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110th Anniversary: Distribution Coefficients of Furfural and 5-Hydroxymethylfurfural in Hydrophobic Deep Eutectic Solvent + Water Systems: Experiments and Perturbed-Chain Statistical Associating Fluid Theory Predictions

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Supporting Information

ABSTRACT: Furfural (FF) and 5-hydroxymethylfurfural (HMF) are intermediates for many products, such as monomers for bioplastics, and can be obtained from various renewable resources. The isolation of these sugar-derived molecules from aqueous solutions is one of the main challenges in biorefinery processes. In the work described in this paper, the separation of FF and HMF from aqueous phases is carried out with hydrophobic deep eutectic solvents (DESs) as new extracting agents. Distribution coefficients of FF and HMF in 10 different hydrophobic DES + water systems have been measured and compared to that of the benchmark extracting agent (toluene). The dependence of the distribution coefficients on the presence of sugars in the system has also been investigated. The hydrophobic DESs were found to selectively extract FF and HMF from aqueous solutions without any co-extraction or precipitation of sugars. Finally, the distribution coefficients have been successfully predicted with PC-SAFT (perturbed-chain statistical associating fluid theory) without the need to fit any parameter to the measured distribution coefficients.

INTRODUCTION

In recent years, biomass has received increasing attention, both as an energy source and as a renewable raw material.¹ The sugar polymers in biomass, i.e., cellulose and hemicellulose, can be hydrolyzed to free sugar monomers (glucose and fructose), which can be further converted into different platform chemicals. For example, furfural (FF) and 5-hydroxymethylfurfural (HMF) can be obtained by acid hydrolysis of these sugar monomers.^{2–4} FF and HMF are the most interesting sugar-derived chemicals, because they are intermediates from which many other products can be made, such as monomers for bioplastics.^{5,6} Moreover, they can be obtained from various renewable agricultural resources and residues from forest products.^{7–9}

Purifications, separations, and solvent recoveries determine the economic feasibility of the FF and HMF production

processes.¹⁰ The isolation of these sugar-derived chemicals is the main challenge in their production.¹¹ Until now, steam stripping and liquid–liquid extraction with toluene have been the most commonly applied isolation methods.^{12–14} Steam stripping is highly energy-intensive. The effectiveness of liquid–liquid extraction depends on the solvent selection. For a rational solvent selection, the following properties should be considered: distribution ratio, selectivity, density, recoverability, environmental impact, viscosity, toxicity, flammability, and thermal and chemical stability. Extraction with toluene causes problems in the solvent recovery step due to the

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Table 1. Chemicals Used, Including Purity (As Provided by the Supplier), Source, CAS Registry Number, and Melting Point (T_m)

name	purity (wt%)	source	CAS no.	T_m (K)
atropine	>99	Sigma-Aldrich	51-55-8	391
decanoic acid	>98	Sigma-Aldrich	334-48-5	300–305
D-fructose	>99	Sigma-Aldrich	57-48-7	373–377
dodecanoic acid	>98	Sigma-Aldrich	143-07-7	316–318
furfural	>99	Sigma-Aldrich	98-01-1	237
glucose	>99.5	Sigma-Aldrich	50-99-7	423–425
5-hydroxymethylfurfural	≥99	Sigma-Aldrich	67-47-0	301–307
<i>n</i> -tetraoctylammonium bromide	~98	Sigma-Aldrich	14866-33-2	368–371
thymol	>99	TCI Chemicals	89-83-8	322–325
menthol	>99	Sigma-Aldrich	98-78-1	304
lidocaine	>99	Sigma-Aldrich	137-58-6	339–342

formation of a heterogeneous azeotrope between toluene and water.^{15,16} Therefore, a lot of research is dedicated to the search for alternative extracting agents.

Recently, various deep eutectic solvents (DESs) were evaluated for their extraction performance for sugar-derived molecules, like FF and HMF from aqueous solutions.¹⁷ Also, DES-impregnated supported liquid membranes (SLMs) were investigated for selective separation of FF and HMF.¹⁸ DESs are mixtures of at least one hydrogen bond acceptor (HBA) and one hydrogen bond donor (HBD).^{19,20} When mixed in the proper molar ratio, they show a large decrease in melting point compared to the initial compounds.²¹ DESs are often assumed to be ionic liquid analogues, as they have similar properties to ionic liquids, e.g., low vapor pressure and tunability.¹ Specifically, hydrophobic DESs²¹ were found to be promising extracting agents for FF and HMF from aqueous solutions.¹⁷ However, to the best of our knowledge, distribution coefficients of FF and HMF in hydrophobic DES/water systems have not yet been reported in the literature.

