Measurement and Modeling of Phase Equilibria in Systems containing Water, Xylose, Furfural, and Acetic Acid

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Abstract

Wood hydrolysates obtained in biotechnological processes are typically aqueous solutions that contain, among others, sugars, acetic acid, and furfural. Only little is known on the influence of the sugars on the phase equilibria in those mixtures. Therefore liquid-liquid equilibria (LLE), solid-liquid equilibria (SLE), and solid-liquid-liquid equilibria (SLLE) in the system (water (W) + xylose (X) + furfural (F)) were studied in the present work at 298.15 K and 333.15 K. Additionally, the LLE in the system (W + X + F + acetic acid (AA)) was studied at 298.15 K. The results show that, up to the solubility limit of xylose, adding xylose to mixtures of (W + F) hardly influences the width of the miscibility gap, and that there is practically no xylose in the furfural-rich phase. However, the miscibility gap in the ternary system (W + F + AA) is

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slightly widened by the addition of xylose. The experimental data on the phase equilibria from the present work were described using the NRTL model. The model describes the experimental data well.

Introduction

Aqueous hydrolysates of lignocellulosic biomass contain sugars and are an attractive renewable raw material for the biotechnological production of chemicals, polymers, and fuels, in particular of ethanol.^{1,2} However, raw hydrolysates are not suited for fermentation, firstly because the sugar concentration is too low, and secondly because they contain components that are toxic for the microorganisms, the so-called inhibitors. Examples of such inhibitors are carboxylic acids (acetic acid, formic acid, and levulinic acid), phenols, furan compounds such as furfural and 5-hydroxymethylfurfural (5-HMF), and inorganic ions.³ Therefore, the hydrolysates need to be concentrated and detoxified before they can be used as substrate in fermentation processes. This is usually done by combining evaporation with other process steps like ion exchange, chemical treatment, or extraction.^{3–6} Some of the inhibitors, like acetic acid and furfural, are valuable chemicals which could be obtained as pure products by further downstream-processing. In a recent work of our group, vapor-liquid equilibria (VLE) in systems containing water (W), xylose (X), glucose (G), and acetic acid (AA) were studied.⁷ Xylose was selected as model substance of C5 sugars, glucose as model substance of C6 sugars. It was found that xylose and glucose have a similar impact on the VLE in the system. The data was used, together with the data of this work, to design an evaporation + distillation downstream process that yields a concentrated sugar solution as well as pure furfural.⁸ Our previous work on VLE⁷ is extended in the present study to furfural (F) and to other types of phase equilibria: liquid-liquid equilibria (LLE), solid-liquid equilibria (SLE), and solid-liquid-liquid equilibria (SLLE), which were measured in the system (W + X + F) at 298.15 K and 333.15 K. Furthermore, the LLE in the system (W + X + F + AA) was studied at 298.15 K. The study is motivated by the fact that the LLE can be used for designing recovery processes by extrac-

tion or hetero-azeotropic distillation.^{5,9–11} The LLE in the system (W + F) is well-studied,^{12–21} but the influence of adding acetic acid and xylose has been studied only scarcely^{22–25} or not at all, respectively.

Sugars are generally well soluble in water but hardly soluble in furfural. Accordingly, it is expected that in LLE in the system (W + X + F) only little sugar is present in the furfural-rich phase whereas most of the sugar should remain in the aqueous phase. Data on the solubility of xylose in water is available,^{26–28} but there was no data on the solubility of xylose in mixtures that contain water and furfural, as it was determined in the present work.

There is also data on VLE of the system (W + AA) at atmospheric pressure, e.g.,^{29–31} as well as at lower pressures,^{7,32–34} and data on VLE of the systems (W + F)^{16,19,35–37} and (F + AA).^{9,38} However, to our knowledge, there is no experimental data of the LLE of the ternary mixture (W + X + F) that is studied in this work.

The phase equilibria that were studied in the present work were modeled using the same approach as in our earlier work,⁷ in which the NRTL model was used for describing the liquid phase non-ideality. The model was parameterized using, among others, the LLE data for the system (W + X + F). It was then applied for predicting the LLE data for the system (W + X + F + AA), for which no experimental data was available, as well as VLE in the system (W + F + AA).

Experimental

Chemicals

Table 1 gives information on the used chemicals, the suppliers, and the purities. All chemicals were used without further purification. Ultrapure water was obtained with a water purification Milli Q system from Merck. For the titration of acetic acid, a sodium hydroxide solution (1 N, Reag. Ph. Eur.) from Carl Roth was used.

