycolic acid	99%	Sigma-Aldrich	79-14-1	75-80
5-Hydroxymethyl furfural	ong. 99%	Sigma-Aldrich	67-47-0	28-34
Imidazole	>99%	Sigma-Aldrich	288-32-4	88-91
Levulinic acid	>97%	Sigma-Aldrich	123-76-2	30-33
N-Tetraethyl ammonium Chloride	>96%	Sigma-Aldrich	56-34-8	
N,N-Dimethyl-4-nitroaniline	>97%	Sigma-Aldrich	619-31-8	160
Tetrahydrofurfuryl alcohol	>99%	Sigma-Aldrich	97-99-4	-80
Tetraoctyl ammonium Bromide	98%	Sigma-Aldrich	14866-33-2	95-98
Urea	>98%	Sigma-Aldrich	57-13-6	133

The most common isolation methods for sugar-derived molecules from biomass mixtures are liquid-liquid extractions and steam stripping. Liquid-liquid extraction of FF from an aqueous solution was first evaluated by using ethyl acetate.⁵ This was proposed as an energy-saving alternative to azeotropic distillation. While giving a satisfactory separation, the high solubility of ethyl acetate in water requires an energy intensive ester recovery unit. Toluene and methyl isobutyl ketone have also been invested as separation media. Knight et al. determined the distribution of FF between toluene and water. However, this work did not include the complete ternary equilibrium data.⁶ Organic carbonates, such as methylisobutylketone (MIBK), 2-methyltetrahydrofuran (2-MTHF), 2-butanol, and ionic liquids (ILs), have also been used for HMF extraction.⁷ Several solvents, for instance *o*-propylphenol and *o*-isopropylphenol, have been identified possessing up to five times higher partitioning coefficients compared to the previously applied solvent 2-MTHF.⁸ These solvents have the potential to significantly improve the HMF synthesis. Unfortunately, most applied extractants are not environmentally benign.

In the search for "greener" solvents for the dissolution and extraction of biomass-derived platform chemicals, deep eutectic solvents (DESs) could be an interesting alternative. DESs were reported for the first time in 2003.⁹⁻¹¹ Last year, synthesis of hydrophobic DESs has been reported for the first time.¹² DESs are mixtures of one or more hydrogen bond acceptors (HBAs) and one or more hydrogen bond donors (HBDs) that, when mixed together in the proper molar ratio, show a large decrease in melting point compared to the initial compounds.¹³⁻¹⁵ It is widely accepted that DESs have a low vapor pressure, wide liquid range, water compatibility, and biodegradability. DESs can be easily prepared using cheap renewable precursors. They have the potential to act as effective solvents for the complete dissolution and extraction of a wide range of nonpolar and polar compounds and have been proposed as alternatives to several conventional and often toxic organic solvents.

In the biomass processing field, DESs can have additional advantages over conventional solvents. These include inhibition of water reactivity (only to some extent), stabilization of carbohydrates and furanic derivatives through hydrogen bond interactions, decrease of polyol viscosity, and compatibility with few enzymes. Recently, DESs have received a particular attention for dehydration of hexoses and pentoses to furanic derivatives such as HMF and FF.¹⁶

In this work, six different DESs will be screened for the first time for FF and HMF extraction capability. The most suited DESs should possess a high solubility for FF and HMF and a low solubility for glucose and fructose. Also, they should possess a resistance to higher temperatures (applied during the production of FF and HMF). Moreover, the viscosity should be as low as possible to ensure fast extraction kinetics. In addition it would be valuable to be able to predict these properties, because experimentation is time-consuming. For example, solubilities may be predicted on the basis of the DES polarity/polarizability and hydrogen-bond acidity or basicity using the Kamlet-Taft parameters.¹⁷⁻²¹

In this work the solubilities of the sugar-derived molecules HMF, FF, dimethyladipate, glucose, fructose, cyclopentanediol, cyclopentanone, tetrahydrofurfuryl alcohol in 6 different DESs (acetic acid: imidazole (1:1), levulinic acid: betaine (2:1), urea: choline chloride (2:1), ethylene glycol: choline chloride (2:1), glycolic acid: *n*-tetraethylammonium chloride (2:1) and decanoic acid: tetraoctylammonium bromide (2:1)) have been studied. These DESs were selected on the basis of their viscosity (too high viscosity makes solubility measurements very complicated) and hydrophobicity (one hydrophobic and five hydrophilic DESs were selected). The solubility of pure compounds (not real biomass) was studied in order to ensure reproducibility of the experiments. Moreover, the thermal stability, viscosity and Kamlet-Taft parameters of the selected DESs were measured.