Moreover, studies predicting the solubilities of FF and HMF in DESs are completely absent. Until now, only CO₂ solubilities in both hydrophilic and hydrophobic DESs have been modeled successfully using perturbed-chain statistical associating fluid theory (PC-SAFT).^{22,23} Two different modeling approaches for the DESs were compared in those works: (i) the “pseudo-pure” component approach, whereby the DES (even though it is a mixture) is considered as one component, and (ii) the individual-component approach, whereby both DES constituents are explicitly taken into account.²⁴ The pure-component PC-SAFT parameters for the individual-component approach of room-temperature solids can be accessed by thermodynamic data (water activity, density) of aqueous mixtures containing one of the DES constituents. However, measuring such data is very difficult and might not provide sufficient input to fit the parameters for very hydrophobic (water-insoluble) DES constituents.²⁵ Therefore, the individual-component approach is not a suitable modeling approach for the hydrophobic DESs studied in this work. Instead, the “pseudo-pure” component modeling approach is more meaningful, and this is applied in this work. The main drawback of this very straightforward modeling approach is that new PC-SAFT parameters are required for each new composition of the DES constituents.

In this paper we present for the first time the distribution coefficients of FF and HMF in 10 hydrophobic DES–water systems and compare them to the benchmark solvent, toluene. First, we have selected one DES (decanoic acid:tetraoctyl-

ammonium bromide in the molar ratio 2:1) to study the effects of the DES:water ratio, the starting concentration of FF and HMF, the addition of impurities (e.g., sugars), the temperature, and the pH value on the distribution coefficient. This DES is known for its high selectivity for FF/HMF over sugars,¹⁷ and so it was used to select suitable extraction conditions. Thereafter, the solubilities of FF, HMF, and glucose were measured in 10 different hydrophobic DESs. Also, the distribution coefficients of FF and HMF for these 10 DESs were measured at the selected extraction conditions and compared with predictions made with PC-SAFT. The parameters for the hydrophobic DESs were adjusted compared to our previous work by additional fitting to experimental volatility data (instead of correlation to density data only).²⁶

■ EXPERIMENTAL SECTION

Chemicals. Table 1 presents information on all the chemicals used in this work, including their purity, source, and melting point. All chemicals were used without any further purification.

DESs Preparation. The 10 different hydrophobic DESs prepared in this work, including their hydrogen bond donors (HBDs) and hydrogen bond acceptors (HBAs) and the ratio between the HBD and HBA, are listed in Table 2. Both solids (HBD and HBA) were weighed in the desired molar ratio in a round-bottom flask, mixed, and heated in an oil bath at 313 K for 2 h to obtain a liquid, the DES, which stayed liquid after

Table 2. DESs Prepared in This Work, Including Their Hydrogen Bond Donor (HBD), Hydrogen Bond Acceptor (HBA), HBD:HBA Ratio, and Abbreviation

HBD	HBA	molar ratio	abbreviation
decanoic acid	<i>n</i> -tetraoctylammonium bromide	2:1	deca-n8888Br
decanoic acid	thymol	1:1	deca-thy
decanoic acid	lidocaine	2:1	deca-lid 2:1
decanoic acid	lidocaine	3:1	deca-lid 3:1
decanoic acid	lidocaine	4:1	deca-lid 4:1
decanoic acid	menthol	1:1	deca-men
thymol	lidocaine	2:1	thy-lid
decanoic acid	atropine	2:1	deca-atr
dodecanoic acid	atropine	2:1	dode-atr
dodecanoic acid	lidocaine	2:1	dode-lid

cooling to room temperature to produce an approximate amount of 25 g of DES.

Solubility Measurements. The solubilities of FF, HMF, and glucose in the 10 selected DESs were measured (in duplicate) by the cloud point method with a standard uncertainty of $u(w) = 0.005$. In a vial, a 5 g portion of each DES was weighed and heated to 303, 323, and 373 K (with a standard uncertainty in temperature of $u(T) = 0.2$ K), respectively. A small amount of FF, HMF, or glucose was added, and only if the small amount was dissolved after 2 h, the experiment was continued by adding a little more the FF, HMF or glucose, until full saturation was achieved.

