# Separation of Furfural from Ternary Mixtures

**Ljudmila Fele* and Viktor Grilc**

National Institute of Chemistry, Hajdrihova 19, P.O.B. 660, 1001 Ljubljana, Slovenia

---

Thermodynamic phase diagrams were investigated that play a very important role in designing the separation of furfural from the ternary mixtures furfural + 5-methylfurfural + water and furfural + acetic acid + water. The saturation vapor pressure of 5-methylfurfural in the temperature range from (359.95 to 450.19) K is reported, as well as VLE data for the two binary systems furfural + 5-methylfurfural and furfural + acetic acid at two pressures and LLE data for furfural + 5-methylfurfural + water at room temperature. The activity coefficients at infinite dilution were determined for water in 5-methylfurfural at a few temperatures by using an ebulliometric technique. Binary interaction parameters of UNIQUAC and NRTL local composition models were evaluated in order to simulate the separation of furfural from both ternary mixtures by means of a rectification process. Binary azeotropic points were estimated for the 5-methylfurfural + water system by using both models as well as residue curves of both ternary systems.

---

## Introduction

Furfural has exceptional physical and chemical properties, due to its unsaturated bonds and aldehyde group; therefore, it is commonly used in the chemical and the petroleum refining industries. It is produced from renewable agricultural sources and residues from forest products processing. The conventional furfural manufacturing process is steam digestion of pentosan-containing plant material under elevated pressure. Treatment of the wood chips with steam produces both furfural and small amounts of acetic acid, 5-methylfurfural, and methanol. Therefore, furfural should be recovered from the condensed reactor vapors by means of a sequence of distillation steps[1] or by using an effective extraction process by means of chlorinated hydrocarbons.[2] Extractive condensation is proposed to remove the acetic acid from the predominantly aqueous vapor stream of a furfural reactor by using triethylamine as an extractant.[3] The new furfural production process is using supercritical fluid in order to remove a reactive product immediately from the reactor and to prevent the side reactions.[4]

In this work, the separation of furfural from two ternary mixtures, furfural + 5-methylfurfural + water and furfural + acetic acid + water, was studied. All of the previously mentioned components appear in the furfural production process, when furfural is produced by steam digestion. Furfural as well as 5-methylfurfural forms a heterogeneous pressure maximum azeotrope with water, and both binary systems are partially miscible. The phase diagram of the first ternary system furfural + 5-methylfurfural + water is of type II; that of the other system, namely furfural + acetic acid + water, is of type I.

Because of the scarcity of data and nonideality of the ternary systems, various experiments were conducted in order to obtain reliable data to simulate the appropriate separations unit. Vapor pressure measurements of furfural and 5-methylfurfural were carried out, as well as vapor−liquid equilibria measurements for the binary pairs furfural + 5-methylfurfural and furfural + acetic acid, for which no published data were found. In addition, activity coefficients at infinite dilution were determined for water in 5-methylfurfural by an ebulliometric technique and ternary liquid−liquid equilibrium data of the system furfural + 5-methylfurfural + water at 298 K were measured. The data reduction procedure was performed including phase equilibrium data from the literature in order to evaluate the UNIQUAC and NRTL binary interaction parameters for both ternary systems, which enable the synthesis, design, and optimization of the appropriate separation process. With the aid of $g^E$ thermodynamic models, the azeotropic information was calculated for the binary system 5-methylfurfural + water using the ASPEN PLUS software package and comparison was made with one datum available in the literature.

## Experimental Section

All chemicals used in this work, furfural, 5-methylfurfural, and acetic acid, were chemicals of high purity (>99, >97, and >99.5 mass %, respectively) purchased from Fluka. Furfural and 5-methylfurfural were redistilled before use under vacuum by using a spinning band column. A nitrogen atmosphere was used to protect furfural and 5-methylfurfural from oxidation during the distillation process. The water used was twice distilled. The purity of all chemicals was checked by gas chromatography using a Carlo Erba apparatus model 8130/FID.

The vapor−liquid equilibrium measurements were performed with a Fischer Labodest 602 dynamic ebulliometer with the recirculation of both phases and sampling of both the liquid and vapor phases. Temperature was measured with a digital precision platinum resistance thermometer (Hart Scientific, model 1506), calibrated according to the MIL-STD-45662-A standard with a resolution of 0.0001 K and an accuracy of ±0.005 K. Pressure was measured by a pressure transducer VKH 300, calibrated with an MKS Baratron type 170M and maintained at its set point with an electric pressure controller within ±0.01 kPa. The same apparatus was used to determine both the activity coef-

---

* To whom correspondence should be addressed. E-mail: ljudmila.fele@ki.si. Telephone: + 386 1 4760 220.