2. EXPERIMENTAL SECTION

Chemicals. The chemicals used in this work, including their source, purity and melting point (as stated by the supplier)²² are presented in Table 1. Demi water ($\geq 18.2 \text{ M}\Omega\cdot\text{cm}$) was obtained from a Purelab flex cell (cartridge packs LC140 and LC141) from Elga. All chemicals were used as such.

DESs preparation and thermophysical characterization. The proper amounts of HBD and HBA were weighed and premixed in the desired molar ratio, and placed in a round-bottom flask to produce an approximate amount of 25 g of DES using a balance “Mettler AX205” with an uncertainty in the measurement of $\pm 0.2 \times 10^{-4} \text{ g}$. The round-bottom flask was stirred and heated in an oil bath at 40°C to obtain a liquid, the DES. Thermostatic bath (IKA RCT basic) with a temperature controller (IKA ETS-DS) with an uncertainty in the measurement of $\pm 0.1^\circ\text{C}$. Karl Fischer analysis with a 899 Coulometer (Metrohm Karl Fischer) with an uncertainty of 1%, was used for measuring the water content of the DESs.

Rheology measurements were performed on an Anton Paar Physica MCR 301 rheometer with the concentric cylinder CC27 system (inner and outer diameter are 26.66 mm and 28.92 mm, respectively). For each sample, first dynamic measurements were performed twice with a constant frequency of 6.3 rad/s and a strain of 0.001 before and between the measurements series the sample was stirred for 100 at 100 s^{-1} . Subsequently, viscosity measurements were performed at different shear rates between 0.001 and 100 s^{-1} until steady state conditions were achieved at $30\text{--}50\text{--}80^\circ\text{C}$. Temperature accuracy is $\pm 0.03^\circ\text{C}$ and the torque uncertainty is max. 0.5%. The rheometer was calibrated with viscosity standards APN7.5, APS3 and APN415 from Anton Paar.

Decomposition temperatures were obtained using thermogravimetric analysis (TGA). TGA was performed using a TA Instruments TGA Q500. The temperature accuracy is $\pm 1^\circ\text{C}$ and the weight uncertainty $\pm 0.1\%$. The data was analyzed with the Universal Analysis 2000 software. A sample of 10 mg was heated from 25 to 600°C at a heating rate of $10^\circ\text{C}\cdot\text{min}^{-1}$ under nitrogen flow. All measurements were carried out in duplo.

Solubility of sugar-derived molecules in DESs. The solubilities of the sugar-derived molecules in the selected DESs were measured (in duplo) via the cloud point method. Five gram of every DES were weighed in a vial. The vials were heated to 30 , 50 , and 80°C , respectively, to which every 2 h a small amount of the sugar-derived molecule was added. Only if the small amount was dissolved after 2 h, the experiment was continued.

Solvatochromic properties of the DESs were determined (in duplo) to predict the solubilities of sugar-derived molecules in DESs. For these measurements, the DESs were dried under vacuum for 3 days and stored in a drybox. The water content of each DES was no more than 50 ppm as measured by Karl Fischer titration (Table 2).

The dye was dissolved in a DES in the concentration range of 10^{-5} to 10^{-4} M . The sample was filled into a dry quartz cell with a light path of 1 cm. The absorbance was recorded with a Shimadzu UV 1800 UV–visible spectrophotometer with automatic baseline correction (accuracy $\pm 0.1 \text{ nm}$ at 656 nm , $\pm 0.002 \text{ Abs}$ at 0.5 Abs , $\pm 0.004 \text{ Abs}$ at 1.0 Abs and $\pm 0.006 \text{ Abs}$ at 2 Abs). The temperature was controlled at 20°C . Each absorbed peak was fitted with a Gaussian profile to obtain the wavelength corresponding to its maximum value.