Extraction Measurements. The extraction of FF and HMF with the 10 hydrophobic DESs was measured using different starting concentrations of FF and HMF in water (i.e., 0.25, 0.50, 1.0, 1.5, 3.0, and 5.0 wt%). First, 5 g portions of these aqueous solutions were put into a centrifuge tube of 50 mL, and different amounts of DES (different solvent-to-feed ratios) were added. After mixing in a shake machine (IKA KS 4000i) during the applied shaking time (i.e., 10, 30, 60, and 300 s and 1 h) at 500 rpm at the selected temperature (i.e., 298, 323, and 353 K), the tubes were centrifuged (Sigma 2-16KL) for 30 min with a speed of 8000 rpm at the selected temperature in order to separate the DES from the aqueous phase. A sample of the aqueous phase was taken (± 1 mL) and analyzed using high-performance liquid chromatography (HPLC).

HPLC Analyses. The concentrations of FF, HMF, glucose, and fructose were measured by HPLC using an Agilent Technologies 1200 series instrument (Agilent Technologies, Santa Clara, USA), equipped with a multiple-wavelength detector (G1365D), an evaporated light scattering detector (ELDS Grace Alltech), and a thermostatic autosampler. Separation was carried out at 298 K (± 1 K); the mobile phase composition was acetonitrile:water (98:2 v/v%) with a 1 mL min⁻¹ flow rate and injection volume of 5 μ L, using a Jordi GEL DVB polyamine column (250 mm $\times$ 4.6 mm, cat. no. 17010, Jordi Labs LLC, Bellingham).

PC-SAFT Modeling. Gross and Sadowski^{27,28} introduced PC-SAFT as an advanced equation of state that combines physical soundness and engineering needs. PC-SAFT is based on statistical thermodynamics, developed by Barker and Henderson.^{29,30} PC-SAFT is a perturbation theory that accounts for perturbations from a hard-chain reference system by association and dispersive forces. It calculates the residual Helmholtz energy a^{res} (difference between the total molar Helmholtz energy and the Helmholtz energy of an ideal gas) as the sum of the free-energy contributions caused by hard-chain repulsion a^{hc} , dispersion forces a^{disp} , and site-site specific hydrogen-bonding interactions a^{assoc} (eq 1):

$$a^{\text{res}} = a^{\text{hc}} + a^{\text{disp}} + a^{\text{assoc}} \quad (1)$$

In PC-SAFT, pure components can be described using five pure-component parameters: (i) the segment number ($m_{\text{seg},i}$), (ii) the temperature-independent segment diameter (σ_i), (iii) the dispersion-energy parameter (u_i/k_B), (iv) the association-energy parameter ($\epsilon^{\text{AiBi}}/k_B$), and (v) the effective-volume parameter of an association site (κ^{AiBi}). The pure-component parameters for water, FF, and HMF and the “pseudo-pure” component parameters for the hydrophobic DESs are already available in the literature²⁶ and are shown in the Supporting Information, Table S1. It should be mentioned that the DESs are treated as “pseudo-pure” components (instead of

mixtures), as it was found previously to be the most convenient strategy for modeling the distribution coefficients of hydrophilic DESs.^{12,26}

The availability of a^{res} allows determination of fugacity coefficients by derivations with respect to density and mole fraction. In this work, fugacity coefficients were used to calculate activity coefficients γ_i (eq 2) by the ratio of the fugacity coefficient of component i in the mixture, φ_i , to the fugacity coefficient of pure component i , φ_{0i} , at the same pressure and temperature:

$$\gamma_i = \frac{\varphi_i(T, p, x_i)}{\varphi_{0i}(T, p, x_i = 1)} \quad (2)$$

At infinite dilution, the distribution coefficient K^x (x refers to mole-fraction scale) for component i between two phases can be predicted with PC-SAFT. For this purpose, the activity coefficients of component i were predicted at infinite dilution in the two phases. In this work, these two phases are the equilibrated DES-rich (DES) and DES-poor aqueous (aq) phases, and the corresponding activity coefficients at infinite dilution are denoted as $\gamma_i^{\text{DES}\infty}$ and $\gamma_i^{\text{aq}\infty}$, respectively. The composition of the equilibrated phases of the binary DES + water system has to be known to model $\gamma_i^{\text{DES}\infty}$ $\gamma_i^{\text{aq}\infty}$. These compositions were experimentally available from previous works.³¹ The ratio of both quantities yields the distribution coefficient of component i at infinite dilution $K_i^{x,\infty}$ (eq 3):

$$K_i^{x,\infty} = \frac{\gamma_i^{\text{DES}\infty}}{\gamma_i^{\text{aq}\infty}} \quad (3)$$