Table 1: CAS registry number, suppliers, and mass fraction purity of the chemicals.

Component	CAS Reg. No.	Supplier	Mass fraction	Analysis method
D(+)-xylose	58-86-6	Alfa Aesar	≥ 0.98	HPLC ^a
Acetic acid	64-19-7	Carl Roth	≥ 0.998	acid-base titration
Furfural	98-01-1	Sigma-Aldrich	≥ 0.985	GC ^b

^a High-performance liquid chromatography.

^b Gas chromatography.

Analysis

The mass fractions of furfural and xylose in the coexisting phases were analyzed with HPLC (Agilent Series 1100/1200). The chromatographic method was adopted from our previous work.⁷ In the present work, however, pure water with a flow rate of 0.7 ml min^{-1} was used as mobile phase. Xylose was detected with a Refractive Index Detector (Agilent 1260 Infinity), while furfural was detected with an UV Detector (Agilent 1100 Series). The HPLC was calibrated with standard solutions and the relative errors for the mass fraction resulting from the analysis of test samples were less than 2%. The mass fraction of water was measured by Karl Fisher titration and the mass fraction of acetic acid was measured by an acid-base titration method with sodium hydroxide as titrant as both described in our previous work.⁷ For the LLE, SLE, and SLLE measurements of the ternary system (W + X + F), the mass fractions of the two components present in lower quantity were analyzed and the mass fraction of the third component was calculated using the following closure condition:

$$\sum_i w_i = 1 \quad i = \text{W, X, F} \quad (1)$$

The accuracy of this method was checked in some random cases with HPLC analysis of furfural for the furfural-rich phase and Karl Fisher titration analysis for the water-rich phase. In these checks the resulting sums of mass fractions were between 0.98 g g^{-1} and 1.02 g g^{-1} . For LLE measurements of the quaternary system (W + X + F + AA), the mass fraction of water was determined as complement to 1 g g^{-1} .

Experimental procedure

The LLE, SLE, and SLLE data reported in this work were measured using thermostated double-jacketed glass vessels as described in a previous work.³⁹ The amounts of pure substances that were filled into the vessels were determined gravimetrically using a balance (METTLER TOLEDO PR1203) with a resolution of 0.001 g. The composition of the feeds that was determined gravimetrically (i.e. disregarding the fact that the feed splits up into two phases for the LLE and the SLE measurements and into three phases for the SLLE measurements) are reported in Table S1 in the Supplementary Information. The heterogeneous mixtures were stirred for at least 24 h with magnetic stirrers and then settled down for another 24 h to reach equilibrium and, in the case of solubility measurements, to enable solid particles to settle on the bottom of the vessel. It was confirmed by experiments in the binary system (W + F) and in the ternary system (W + F + AA) for the measurement of the LLE and experiments in the binary system (W + X) for the measurement of the SLE that the equilibrium is established by this procedure. The experiments were carried out at 298.15 K or 333.15 K at atmospheric pressure. The temperature was controlled by a water thermostat and measured with a Pt 100 resistance thermometer that was calibrated against a standard certified by PTB Braunschweig. The uncertainty of the temperature measurement is ± 0.05 K. The temperatures of 298.15 K and 333.15 K were reached with a precision of ± 0.2 K. Samples from the top and the bottom phases were drawn with a syringe through a septum placed on the top or at the bottom of the vessel, respectively, such as to avoid any penetration of the liquid-liquid interface upon sampling. For measurements with three phases present (S + L + L), samples of both the top and the bottom liquid phase were drawn through the septum placed on the top of the vessel because of the presence of solid xylose at the bottom. To ensure an accurate sampling of the bottom phase prior to sampling, the syringe was filled with air and air bubbles were injected carefully into the solution until the needle of the syringe was in the bottom phase. In the case of SLE and SLLE measurements, samples of the liquid phases were withdrawn using a pre-warmed syringe at a slightly higher temperature than the sample such as to avoid any precipitation. The reproducibility of the results was checked by a triple measurement of at least one tie line for each

system. The relative deviation did not exceed the analysis error reported in the previous section.

Model

The model used in the present work is the same as the one that was developed in our previous work.⁷ However, in that work only a liquid phase and a gas phase were considered. The solid phases that occur in some of the experiments from the present work are assumed to be pure xylose. This is confirmed by the experimental data as shown below. As only equilibria with solid and liquid phases are studied here, the gas phase part of the model is not needed in principle. It is included in the present discussion as it was used for making predictions on VLE based on the present experimental results as described below in more detail.