Table 2. Water Content of the Six Different DESs after Drying under Vacuum for 3 days

DES	Water content (ppm)
Deca-N8888Br	35
EG-ChCl	39
AcAc-Im	43
Le-Be	42
Urea-ChCl	37
Gly-N2222Cl	48

The Kamlet–Taft parameters were calculated according to the following eqs (eqs 1–(5)):

$$\nu(\text{dye}) = 1/(\lambda_{\text{max}}(\text{dye}) \times 10^{-4}) \quad (1)$$

The normalized E_{TN} polarity is obtained by measuring the wavelength corresponding to maximum absorption in a solvent:

$$E_{\text{TN}} = E_{\text{T}}(30) - 30.7/32.4 \quad (2)$$

where $E_{\text{T}}(30)$ in $\text{kcal}\cdot\text{mol}^{-1}$ is $28591/\lambda_{\text{max}}(\text{reich})$ (nm); here, λ_{max} is the wavelength corresponding to maximum absorption. The Kamlet–Taft parameter π^* is obtained by measuring the wavelength of maximum absorbance, ν_{max} in kK ($\text{kilokeyser}, 10^{-3} \text{ cm}^{-1}$), of the dye *N,N*-diethyl-4-nitroaniline:

$$\pi^* = \nu_{\text{max}} - \nu_0/s \quad (3)$$

where $\nu_0 = 27.52 \text{ kK}$ and $s = -3.182$; here, ν_0 is the regression value for a reference solvent system, and s the susceptibility of intensity of the spectral absorption due to changing solvent dipolarity/polarizability. Parameter π^* provides a measure of a solvent's dipolarity/polarizability ratio. The Kamlet–Taft parameter α was determined with

$$\alpha = (E_{\text{T}}(30) - 14.6(\pi^* - 0.23) - 30.31)/16.5 \quad (4)$$

Parameter α provides a measure of a solvent's hydrogen-bond donating acidity (HBD). The Kamlet–Taft parameter β was obtained by measuring the relative difference of solvatochromism between 4-nitroaniline (1) and *N,N*-diethyl-4-nitroaniline (2):

$$\beta = (1.035\nu_{(2)\text{max}} - \nu_{(1)\text{max}}) + 2.64/2.8 \quad (5)$$

where $\nu_{(1)\text{max}}$ and $\nu_{(2)\text{max}}$ are the wavelengths of maximum absorbance of dissolved 4-nitroaniline and *N,N*-diethyl-4-nitroaniline, respectively. Parameter β provides a measure of a solvent's hydrogen-bond-accepting basicity (HBA).

3. RESULTS AND DISCUSSION

DESs preparation and thermophysical characterization. Six different DESs were prepared by weighing, i.e. acetic acid:imidazole (1:1), levulinic acid:betaine (2:1), urea:choline chloride (2:1), ethylene glycol:choline chloride (2:1), glycolic acid:*n*-tetraethylammonium chloride (2:1), and decanoic acid:tetraoctylammonium bromide (2:1) (Table 3). It should be noted that acetic acid:imidazole shows some proton transfer and could in principle be partly considered as a protic IL. Thereafter, the viscosity, thermal stability, and solubilities of sugar-derived molecules in these different DESs were determined at different temperatures at atmospheric pressure.

Figure 1 shows the dynamic viscosities and shear stresses at different shear rates and temperatures. The dynamic viscosities at a shear rate of 100 s^{-1} are presented in Table 4. The viscosities of all the tested DESs are much higher than the

Table 3. DESs Prepared in This Work Including their HBD, HBA, HBD:HBA Ratio, and Abbreviation

HBD	HBA	Molar ratio ^a	Abbreviation
acetic acid	imidazole	1:1	AcAc-Im
levulinic acid	betaine	2:1	Le-Be
urea	choline chloride	2:1	Urea-ChCl
ethylene glycol	choline chloride	2:1	EG-ChCl
glycolic acid	<i>n</i> -tetraethyl ammonium chloride	2:1	Gly-N2222Cl
decanoic acid	tetraoctyl ammonium bromide	2:1	Deca-N8888Br

^aStandard uncertainties in mole fraction are $u(x) = 0.001$.