The use of this $K_i^{x,\infty}$ value is only reasonable given that component i is present at very low concentrations. This assumption is reasonable in this work. As $K_i^{x,\infty}$ is a mole-based quantity, conversion to mass-based units is required, which can be done using the molar masses of water, $M_{\text{H}_2\text{O}}$, and the DES, M_{DES} :

$$K_i^{w,\infty} = \frac{\gamma_i^{\text{DES}\infty}}{\gamma_i^{\text{aq}\infty}} \frac{M_{\text{DES}}}{M_{\text{H}_2\text{O}}} \quad (4)$$

For more information regarding the PC-SAFT model, the corresponding formulas, the mixing rules, and the parametrization, the interested reader is referred to previous works.^{26–28}

RESULTS AND DISCUSSION

Distribution coefficients (K) for FF and HMF in various DES + water systems were experimentally determined via eq 5:

$$K = \frac{w_O}{w_A} \quad (5)$$

where w_O and w_A stand for the weight fraction of FF or HMF in the organic and aqueous phases, respectively. It should be noted that these values correspond to the K_i^w values calculated using the PC-SAFT model (eq 4).

Extraction Optimization. The extraction of the pure components FF and HMF using one selected DES (deca-n8888Br(2:1)) was performed in order to study the effects of the DES:water ratio, the starting concentration of FF and HMF, the addition of impurities (e.g., sugars), the temperatures, and the pH values on the distribution coefficients. First, the extraction of FF and HMF at a temperature of 298 K and

at different solvent-to-feed ratios (DES: water) was carried out by bringing both phases into contact via shaking during 5, 10, 20, 30, and 60 min. The results for the obtained distribution coefficients are presented in Table S2 in the [Supporting Information](#). From this table it can be noticed that the extraction is already complete after 5 min of shaking time. In the rest of this work, a shaking time of 2 h was selected (as usually applied in literature), and this means that equilibrium was guaranteed. Next, three different starting concentrations of pure FF and HMF (0.25, 0.5, and 1.5 wt%) were extracted with the selected DES (deca-n8888Br) at three different solvent-to-feed ratios (DES:water = 1:1, 1:2, and 1:10, which are equivalent to water mole fractions of 0.500, 0.667, and 0.909, respectively). The results for the obtained distribution coefficients are shown in [Table 3](#). The following two

Table 3. Distribution Coefficients for Extraction of the Pure Components FF and HMF at 298 K and 1.01 bar Using deca-n8888Br as Extracting Agent at Different Solvent-to-Feed (DES:Water) Ratios and Different Starting Concentrations^a

starting concn of FF/HMF (wt%)	DES:water ratio	K	
		FF	HMF
1.5	10:10	4.6	1.6
	5:10	4.2	2.3
	1:10	2.5	1.8
0.5	10:10	4.6	1.6
	5:10	3.6	1.1
	1:10	2.2	1.8
0.25	10:10	5.3	1.7
	5:10	4.3	2.2
	1:10	2.3	1.9

^aStandard uncertainties are $u(T) = 1$ K, $u(p) = 0.03$ bar and $u(K) = 0.5$.

observations can be made: (i) the starting concentration of the solute does not have a significant influence on the distribution coefficients of FF and HMF, and (ii) the solvent-to-feed ratio has a large influence on the distribution coefficient—the higher the better, especially for FF. This is a general trend that is commonly observed in many systems.¹⁶ Of course, the ratio between the DES and the water is also changing when the amount of FF or HMF in the feed is changing, but this effect will be very small, as the concentrations of FF and HMF in the feed are very low. This is the reason why the feed concentration does not have a significant influence on the measured distribution coefficients. The difference in distribution coefficients between FF and HMF can be explained by the difference in hydrophobicities of the two components. HMF (completely water-miscible) is much more hydrophilic than FF (maximum water solubility at 298 K is only 77 g·L⁻¹, as stated by the supplier), and therefore the hydrophobic DESs are more selective for FF.