Acetic acid is assumed to form dimers only in the vapor phase⁷ and xylose is present only as solid or in the liquid phase. All concentrations reported here for vapor phases are overall concentrations, i.e. those obtained disregarding the dimerization.

The LLE was modeled using the isoactivity criterion:

$$x_i' \gamma_i' = x_i'' \gamma_i'' \quad i = W, X, F, AA \quad (2)$$

where x_i' , x_i'' are the mole fractions of the component i in equilibrium in the two liquid phases and γ_i' , γ_i'' are the corresponding activity coefficients normalized according to Raoult's law. $'$ indicates the upper phase and $''$ the lower phase.

The SLE was modeled using the following expression:⁴⁰

$$\ln(x_X \gamma_X) = -\frac{\Delta h_{f,X}}{RT} \left(1 - \frac{T}{T_{f,X}}\right) + \frac{\Delta c_{p,X}}{R} \left(\frac{T_{f,X} - T}{T}\right) + \frac{\Delta c_{p,X}}{R} \ln\left(\frac{T}{T_{f,X}}\right) \quad (3)$$

where x_X is the mole fraction of xylose, γ_X is the activity coefficient of xylose, $T_{f,X}$ is the melting temperature of pure xylose, $\Delta h_{f,X}$ is the enthalpy of fusion of pure xylose at the normal melting temperature of pure xylose, $\Delta c_{p,X}$ is the difference between the heat capacities of the pure liquid

and the pure solid xylose and R is the universal gas constant. $T_{f,X}$, $\Delta c_{p,X}$ (assumed constant⁴¹) and $\Delta h_{f,X}$ were taken from the literature⁴¹ and have the following values: $T_{f,X} = 423.15$ K, $\Delta c_{p,X} = 120$ J/(mol K) and $\Delta h_{f,X} = 31.65$ kJ/mol. Eq. (3) is valid assuming that xylose is in anhydrous form, and that $\Delta c_{p,X}$ is not temperature-dependent.

The VLE for water, furfural, and monomeric acetic acid was modeled as described by Galeotti *et al.*⁷ It is assumed that xylose is non-volatile, i.e. it has a negligible vapor pressure. The vapor pressures of the pure substances water, furfural, and acetic acid are given in Table S3 in the Supplementary Information. The non-ideality of the liquid phase is described with the NRTL model.⁴² The non-randomness parameter $\alpha_{i,j}$ was set to 0.3 for all binary subsystems without acetic acid and to 0.47 for all binary subsystems with acetic acid following our previous work.⁷ The binary interaction parameters $\tau_{i,j}$ were obtained by fitting the following temperature-dependent correlation to the experimental data.

$$\tau_{i,j} = a_{i,j} + \frac{b_{i,j}}{T} \quad (4)$$

For the two binary subsystems (W + F) and (W + AA) all four parameters of the correlation were used and fit to experimental data, while for all other binary subsystems the use of $a_{i,j}$ was sufficient to yield a good description of the equilibrium data, i.e. $b_{i,j}$ was set to zero. Not all parameters that could have been adopted from our previous work⁷ were actually adopted for the present study. This because the previous work⁷ was focused on VLE and the present study is focused on LLE and SLE. The differences are discussed along with the description of the way the parameters were fitted here.

The experimental data used for the fitting of NRTL parameters are reported in Table 2. The binary interaction parameters were obtained from a fit to the corresponding binary data except for the binary interaction parameters $\tau_{X,F}$ and $\tau_{F,X}$ between xylose and furfural and $\tau_{X,AA}$ and $\tau_{AA,X}$ between xylose and acetic acid because of the lack of corresponding binary data. The binary interaction parameters $\tau_{X,F}$ and $\tau_{F,X}$ between xylose and furfural were obtained from a fit to ternary LLE experimental data of the system (W + X + F) of this work. The binary interaction parameters $\tau_{X,AA}$ and $\tau_{AA,X}$ between xylose and acetic acid were adopted from our previous work⁷ in which

they were fitted to VLE in the ternary system (W + X + AA). Unlike the previous work,⁷ the binary interaction parameters $\tau_{W,X}$ and $\tau_{X,W}$ between water and xylose were not set to zero but they were fitted to the corresponding SLE data. These parameters are necessary for an accurate description of the solubility of xylose. The other difference with the previous work⁷ is in the fitting of the interaction parameters $\tau_{W,AA}$ and $\tau_{AA,W}$ between water and acetic acid. In the present work the fitting was done using all the VLE experimental data of the binary system (W + AA) at 20.0 kPa from the previous work,⁷ as done usually, and not only the data having an acetic acid concentration lower than 0.4 mol mol⁻¹.