10.1021/je020117y CCC: $25.00

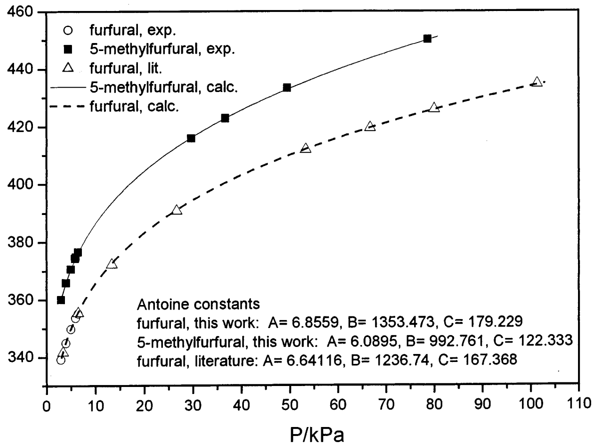

**Figure 1.** Vapor pressure data of furfural and 5-methylfurfural.

ficients at infinite dilution of water in 5-methylfurfural and the vapor pressures of pure furfural and 5-methylfurfural.

The theoretical basis for the direct determination of activity coefficients at infinite dilution via the ebuliometric technique was given by Gautreaux and Coates.[5] They derived analytical expressions, which contain only pure-component properties and the limiting slope of pressure or temperature versus liquid or vapor composition curves. The experimental procedure proposed by Olsson[6] was used in this work. The activity coefficient at infinite dilution is not a directly measured quantity; thus, error propagation was applied to estimate its uncertainty.

Ternary LLE measurements were conducted by using centrifuge tubes. The prepared synthetic mixtures were shaken for 6 h at room temperature, followed by a settling period of 18 h, and final separation of two liquid phases was achieved by centrifuging for 10 min at 3000 rpm. Both liquid phases were sampled and analyzed.

The model mixtures for all experiments were prepared by weighing on an analytical Mettler AT 261 balance with an accuracy of ±0.000 05 g. The amount of water in the initial mixtures and in the samples was determined by Karl Fischer titration (Metrohm 684 KF Coulometer, without the diaphragm); the volatile components were analyzed by gas chromatography using a flame ionization detector and a capillary column HP-FFAP at 423.15 K. The internal standard (propionic acid) method was applied.

## Results and Discussion

The phase equilibrium data available in the literature for the constituent binary systems and subject ternary mixtures are binary LLE[7] data (furfural + water, 5-methylfurfural + water), binary VLE[8,9] data (furfural + water, acetic acid + water), binary azeotropic[10] data (furfural + water, 5-methylfurfural + water), and ternary LLE[11] data for the furfural + acetic acid + water system.

In this work, vapor pressures of pure furfural and 5-methylfurfural were measured in the temperature ranges from (339 to 355) K and from (359 to 450) K, respectively. The experimental vapor pressure temperature dependence was correlated using the Antoine equation:

$$\log_{10} P_i^{\mathrm{S}}/\mathrm{mmHg} = A - B/(C + t/°\mathrm{C}) \qquad (1)$$

Furfural vapor pressure data were in good agreement with DDB (Dortmund Data Bank) data, shown in Figure 1. Unfortunately, no data were available for 5-methylfurfural. The Antoine constants for 5-methylfurfural were determined by a maximum likelihood (ML) procedure and are ($A$ = 6.0895, $B$ = 992.761, and $C$ = 122.333). The experimental and calculated vapor pressure data for furfural and 5-methylfurfural together with the literature data for furfural are shown in Figure 1.