Table 4. Dynamic Viscosity (η) at Different Temperatures for Six Different DESs (Stirred for 100 at 100 s^{-1}) at $p = 1.01 \text{ bar}$

DES	$\eta/\text{Pa}\cdot\text{s}^a$ (at $30 \text{ }^\circ\text{C}$)	$\eta/\text{Pa}\cdot\text{s}^a$ (at $50 \text{ }^\circ\text{C}$)	$\eta/\text{Pa}\cdot\text{s}^a$ (at $80 \text{ }^\circ\text{C}$)
Deca-N8888Br	0.469	0.174	0.056
EG-ChCl	0.035	0.019	0.009
AcAc-Im	0.054	0.020	0.006
Le-Be	0.838	0.221	0.056
Urea-ChCl	0.893	0.197	0.044
Gly-N2222Cl	0.268	0.087	0.027

^aStandard uncertainties are $u(\eta) = 0.005 \text{ Pa}\cdot\text{s}$, $u(T) = 0.03 \text{ }^\circ\text{C}$, and $u(p) = 0.03 \text{ bar}$.

Figure 1. Shear stress and dynamic viscosity versus shear rate of six different DESs at (a) $30 \text{ }^\circ\text{C}$, (b) $50 \text{ }^\circ\text{C}$, (c) $80 \text{ }^\circ\text{C}$, and atmospheric pressure ($p = 1.01 \text{ bar}$): (black boxes) Urea-ChCl; (red circles) Le-Be; (blue triangles) Gly-N2222Cl; (magenta triangles) Deca-N8888Br; (green diamonds) AcAc-Im; (dark blue left pointing triangles) EG-ChCl.

Table 5. Comparison of the Viscosity (η in mPa·s) of Urea-ChCl at Different Temperatures in the Present Work and Literature

T (°C)	Xie et al. ²⁵	Chemat et al. ²⁶	Abbot et al. ¹¹	Agostino et al. ²⁷	This work
25	1571.0	748.09	447.0	449	
30	953.7	511.61		330	893
35	403.2	351.46	208.0	231	
45	195.9	169.57		161	
50	143.6	86.09	108.0	119	197
55	107.7	63.20		95	
80		24.81			44.0

Table 6. Comparison of the Viscosity (η in mPa·s) of EG-ChCl at Different Temperatures in the Present Work and Literature

T (°C)	Mjalli et al. ²⁸	Zhang et al. ¹⁴	D'Agostino et al. ²⁷	This work
20		36	37	
25	41	36	35	
30			33	35

Table 7. Loss Modulus (G'') for the Six Different DESs at 30–50–80 °C at $p = 1.01$ bar

DES	G''/Pa^a (at 30 °C)	G''/Pa^a (at 50 °C)	G''/Pa^a (at 80 °C)
Deca-N8888Br	3.027	0.992	0.298
EG-ChCl	0.211	0.117	0.061
AcAc-Im	0.324	0.116	0.048
Le-Be	4.792	1.176	0.281
Urea-ChCl	5.207	1.036	0.225
Gly-N2222Cl	1.634	0.502	0.175

^aStandard uncertainties are $u(G'') = 0.005$ Pa, $u(T) = 0.03$ °C, and $u(p) = 0.03$ bar.

Figure 2. Thermostability of the six different DESs: (solid black line) Gly-N2222Cl; (dashed red line) EG-ChCl; (dotted blue line) Deca-N8888Br; (dashed dotted magenta line) AcAc-Im; (dash-dot-dot green line) Le-Be; (short dashed dark blue line) Urea-ChCl.

viscosity of water and similar to that of ILs.^{23,24} As expected, the viscosity decreases upon an increase of temperature. Furthermore, it can be observed that the viscosity of all the DESs is in the same order of magnitude and comparable previous measurements for urea:ChCl (Table 5)^{11,25–27} and EG-ChCl (Table 6).^{14,27,28} It should be mentioned that in most previous studies, kinetic viscosities (ν) instead of dynamic viscosities (η) were reported; these properties are related to each other by density via: $\nu = \eta/\rho$. Moreover, in previous

Table 8. Onset Thermal Decomposition Point from TGA for Glucose and Fructose, Six Different DESs, and Mixtures of Sugars in the DES (Gly-N2222Cl) at $p = 1.01$ bar

DES	onset point TGA (°C) ^a
AcAc-Im	93
Le-Be	166
Urea-ChCl	186
EG-ChCl	84
Gly-N2222Cl	143
Deca-N8888Br	142
fructose	185
glucose	65
Gly-N2222Cl + fructose	76
Gly-N2222Cl + glucose	121

^aStandard uncertainties are $u(T) = 1$ °C and $u(p) = 0.03$ bar.