Table 2: Experimental data used for fitting NRTL parameters.

System	Experimental data	References
W + X	SLE of the binary subsystem at 101.3 kPa	26–28
W + F	VLE and LLE of the binary subsystem at 101.3 kPa	12,16
W + AA	VLE of the binary subsystem at 20.0 kPa	7
X + F	LLE of the ternary system (W + X + F) at 298.15 K and 333.15 K	This work
X + AA	VLE of the ternary system (W + X + AA) at 20.0 kPa	7
F + AA	VLE of the binary subsystem at 49.3 and 88.9 kPa	9

For the fitting of the binary interaction parameters $\tau_{W,F}$ and $\tau_{F,W}$ between water and furfural, a weight of 1 was used for the LLE data and a weight of 0.05 for the VLE data. The SLE, being the focus of this paper, has a higher weight. To ensure that VLE was not completely off, the VLE was added to the fit with a small weight.

For the fit to the SLE data of the binary system (W + X), the temperature was set to the experimental value and the objective function was the sum of the squared relative deviations of the experimental values and the model results for the liquid phase concentration of xylose. For all the fits to VLE and LLE data, a maximum likelihood method was applied in which deviations in the temperature, the pressure as well as in the gas and liquid phase concentration or in the two liquid phases concentration were considered after weighing with the corresponding experimental uncertainties. The fitting of the parameters and the modeling of phase equilibria was realized using the software packages MATLAB (in case of SLE of the ternary system (W + X + F)) and Aspen Plus (in case of all other phase equilibria).

Results and Discussion

To test the experimental method, the LLE of the system (W + F) was studied at 298.15 K and 333.15 K. The experimental results are compared to literature data¹² and the model in the lower part of Figure 1. To make the figure clearer, the experimental results are compared with a single data set from literature. A deviation plot including several data sets from literature is reported for completeness in Figure S2 and Figure S3 in Supplementary Information. In Figure 1 also the VLE of the system (W + F) is shown.

Figure 1: Phase diagram of the system (W + F) at 101.3 kPa. Experimental values: VLE $\circ$ Mains,¹⁶ LLE $\square$ Stephenson,¹² $\bullet$ this work. NRTL model (this work): —.

The NRTL parameters for the system (W + F) are reported in Table 3 together with those for the other binary systems.

Table 3: NRTL parameters.

	$a_{i,j}$	$a_{j,i}$	$b_{i,j}/K$	$b_{j,i}/K$	$\alpha_{i,j} = \alpha_{j,i}$
W + X	1.29480	-1.54200	0.000	0.000	0.30
W + F	3.75496	-3.21520	-55.438	1221.700	0.30
W + AA	-11.37710	7.29431	4318.650	-2532.240	0.47
X + F	3.17074	6.51710	0.000	0.000	0.30
X + AA	3.41027	2.24623	0.000	0.000	0.47
F + AA	0.00045	0.67716	0.000	0.000	0.47

The experimental data of this work agree well with the literature data which shows that the experimental method is suitable for these measurements. The model matches the experimental data also well.

The LLE, SLLE, and SLE experimental results for the ternary system (W + X + F) at 298.15 K and 333.15 K are given in Table 4 and in Table 5. An inversion of the phase order in the LLE was observed: for low xylose mass fraction, the upper phase is water-rich but if a certain xylose concentration is exceeded, the water-rich phase becomes the lower phase. This is due to the fact that increasing the xylose concentration, the water-rich phase increases the density up to higher values than the density of the furfural-rich phase.

Table 4: Experimental data for LLE and SLLE in the system (W + X + F) at $p = 101.3$ kPa.^a For data above the dashed line, the water-rich phase is the upper phase, while for data under the dashed line, the water-rich phase is the lower phase. The last row for each temperature gives the composition of the liquid phases of the SLLE. The solid phase in the SLLE is pure xylose.