It is interesting to investigate the influence of other (side-)components on the obtained distribution coefficients of FF and HMF. First, the influence of a mixture of FF and HMF (in different mixing ratios) on the distribution coefficients K_{FF} and K_{HMF} was studied. Therefore, three different starting solutions with both components at different concentrations (mixture 1 consisted of 1.5 wt% FF and 1.5 wt% HMF; mixture 2

consisted of 0.5 wt% FF and 1.5 wt% HMF; mixture 3 consisted of 1.5 wt% FF and 0.5 wt% HMF) were prepared. The results are shown in [Table 4](#).

Table 4. Distribution Coefficients Obtained by Extraction with deca-n8888Br at 298 K and 1.01 bar from Different Starting Mixtures of FF and HMF at Different Solvent-to-Feed (DES:Water) Ratios^a

feed composition	DES:water ratio	K	
		FF	HMF
mixture 1 (1.5 wt% FF + 1.5 wt% HMF)	10:10	4.3	2.4
	5:10	4.0	1.9
	1:10	2.5	1.7
mixture 2 (0.5 wt% FF + 1.5 wt% HMF)	10:10	4.0	1.8
	5:10	4.3	1.6
	1:10	3.2	1.2
mixture 3 (1.5 wt% FF + 0.5 wt% HMF)	10:10	4.0	1.6
	5:10	4.3	2.0
	1:10	2.3	1.9

^aStandard uncertainties are $u(T) = 1$ K, $u(p) = 0.03$ bar, $u(K) = 0.5$.

From [Tables 3](#) and [4](#), it can be concluded that K_{FF} and K_{HMF} were almost not influenced by addition of the other component, so cross-component interactions were negligible, which is reasonable at the very low concentrations of FF and HMF.

Usually, FF and HMF are produced from biomass-derived sugars. Thus, sugars are often present in reaction mixtures containing FF and HMF. Therefore, the influence of the addition of both glucose and fructose on K_{FF} and K_{HMF} was also investigated using the following multi-component starting concentrations: 1.0 wt% FF + 1.0 wt% HMF + 1.0 wt% glucose + 1.0 wt% fructose. The results for the obtained distribution coefficients at two different solvent-to-feed ratios are listed in [Table 5](#).

Table 5. Distribution Coefficients Obtained by Extraction with deca-n8888Br at 298 K and 1.01 bar from a Multi-Component Starting Solution (FF + HMF + Glucose + Fructose) at Different Solvent-to-Feed Ratios^a

feed composition	DES:water ratio	K			
		FF	HMF	glucose	fructose
FF (1 wt%) + HMF (1 wt%) + glucose (1 wt%) + fructose (1 wt%)	10:10	4.3	1.4	0	0
FF (1 wt%) + HMF (1 wt%) + glucose (1 wt%) + fructose (1 wt%)	05:10	4.1	1.6	0	0

^aStandard uncertainties are $u(T) = 1$ K, $u(p) = 0.03$ bar, $u(K) = 0.5$.

When comparing the results in [Table 5](#) (presence of sugars) with the values in [Table 4](#) (absence of sugars), it can be noticed that also the addition of glucose and fructose to the starting solution hardly influences the obtained values for K_{FF} and K_{HMF} . Moreover, both sugars are not obtained in the extract phase. This means that the extraction is highly selective for FF and HMF over sugars. Thus, during the production of FF and HMF from biomass-derived sugars, the sugars will stay

in the reaction mixture, while only FF and HMF are selectively extracted into the DES phase.

The measured distribution coefficients for FF and HMF using the DES deca-n8888Br have been compared with those obtained using toluene as extracting agent. Therefore, the extraction of FF and HMF from a 1 wt% FF + 1 wt% HMF starting mixture at a temperature of 298 K was carried out using different solvent-to-feed ratios (10:10, 8:10, 5:10, 4:10, 3:10, 2:10, and 1:10), where both the DES and toluene were compared as solvents. The results for the obtained distribution coefficients are shown in Table 6. The measured distribution

Table 6. Distribution Coefficients Obtained by Extraction with deca-n8888Br and Toluene at 298 K and 1.01 bar from a Starting Solution Consisting of 1 wt% FF + 1 wt% HMF at Different Solvent-to-Feed Ratios^a