Figure 3. Thermostability of sugars and Gly-N2222Cl with sugars dissolved: (solid black line) fructose; (dashed red line) glucose; (dotted blue line) Gly-N2222Cl + fructose; (dashed dotted magenta line) Gly-N2222Cl + glucose.**Table 9.** Comparison of the Solubility (in weight fraction, w) of Furfural in Water at Different Temperatures in the Present Work and the Literature at $p = 1.01$ bar

T (°C)	CRC hand book ³³	Wongsawa et al. ³⁴	Sigma-Aldrich ²²	This work ^a
20	0.0766		0.0715	0.061
25		0.0408		

^aStandard uncertainties are $u(w) = 0.005$, $u(T) = 0.2$ K, and $u(p) = 0.03$ bar.

Table 10. Comparison of the solubility (in mole fraction, x) of glucose in water at different temperatures in the present work and literature at $p = 1.01$ bar

T (°C)	Alves et al. ³⁵	Gray et al. ³⁶	This work ^a
20	0.0451	0.08029	0.0797
25		0.09147	
30	0.0571	0.11386	0.1122
50			0.1336

^aStandard uncertainties are $u(x) = 0.005$, $u(T) = 0.2$ K, and $u(p) = 0.03$ bar.

studies, the shear stress used and water content of the DES were not always reported.

Figure 1 shows a linear behavior of the shear stress as a function of the shear rate (for sufficiently high shear rates) for all the different DESs at all three investigated temperatures, from which it can be concluded that these DESs behave as

Table 11. Solubility (in weight fraction, w_i) of HMF, FF, Dimethyladipate, Glucose, Fructose, Cyclopentanediol, Cyclopentanone, and Tetrahydrofurfuryl alcohol in the Six Selected DESs at Three Different Temperatures at $p = 1.01 \text{ bar}^a$

component		HMF ^b	FF ^b	Dimethyl adipate ^b	furfuryl alcohol ^b	cyclopenta none ^b	Cyclopentane diol ^b	Glucose ^b	Fructose ^b
AcAc-Im (1:1)	30 °C	m	m	m	m	m	0.90	0.50	0.35
	50 °C	m	m	m	m	m	0.90	0.51	0.35
	80 °C	m	m	m	m	m	0.90	m	m
Le-Be (2:1)	30 °C	m	m	m	m	0.75	0.75	0.20	0.20
	50 °C	m	m	m	m	0.75	0.75	0.20	0.20
	80 °C	m	m	m	m	m	0.75	0.20	0.20
Urea-ChCl (2:1)	30 °C	0.80	0.80	<0.02	m	0.25	0.03	0.35	0.35
	50 °C	0.85	0.85	<0.02	m	0.25	0.15	0.35	0.35
	80 °C	0.90	0.90	<0.02	m	0.26	0.15	m	m
EG-ChCl (2:1)	30 °C	m	0.95	0.05	m	0.50	m	0.20	0.50
	50 °C	m	0.95	0.05	m	0.50	m	0.20	0.50
	80 °C	m	0.96	0.06	m	0.51	m	m	m
Gly-N2222Cl (2:1)	30 °C	m	m	0.15	m	m	m	0.24	0.14
	50 °C	m	m	0.16	m	m	m	0.24	0.14
	80 °C	m	m	0.16	m	m	m	m	m
Deca-N8888Br (2:1)	30 °C	m	m	m	m	m	m	0.10	0.10
	50 °C	m	m	m	m	m	m	0.10	0.10
	80 °C	m	m	m	m	m	m	0.10	0.10

^aStandard uncertainties are $u(w) = 0.005$, $u(T) = 0.2 \text{ K}$, and $u(p) = 0.03 \text{ bar}$. ^bm = completely miscible.

Table 12. Solubility (in weight fraction, w_i) of HMF and FF in EG-ChCl at different molar ratios (1:1, 2:1, 3:1 and 4:1) and temperatures at $p = 1.01 \text{ bar}^a$

component		HMF ^b	FF ^b
EG-ChCl (1:1)	30 °C		
	50 °C		
	80 °C	m	0.90
EG-ChCl (2:1)	30 °C	m	0.95
	50 °C	m	0.95
	80 °C	m	0.96
EG-ChCl (3:1)	30 °C	m	0.95
	50 °C	m	0.95
	80 °C	m	0.95
EG-ChCl (4:1)	30 °C	m	m
	50 °C	m	m
	80 °C	m	m

^aStandard uncertainties are $u(w) = 0.005$, $u(T) = 0.2 \text{ K}$, and $u(p) = 0.03 \text{ bar}$. ^bm = completely miscible.