T/K	Water-rich phase			Furfural-rich phase		
	$w_W / g\ g^{-1}$	$w_X / g\ g^{-1}$	$w_F / g\ g^{-1}$	$w_W / g\ g^{-1}$	$w_X / g\ g^{-1}$	$w_F / g\ g^{-1}$
298.15	0.9137	0.0000	0.0863	0.0511	0.0000	0.9489
	0.8432	0.0794	0.0774	0.0498	0.0000	0.9502
	0.7799	0.1480	0.0721	0.0457	0.0000	0.9543
	0.6767	0.2601	0.0632	0.0434	0.0000	0.9566
	0.6183	0.3210	0.0607	0.0405	0.0006	0.9589
	0.5412	0.4058	0.0530	0.0358	0.0000	0.9642
	0.4838	0.4687	0.0476	0.0334	0.0032	0.9634
	0.4278	0.5281	0.0441	0.0314	0.0023	0.9663
	0.9071	0.0000	0.0929	0.0830	0.0000	0.9170
	0.7459	0.1791	0.0750	0.0808	0.0002	0.9190
333.15	0.6465	0.2716	0.0819	0.0673	0.0011	0.9316
	0.5582	0.3726	0.0692	0.0676	0.0010	0.9314
	0.4400	0.5036	0.0564	0.0626	0.0007	0.9367
	0.2979	0.6521	0.0500	0.0576	0.0016	0.9408

^a Standard uncertainties: $u(T) = 0.2$ K, $u(p) = 1$ kPa. Relative standard uncertainties: $u_r(w) = 0.02$.

Table 5: Experimental data for the liquid phase in SLE in the system (W + X + F) at $p = 101.3$ kPa.^a The solid phase is pure xylose.

T/K	$w_W / \text{g g}^{-1}$	$w_X / \text{g g}^{-1}$	$w_F / \text{g g}^{-1}$
298.15	0.4489	0.5511	0.0000
	0.4419	0.5444	0.0137
333.15	0.3040	0.6960	0.0000
	0.3022	0.6821	0.0157

^a Standard uncertainties: $u(T) = 0.2$ K, $u(p) = 1$ kPa.
Relative standard uncertainties: $u_r(w) = 0.02$.

The experimental results are plotted and compared to the model in the phase diagrams in Figure 2.

(a)

(b)

Figure 2: Phase diagrams of the system (W + X + F) at 298.15 K (panel (a)) and 333.15 K (panel (b)). $\square$ - - - - $\square$ Experimental tie lines, $\circ$ Experimental solubility of xylose, $\blacksquare$ Feed in L + L region, $\bullet$ Feed in S + L + L region, $\blacktriangle$ Feed in S + L region. — NRTL calculation of tie lines, binodal curve, and solubility of xylose. delimits the S + L + L region.

Five regions are observed in the phase diagrams. The region L represents the homogeneous water-rich liquid, the region L + L represents the region where two liquid phases are in equilibrium: a water-rich and a furfural-rich phase. In the regions S + L, a liquid phase coexists with a solid phase that is pure anhydrous xylose. In the region S + L + L, two liquid phases coexist with this solid. The experimental feed points for the LLE experiments in the L + L region are located on the experimental tie lines, or near to them, indicating a good quality of the sample analysis and experimental procedure. Figure 2 shows that in the furfural-rich phase the concentration of xylose is very low. No xylose or only small amounts of xylose were found in that phase (highest mass fraction 0.032 g g⁻¹, cf. Table 4). Comparing the two panels of Figure 2 reveals that the temperature dependence of the phase behavior of the studied system is very weak; the only noticeable difference is the increase in the solubility of xylose in the (W + F) system with increasing temperature.

The experimental data are well described by the NRTL model, with a slightly better description at 298.15 K. More information on the simulation of the phase equilibria, including numerical results and a statistical evaluation of the deviations is given in the Supplementary Information. The experimental results for the LLE in the ternary system (W + F + AA) and for the quaternary system (W + X + F + AA) at 298.15 K are given in Table 6.

Table 6: Experimental data for LLE in the system (W + X + F + AA) at 298.15 K and 101.3 kPa. The water-rich phase is the upper phase for all three measurements.

Water-rich phase				Furfural-rich phase			
x_W mol mol ⁻¹	x_X mol mol ⁻¹	x_F mol mol ⁻¹	x_{AA} mol mol ⁻¹	x_W mol mol ⁻¹	x_X mol mol ⁻¹	x_F mol mol ⁻¹	x_{AA} mol mol ⁻¹
0.8896	0.0000	0.0526	0.0578	0.5260	0.0000	0.3667	0.1073
0.8661	0.0405	0.0392	0.0542	0.4092	0.0054	0.4613	0.1241
0.9422	0.0000	0.0284	0.0294	0.3639	0.0000	0.5651	0.0710

^a Standard uncertainties: $u(T) = 0.2$ K, $u(p) = 1$ kPa. Relative standard uncertainties: $u_r(x) = 0.02$.