**Table 1. Activity Coefficients of Water in 5-Methylfurfural at Infinite Dilution**

| $T$/K | $\gamma^{\infty}$ |
|---|---|
| 360.38 | 5.24 |
| 365.99 | 5.04 |
| 370.64 | 4.88 |

**Table 2. Experimental VLE Data[a] for the System Furfural (1) + 5-Methylfurfural (2)**

| $T$/K | $x_1$ | $y_1$ | $T$/K | $x_1$ | $y_1$ |
|---|---|---|---|---|---|
| $P$ = 3.49 kPa | | | $P$ = 4.98 kPa | | |
| 342.70 | 1 | 1 | 349.76 | 1 | 1 |
| 343.32 | 0.9761 | 0.9950 | 350.45 | 0.9764 | 0.9924 |
| 344.04 | 0.9653 | 0.9925 | 350.49 | 0.9657 | 0.9891 |
| 345.19 | 0.8822 | 0.9707 | 352.01 | 0.8831 | 0.9624 |
| 346.94 | 0.7522 | 0.9217 | 353.55 | 0.7535 | 0.9103 |
| 348.06 | 0.6950 | 0.8923 | 354.67 | 0.6963 | 0.8803 |
| 352.12 | 0.4780 | 0.7304 | 358.48 | 0.4791 | 0.7201 |
| 353.76 | 0.4093 | 0.6587 | 360.37 | 0.4103 | 0.6497 |
| 354.45 | 0.3768 | 0.6215 | 360.69 | 0.3776 | 0.6142 |
| 355.99 | 0.3027 | 0.5279 | 363.31 | 0.3034 | 0.5210 |
| 358.54 | 0.2034 | 0.3806 | 364.72 | 0.2036 | 0.3794 |
| 361.28 | 0.1176 | 0.2327 | 368.00 | 0.1175 | 0.2335 |
| 362.55 | 0.0734 | 0.1497 | 369.20 | 0.0733 | 0.1510 |
| 363.45 | 0 | 0 | 370.70 | 0 | 0 |

[a] $x_i$, $y_i$ = mole fractions of component $i$ in the liquid and vapor phases, respectively.

**Table 3. Experimental LLE Tie Lines for the System Furfural (1) + 5-Methylfurfural (2) + Water (3) at 298.15 K**

| phase 1 | | phase 2 | |
|---|---|---|---|
| $x_2$ | $x_3$ | $x_2$ | $x_3$ |
| 0.6172 | 0.2123 | 0.0060 | 0.9911 |
| 0.5124 | 0.2014 | 0.0050 | 0.9902 |
| 0.3759 | 0.2056 | 0.0039 | 0.9884 |
| 0.2990 | 0.2097 | 0.0032 | 0.9875 |
| 0.3955 | 0.2059 | 0.0038 | 0.9895 |
| 0.1500 | 0.2189 | 0.0017 | 0.9854 |
| 0.2455 | 0.2047 | 0.0026 | 0.9873 |

Activity coefficients at infinite dilution were determined for water in 5-methylfurfural at the temperatures (360, 366, and 371) K (Table 1), using differential ebulliometry. Activity coefficients of water in 5-methylfurfural are small, and only very slight temperature dependence is observed. Like the binary water + furfural system, the binary system water + 5-methylfurfural also exhibits partial miscibility of components and azeotropy. From an analogy with the water + furfural system, it can be expected that the activity coefficients of 5-methylfurfural in water at infinite dilution will be considerably larger. The experiments with water as the solvent and very small additions of 5-methylfurfural were not successful; the circulation problems were observed in the still associated with high surface tension of water at the measured conditions of (3, 4, 5) kPa.

Vapor−liquid equilibrium measurements of the binary furfural + 5-methylfurfural system at two pressures, (3.5 and 5.0) kPa, were conducted. The data measured are given in Table 2 and are graphically presented in Figure 2 (cigar shape).

Measurements of the LLE of the conjugate phases for the ternary system furfural + 5-methylfurfural + water at 298 K were performed and are reported in Table 3. The phase diagram is type II, as shown in Figure 3.