DES:water ratio	K (solvent = deca-n8888Br)		K (solvent = toluene)	
	FF	HMF	FF	HMF
10:10	5.7	2.3	5.0	0.2
8:10	4.7	1.9	4.1	0.1
5:10	4.9	2.0	3.8	0.1
4:10	3.8	1.6	3.8	0.1
3:10	3.9	1.5	3.6	0.1
2:10	3.9	1.7	3.7	0.1
1:10	3.1	1.4	3.5	0.1

^aStandard uncertainties are $u(T) = 1$ K, $u(p) = 0.03$ bar, $u(K) = 0.5$.

coefficients for FF using both solvents (deca-n8888Br or toluene) are comparable, with slightly higher values for the DES. However, the obtained distribution coefficients for HMF are much higher using the DES compared to the benchmark toluene or methyl isobutyl ketone (MIBK, $K_{\text{HMF}} = 1.0$).³³ This suggests that the DES is a better extracting agent for HMF compared to toluene, most likely due to its higher polarity. Again, as expected, it is observed that higher solvent-to-feed ratios result in higher distribution coefficients.

In biorefinery processes, the reaction of xylose to FF usually takes place at high temperatures and low pH values. Therefore, the influences of a temperature increase and a pH decrease on the distribution coefficients of FF and HMF have also been studied. The results for the obtained distribution coefficients at three different temperatures (298, 323, and 353 K) and two different pH values (7 and 2) are presented in Table 7. It can be noted that both the temperature and the pH do not have a significant influence on the extraction of both FF and HMF.

Table 7. Distribution Coefficients Obtained by Extraction with deca-n8888Br at Different Temperatures (298, 323, and 353 K) and pH Values (7 and 2) at 1.01 bar from a Starting Solution Consisting of 1 wt% FF + 1 wt% HMF at Different Solvent-to-Feed Ratios (1:1 and 1:2)^a

ratio –		1:1			1:2		
temp –		298 K	323 K	353 K	298 K	323 K	353 K
FF	pH 7	3.0	3.8	3.6	5.6	5.4	4.2
	pH 2	3.3	4.0	3.8	4.8	4.7	5.1
HMF	pH 7	1.4	1.7	1.5	2.4	2.3	1.6
	pH 2	1.5	1.8	1.6	2.5	1.9	2.0

^aStandard uncertainties are $u(T) = 1$ K, $u(p) = 0.03$ bar, $u(K) = 0.5$.

This can be explained by the fact that the polarity of the DES phase is not significantly affected by a change in either temperature or pH.

In conclusion, the only factor having a significant effect on the distribution coefficients of both FF and HMF in the selected DES is the solvent-to-feed ratio, and the distribution coefficients hardly depend on the feed composition, extraction time (beyond 5 min), temperature, and pH value. It is suspected that the interaction between the FF or HMF and the DES (i.e., the activity coefficient of FF or HMF in the DES) is the most important factor determining the observed distribution ratios, and not the mutual solubilities between DES and water. Any co-extraction of water (more occurring at lower solvent-to-feed ratios) cannot explain the observed higher distribution coefficients of the more hydrophilic HMF at higher solvent-to-feed ratios.

Extraction of FF and HMF Using 10 Different Hydrophobic DESs. Next, the extraction of FF and HMF in 10 different hydrophobic DESs is investigated. The solubilities of FF, HMF, and glucose in these 10 different DESs³² at 298, 323, and 353 K were determined first. The results are presented in Table 8. It should be noted that the

Table 8. Solubilities (in Weight Fraction, w_i) of FF, HMF, and Glucose in 10 Different DESs at 298, 323, and 353 K and 1.01 bar (Same Reported Values for Solubilities Are Achieved at the Three Temperatures)^a

DES	FF miscibility (%) ^b	HMF solubility (%) ^c	glucose solubility (%)
deca-n8888Br	m	s	0.10
deca-thy	m	s*	0.10
deca-men	m	0.50	0.10
deca-atr	m	0.10	0.10
deca-lid 2:1	m	s	0.10
deca-lid 3:1	m	s	0.10
deca-lid 4:1	m	s*	0.10
dode-atr	m	s	0.10
dode-lid	m	s*	0.10
thy-lid	m	s	0.10

^aStandard uncertainties are $u(w) = 0.005$, $u(T) = 0.2$ K, and $u(p) = 0.03$ bar. ^bm = completely miscible, no heterogeneous regions. ^cs = completely soluble, no precipitates; s* = crystallizes after cooling to room temperature.

solubility data involve solid solubilities for HMF and glucose; however, for FF the stated solubilities are, in fact, liquid miscibilities (as this compound is a liquid at the temperatures applied, see Table 1).