In the LLE measurement with xylose, an amount of 100 g xylose per kg of the two-phase solvent mixture was used. LLE phase envelopes for the systems (W + F + AA) and (W + X + F + AA) at 298.15 K are plotted and compared to the model in Figure 3. In Figure 3, the results of the quaternary system (W + X + F + AA) are projected to the ternary subsystem (W + F + AA) via

mole fractions on a sugar-free basis $x_i^{*'}, x_i^{*''}$ defined as:

$$x_i^{*'} = \frac{x_i'}{x_F' + x_W' + x_{AA}'} \quad i = W, F, AA \quad (5)$$

$$x_i^{*''} = \frac{x_i''}{x_F'' + x_W'' + x_{AA}''} \quad i = W, F, AA \quad (6)$$

This projection makes it possible to plot the data of the quaternary system with a xylose concentration of 100 g xylose per kg solvent together with the data of the ternary system without xylose.

Figure 3: LLE of the ternary system (W + F + AA) at 298.15 K and projection of the LLE of the quaternary system (W + X + F + AA) at 298.15 K to the ternary subsystem (W + F + AA), as explained in the text. Experimental tie lines without xylose: □ ---- □ Heric,²² ○ ---- ○ this work. Experimental tie lines with 100 g xylose in kg solvent: △ ---- △ this work. NRTL model (this work): without xylose —, with 100 g xylose per kg solvent — .

For the ternary system (W + F + AA), the experimental data of this work are in good agreement with the results of Heric.²² Also in this case, to make the figure clearer, the experimental results are compared with a single data set from literature. A deviation plot including four data sets from literature^{22–25} is reported for completeness in Figure S6 and Figure S7 in the Supplementary Information. The addition of 100 g xylose per kg of solvent causes a slight widening of the miscibility gap. The NRTL model predicts the LLE of the ternary system (W + F + AA) reasonably well for low concentrations of AA, but shows considerable deviations between experiment and model for increasing concentrations of acetic acid. The NRTL model predicts also the effect of the addition of xylose to the ternary system fairly well. Quantitative information on the model predictions is

given in the Supplementary Information. Literature VLE data of the ternary system (W + F + AA)⁴³ is compared against model values in Figure 4. The experimental data are well described by the NRTL model.

Figure 4: VLE data of the ternary system (W + F + AA) at 101.32 kPa. Experimental values: • liquid phase, ○ vapor phase, - - - tie lines, Tsirlin.⁴³ NRTL model (this work): —.

Conclusions

The influence of adding xylose to mixtures of water, furfural, and acetic acid was studied. LLE, SLE, and SLLE measurements were carried out at 298.15 K and 333.15 K for the ternary system (W + X + F). The study is interesting for the processing of hydrolysates from lignocellulosic biomass. The LLE of furfural and water depends only weakly on the xylose concentration and xylose is present in the furfural-rich phase only in small amounts. Some LLE measurements were carried out also for the ternary system (W + F + AA) as well as for the the quaternary system (W + X + F + AA) at 298.15 K. The addition of xylose causes a slight increase of the miscibility gap.

A thermodynamic model of the studied system was developed. It follows the approach proposed in the previous work of the authors⁷ and is based on the NRTL model. The model describes the LLE, SLE, and SLLE experimental results of the ternary system (W + X + F) well. The model gives moreover a good prediction of the VLE and LLE of the ternary system (W + F + AA) and of the effect that the addition of xylose to this ternary system has on the LLE. The model is therefore reliable and can be used for the conceptual design of a process for the recovery of furfural from an aqueous solution containing acetic acid and xylose.

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Supporting Information Available

The following files are available free of charge.

- Supplementary Information: In Supplementary Information the composition of feed solutions, both for LLE, SLE, and SLLE measurements of the ternary system (W + X + F) and for the LLE measurements of the quaternary system (W + X + F + AA), are reported. Moreover, all information on the simulation of the phase equilibria, including the pure component vapor pressures, numerical results, and a statistical evaluation of the deviations is given.

This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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Graphical TOC Entry