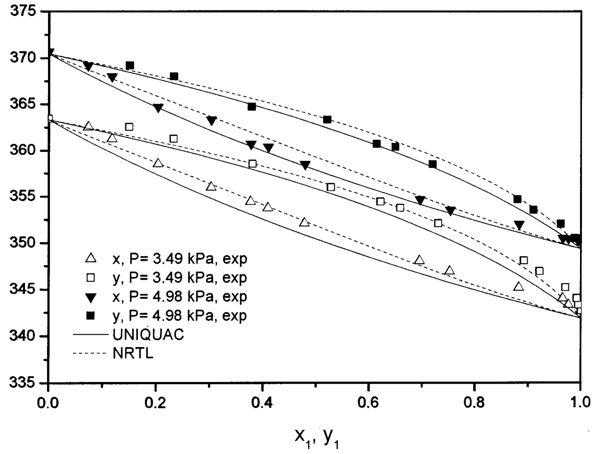

**Figure 2.** Measured and calculated *TPxy* data for the system furfural (1) + 5-methylfurfural (2).

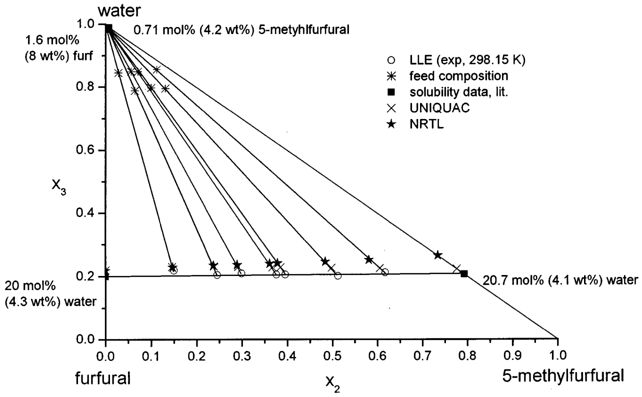

**Figure 3.** LLE data at 298.15 K for the system furfural (1) + 5-methylfurfural (2) + water (3).

**Table 4. Experimental VLE Data[a] for the System Furfural (1) + Acetic Acid (2)**

| $T$/K | $x_2$ | $y_2$ | $T$/K | $x_2$ | $y_2$ |
|---|---|---|---|---|---|
| $P = 49.34$ kPa | | | $P = 88.98$ kPa | | |
| 368.10 | 1 | 1 | 386.07 | 1 | 1 |
| 369.12 | 0.9799 | 0.9936 | 386.95 | 0.9796 | 0.9935 |
| 370.30 | 0.9499 | 0.9863 | 387.79 | 0.9587 | 0.9863 |
| 371.06 | 0.9281 | 0.9819 | 388.47 | 0.9364 | 0.9817 |
| 371.37 | 0.9165 | 0.9771 | 388.90 | 0.9277 | 0.9786 |
| 371.98 | 0.8962 | 0.9760 | 389.94 | 0.9046 | 0.9726 |
| 373.40 | 0.8451 | 0.9614 | 391.67 | 0.8436 | 0.9559 |
| 376.37 | 0.7522 | 0.9369 | 395.03 | 0.7472 | 0.9214 |
| 380.13 | 0.6634 | 0.9016 | 397.05 | 0.6715 | 0.8959 |
| 382.27 | 0.5689 | 0.8606 | 401.03 | 0.5676 | 0.8526 |
| 385.60 | 0.4720 | 0.8046 | 404.86 | 0.4677 | 0.7893 |
| 391.13 | 0.3466 | 0.6973 | 409.60 | 0.3499 | 0.6803 |
| 395.45 | 0.2336 | 0.5655 | 415.08 | 0.2344 | 0.5436 |
| 402.04 | 0.1165 | 0.3431 | 422.33 | 0.1003 | 0.2936 |
| 409.50 | 0 | 0 | 429.50 | 0 | 0 |

[a] $x_i$, $y_i$ = mole fractions of component $i$ in the liquid and vapor phases, respectively.

Binary vapor–liquid equilibrium measurements were also carried out for the binary pair furfural + acetic acid in the second ternary system furfural + acetic acid + water at 49.4 and 89.0 kPa by an ebulliometric technique with sampling of both the vapor and liquid phases. The data are listed in Table 4 and shown in Figure 4.

By including the binary data from the literature[7–10] and ternary LLE data[11] for the ternary system furfural + acetic acid + water, a data reduction procedure was performed in order to evaluate binary interaction parameters of the UNIQUAC and NRTL $g^E$ models for both ternary systems.