Table 13. Kamlet–Taft Parameters for the Six Different DESs and Ethanol as Reference from the Literature

	Et(30)	EtN	π	A	β
Ethanol	52.269	0.666	0.549	0.945	0.732
Ethanol lit	51.900	0.654	0.540	0.830	0.770
AcAc-Im	81.224	1.559	0.850	1.909	0.345
Le-Be	85.859	1.702	0.908	2.064	0.376
urea-ChCl	58.112	0.846	1.112	1.140	0.913
EG-ChCl	57.760	0.835	1.021	1.128	0.908
Gly-N2222Cl	87.434	1.751	1.021	2.116	0.391
Deca-N8888Br	58.951	0.872	1.649	1.168	0.334

Newtonian fluids (= constant viscosity with shear rate) in the measured temperature range.

At a constant strain of 0.001 and a frequency of 6.3 rad s^{-1} the storage modulus G' (elastic energy “returning”) and the loss modulus G'' (dissipative energy “absorbance”) for the six different DESs at 30 °C, 50 °C, and 80 °C were determined. The results are presented in Figures S1–S6 in the [Supporting](#)

Information. An overview of the results for the G'' can be found in [Table 7](#). G' was in all cases below 0.1 Pa, which is below the detection limit.

It can be noted that all measured DESs show constant and reversible viscoelastic behavior, although their G'' differ from each other and they are temperature dependent. Higher temperatures result in lower G'' , and smaller differences between the different DESs. In general, it can be observed that a DES with a higher viscosity shows a higher loss modulus.

Next, the thermostability of the six different DESs was measured. The TGA results are plotted in [Figure 2](#) and the onset data can be found in [Table 8](#). Some DESs (EG-ChCl, Gly-N2222Cl, Le-Be) showed more than one transition, but in these cases only the lowest transition is reported in [Table 8](#). Except for AcAc-Im and EG-ChCl, the DESs are stable up to approximately 150 °C or higher. The reaction temperature of sugars hydrolysis is typically 180 °C; thus, for in situ extraction the tested DESs are not (yet) optimized.

Moreover, the thermal stability of the sugars glucose and fructose was determined, as they can degrade under influence of temperature. At higher temperatures, caramelization and subsequent pyrolysis become more pronounced. The so-called maillard reaction is a chemical reaction between amino acids and reducing sugars. This process is accelerated in an alkaline environment.²⁹ The thermal stability of mixtures of DESs with sugars was determined and plotted in [Figure 3](#). The results show that the DES phase is less thermally stable when sugars are added. Also, the sugars are more stable without the presence of the DES. Thus, the DES probably accelerates the degradation reaction of the sugars.

Solubility of sugar-derived molecules in DESs. The solubility of FF^{22,33,34} and glucose^{35,36} in water was determined first to validate the experimental method used. As can be seen in [Tables 9](#) and [10](#), these solubilities are in the same order of magnitude as previously measured in literature. Next, the solubility of the following sugar-derived components in the six different DESs at 30–50–80 °C was determined: HMF, FF, dimethyladipate, glucose, fructose, cyclopentanediol, cyclopentanone, tetrahydrofurfuryl alcohol. For all compounds

Figure 4. Solubility of (blue circles) HMF and (orange circles) glucose versus the Kamlet–Taft parameters of the six DESs: A, dipolarity; B, acidity; C, basicity.

(except FF and HMF) the stated solubilities are the solid solubilities, but for FF and HMF the stated solubilities are in fact liquid miscibilities (as these compounds are liquid at the temperatures applied, see Table 1). The solubility results are presented in Table 11.

It can be observed that the temperature does not have a significant influence on the solubility in the DESs. Only the solubility of glucose and fructose in the different DESs show some significant differences at higher temperatures, but most likely this is related to the fact that these sugars are degraded or converted to other components at higher temperatures. This can also provide an explanation for the observed higher solubility of the sugars in the DESs at higher temperatures.