It was observed that the temperature does not have any influence on the solubility of FF, HMF, and glucose in the DESs. In fact, exactly the same values are obtained for the solubilities at 298, 323, and 353 K. The same behavior was found previously for other DESs in literature.¹⁷ FF is completely miscible with all 10 DESs, while glucose is nearly insoluble in all 10 DESs (only 0.1% of the glucose dissolves in the DESs). The solubility of HMF depends on the choice of the DES. HMF is fully soluble in five hydrophobic DESs (deca-N8888Br, deca-lid 2:1, deca-lid 3:1, dode-atr, and thy-lid), while it is not fully soluble (or crystallizes after cooling back to room temperature) in the other five DESs. The fact that glucose is nearly insoluble in all DESs while they are much better solvents for FF and HMF is beneficial for industrial

applications. When the DESs are applied as extracting agents, they will selectively remove the FF and HMF from the reaction mixture with sugars. It is expected that DESs showing the highest solubilities for FF and HMF will be the most promising extracting agents.

Subsequently, the 10 DESs were applied as extracting agents for the removal of FF and HMF from aqueous solutions, and the data were compared to those obtained with the benchmark extracting agent toluene. The obtained distribution coefficients for FF and HMF using a solvent-to-feed ratio (DES: water) of 1:1, a starting concentration of pure FF or pure HMF of 1 wt %, a shaking time of 2 h, and a shaking speed of 500 rpm at 298 K and 1.01 bar are reported in Table S3 in the [Supporting Information](#). The results are also graphically presented in [Figure 1](#). From this figure, it can be concluded that the DESs

Figure 1. Distribution coefficients of FF (black square) and HMF (blue circle) in 10 different DESs and toluene, with solvent-to-feed ratio 1:10, shaking time 2 h, shaking speed 500 rpm at 298 K and 1.01 bar, and starting concentration 1 wt% of HMF or FF.

deca-thy and thy-lid outperform the benchmark solvent regarding the extraction of FF, while deca-n8888Br, deca-lid 2:1, deca-lid 3:1, and deca-lid 4:1 show a similar performance compared to toluene. The other four DESs show worse performance. All DESs show better extraction of HMF compared to toluene. The explanation is that the DESs are all less hydrophobic than toluene. Remarkably, the DESs showing the highest solubilities for FF and HMF ([Table 8](#)) were not always the best extracting agents. In fact, the obtained distribution coefficient data do not seem to be correlated with the measured solubility data. This is most probably caused by the fact that the distribution coefficients depend on both the interaction of the FF and HMF with (one of) the DES' constituents and with water, while the solubilities were measured in a water-free system.

Other relations for the observed trends in the distribution coefficients were also investigated. For example, for the 10 different DESs, the Kamlet–Taft parameters were measured. These parameters are reported in Table S4 of the [Supporting Information](#). However, there was no correlation between any of the three Kamlet–Taft parameters and the distribution coefficient, a finding that coincides with previous observations.²³ It was also found that the starting concentrations of FF (0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 3.0, and 5.0 wt

%) and HMF (0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 10, and 20 wt%) did not have a significant influence on the obtained distribution coefficients (see Tables S5 and S6 in the [Supporting Information](#)).

The recovery of FF and HMF from the DES, which is very important for a full techno-economical evaluation, was not investigated in this work but will be addressed in a separate future study. Specifically, vacuum distillation and the use of DES impregnated supported liquid membranes are currently being investigated as promising recovery methods.

PC-SAFT Modeling. PC-SAFT was applied to estimate the distribution coefficients at infinite dilution of FF and HMF in ternary DES + water + FF/HMF LLE systems. The results can be found in Tables S7 and S8 of the [Supporting Information](#). These results are based on PC-SAFT pure-component parameters for the DESs, water, FF, and HMF. These are listed in Table S1 in the [Supporting Information](#).