Furfuryl alcohol dissolves completely in all DESs. The solubility of FF and HMF is good in all DESs except the DESs containing ChCl, where their solubilities are slightly lower. All DESs have a low solubility for sugars. The hydrophobic DES Deca-N8888Br is most interesting for biomass extractions, because it is water-immiscible (earlier published data shows that the water solubility in deca-N8888Br is only 920 ppm¹²). and shows high solubility for all sugar-derived components except the sugars themselves.

The DES EG-ChCl was selected to test whether the ratio of the HBA and HBD influences the solubility of HMF and FF, since FF is not completely miscible in this DES. The results are presented in Table 12, showing that HMF is miscible in all ratios, whereas FF is not completely miscible for the ratios 1:1, 2:1 and 3:1. The solubility increases with increasing amount of ethylene glycol (HBD) in the DES. Again, the temperature was not found to have a significant influence on the solubility of HMF and FF. The viscosity of the DES EG-ChCl (1:1) at 30 and 50 °C was too high to dissolve any HMF or FF (kinetically limited).

Kamlet–Taft parameters. After drying, the DESs have a water content below 50 ppm, and their Kamlet–Taft parameters were measured. To validate the experimental method, the Kamlet–Taft parameters of ethanol were measured first and compared to literature (see Table 8). It was concluded that method was reproducible and gave similar results for ethanol as reported before in the literature. The measured Kamlet–Taft parameters for the six different DESs are summarized in Table 13. The solubility of both HMF and glucose (which have the largest difference in solubility in the different DESs) versus the different Kamlet–Taft parameters

are plotted in Figure 4. Since FF and HMF have almost the same solubilities and similar behavior, the plots for FF has been omitted here for brevity. From this figure, it can be observed that the glucose solubility decreases with increasing dipolarity (π) of the DES. The other Kamlet–Taft parameters do not strongly correlate with the glucose and HMF solubilities. In general, it can be observed that if the dipolarity (π) is high (and α and β are relatively low), the solubility of HMF and FF is higher and the solubility of the sugars is lower in the DES. This results in the highest selectivity for HMF and FF over glucose in biomass extraction processes. This is the case for Deca-N888Br, which is the only hydrophobic DES tested, and therefore the most interesting for biomass extraction processes. Other hydrophobic DESs will be tested in future research.

The performance of the DESs studied in this work is quite similar to the performance of previously investigated ILs. For example, it was previously shown that solubilities of fructose and glucose in ILs are in the range of 0.02–0.35 in mole fraction,^{30,31} which are in the same range as the solubilities found for fructose and glucose in the DESs tested in this work. Moreover, FF and HMF were also fully miscible with many ILs and therefore ILs could be used as water-immiscible extractants for the recovery of furfural derivatives.³² The main advantage of the DESs over the ILs is probably their higher “greenness” and their lower cost, making them interesting alternative extractants compared to ILs for selective removal of FF and HMF by liquid–liquid extraction from aqueous biomass solutions, e.g. in biorefineries.

4. CONCLUSIONS

In this study the physical properties and the solubility of various sugar-derived molecules in six different DESs (viz., acetic acid:imidazole (1:1), levulinic acid:betaine (2:1), urea:choline chloride (2:1), ethylene glycol:choline chloride (2:1), glycolic acid:*n*-tetraethylammonium chloride (2:1), and decanoic acid:tetraoctylammonium bromide (2:1)) have been experimentally determined. The dynamic viscosity of all six DESs is comparable to those observed for other DESs, and they all show Newtonian behavior. In general, it is observed that a DESs with a higher viscosity possesses a higher loss modulus. All DESs are thermally stable up to at approximately 150 °C. Sugars have a detrimental influence on the thermostability of the DESs. The solubility of sugars (glucose and fructose) is low in the six different DESs. A lower ratio of HBA:HBD results in a higher solubility for FF for the DES consisting of EG:ChCl. The hydrophobic DES (decanoic acid: tetraoctylammonium bromide (2:1)) showed the highest solubility for all other sugar-derived molecules (except for the sugars themselves). Therefore, this DES is most interesting as solvent for actual biomass extractions. Finally, the Kamlet–Taft parameters of the different DESs were also determined and it was found that especially the dipolarity parameter (π) correlates well with a decreasing solubility of glucose and, therefore, an increasing selectivity for HMF and FF over glucose.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jced.7b00184.

Storage and loss modulus versus time of all six DESs (PDF)

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Notes

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