[Figure 2](#) shows the comparison between the experimentally obtained FF distribution coefficients and the ones calculated

Figure 2. Distribution coefficient of FF between DES phase and aqueous phase in ternary systems (DES + H₂O + FF). Black bars represent experimental data and gray bars PC-SAFT predictions using parameters from Table S1 in the [Supporting Information](#) ($k_{\text{DES-water}} = 0$).

using PC-SAFT in a purely predictive mode (i.e., the three binary interaction parameters k_{ij} of the pairs DES–water, DES–FF, and water–FF were set to zero). It can be noticed that the PC-SAFT predictions are qualitatively correct (i.e., showing comparable trends as experimentally observed). That is, PC-SAFT allows predicting a priori in which DES the highest distribution coefficients can be found for FF. These results further cross-validate the experimental findings from [Figure 1](#), in which the two DESs deca-thy and thy-lid were found to outperform the benchmark extracting agent toluene.

PC-SAFT was not able to quantitatively predict the experimental values when all binary interaction parameters were set to zero. PC-SAFT systematically underestimated the distribution coefficients of HMF slightly. Thus, two binary interaction parameters k_{ij} (for the binary DES + water system, and for the binary DES + HMF system) were introduced to

account for the interaction of the DES with HMF and water. This allowed much more quantitative PC-SAFT predictions. Figure 3 shows the comparison between the experimentally

Figure 3. Distribution coefficient of HMF between the DES phase and the aqueous phase in the system (DES/H₂O/HMF). Black bars represent experimental data, light gray bars represent PC-SAFT predictions with $k_{DES-water} = 0$, dark gray bars represent PC-SAFT predictions with $k_{DES-water} \neq 0$, and white bars represent PC-SAFT predictions using $k_{DES-water} \neq 0$ and $k_{DES:HMF} \neq 0$. The latter were adjusted to solubility data; i.e., they are independent of any experimental K value. The PC-SAFT parameters are listed in Tables S1 and S9 in the Supporting Information.

obtained HMF distribution coefficients and the so-obtained PC-SAFT calculated values. Nevertheless, these results are still predictive in the sense that no parameter was adjusted to experimental distribution coefficient data or any other data of the ternary water + DES + FF (HMF) systems under investigation. That is, all binary parameters were fitted to experimental data of binary systems only, i.e., LLE of water + DES and solubility data of HMF in DES; all these parameters were available already in the literature.³⁴ Concluding from the results in Figures 2 and 3, k_{ij} values between DES and water are not crucial for quantitative PC-SAFT modeling results, whereas the k_{ij} between the goal component (HMF) and the DES is the decisive parameter that guarantees quantitatively correct predictions.

Thus, PC-SAFT was able to qualitatively predict the distribution coefficients of FF and HMF in ternary DES + water + FF/HMF LLE systems, although in some cases binary interaction parameters were required to make the predictions quantitatively correct. It should be noted that all DESs were treated as “pseudo-pure” components in this study. It is expected that binary interaction parameters may not need to be introduced in the case that the DESs are treated as mixtures of HBA and HBD.

CONCLUSIONS

The influence of the feed composition, temperature, pH, and solvent-to-feed ratio on the distribution coefficients of FF and HMF in the selected DES (deca-n8888Br) + water system was

investigated. Only the solvent-to-feed ratio was found to have a significant effect on the distribution coefficient; the other variables did not have a significant effect. Thereafter, the distribution ratios of FF and HMF in 10 different hydrophobic DESs were measured at the optimized conditions. All hydrophobic DESs show much better extraction of HMF compared to the benchmark solvent toluene. The DESs deca-thy and thy-lid perform excellently for the extraction of FF, while deca-n8888Br, deca-lid 2:1, deca-lid 3:1, and deca-lid 4:1 show similar performance compared to toluene. Finally, PC-SAFT was used to predict the distribution coefficients of FF and HMF in ternary LLE systems (DES + water + FF/HMF). PC-SAFT also predicted that deca-thy and thy-lid are the best extracting agents, for which the predictions were in quantitative agreement with the obtained experimental data.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.iecr.8b06234.

Table S1, pure-component PC-SAFT parameters for DESs, water, FF, and HMF; Table S2, extraction coefficients of pure wt% HMF + 1 wt% FF for different shaking times; Table S3, pure-component distribution coefficients obtained by extraction with 10 different DESs; Table S4, Kamlet–Taft parameters for the 10 different DESs and toluene and ethanol as reference; Tables S5 and S6, distribution coefficients obtained by extraction with four selected DESs from different starting solution; Table S7, distribution coefficient from FF in a ternary LLE system; and Table S8, distribution coefficient from HMF in a ternary LLE system (PDF)

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