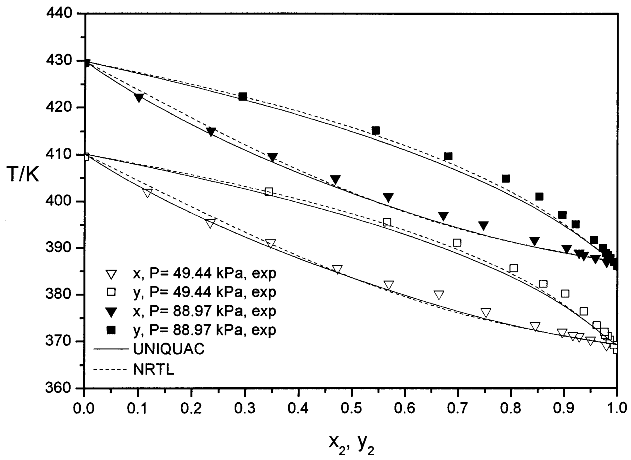

**Figure 4.** Measured and calculated *TPxy* data for the system furfural (1) + acetic acid (2).

**Table 5. UNIQUAC Size and Surface Parameters**

| component | $r$ | $q$ |
|---|---|---|
| furfural | 3.1680 | 2.4840 |
| 5-methylfurfural | 3.9030 | 3.0520 |
| acetic acid | 2.2024 | 2.0720 |
| water | 0.9200 | 1.4000 |

Binary interaction parameters of the furfural + 5-methylfurfural system were obtained by regression on our measured VLE binary data for furfural + 5-methylfurfural at two pressures. Published azeotropic[10] data (AZ1) and solubility[7] and VLE[8] data for the furfural + water system were used to calculate interaction parameters of the binary pair furfural + water. With binary parameters obtained in previous calculations for both mentioned binary systems, the regression procedure was performed on the ternary liquid–liquid equilibrium data of the furfural + 5-methylfurfural + water system, LLE[7] of the binary system 5-methylfurfural + water, and azeotropic[10] data (AZ2) to determine the interaction parameters for the 5-methylfurfural + water system. For the second ternary system (furfural + acetic acid + water) binary interaction parameters of the furfural + acetic acid pair were evaluated from the regression on our experimental binary VLE data. Using the interaction parameters for two binary pairs, furfural + acetic acid and furfural + water, the regression procedure was carried out on binary VLE[9] data of the acetic acid + water system and ternary LLE[11] data of the furfural + acetic acid + water system to derive the binary parameters of the acetic acid + water pair.

Vapor-phase imperfections were taken into account by using the Redlich–Kwong[12] equation of state. The Hayden–O'Connell[13] equation of state is generally proposed for systems containing organic acids that tend to associate in the vapor phase. Since our purpose was to design the separation unit for a mixture with a smaller amount of acetic acid, the association effect was not considered. UNIQUAC[14] and NRTL[15] temperature dependent parameters were employed to account for nonidealities in the liquid phase. The values of the area parameter $q_i$ and the volume parameter $r_i$ in the UNIQUAC equation are shown in Table 5. The ASPEN PLUS data regression option was used with a generalized least-squares method, based on the ML principle.[16] The objective function was used as follows:

$$F = \Sigma_i[(\Delta x_i)^2/\sigma^2_{\ x} + (\Delta y_i)^2/\sigma^2_{\ y} + (\Delta T_i)^2/\sigma^2_{\ T} + (\Delta P_i)^2/\sigma^2_{\ P}], \quad i = 1, n \qquad (2)$$

**Table 6. Values of the UNIQUAC Temperature Dependent Binary Interaction Parameters**

| binary system | $a_{ij}$ | $b_{ij}$/K | $a_{ji}$ | $b_{ji}$/K |
|---|---|---|---|---|
| Furfural (1) + 5-Methylfurfural (2) + Water (3) | | | | |
| furfural (1) + water (3) | 2.1345 | −826.83 | −1.1433 | 244.675 |
| furfural (1) + 5-methylfurfural (2) | 0 | −307.398 | 0 | 234.087 |
| 5-methylfurfural (2) + water (3) | 2.8689 | −1104.191 | −2.0056 | 478.375 |
| Furfural (1) + Acetic acid (2) + Water (3) | | | | |
| furfural (1) + acetic acid (2) | 0 | 340.9738 | 0 | −589.8015 |

**Table 7. NRTL Temperature Dependent Parameters with $\alpha_{ij} = 0.2$**

| binary system | $a_{ij}$ | $b_{ij}$/K | $a_{ji}$ | $b_{ji}$/K |
|---|---|---|---|---|
| Furfural (1) + 5-Methylfurfural (2) + Water (3) | | | | |
| furfural (1) + water (3) | −3.1078 | 964.0374 | 4.4233 | −95.0897 |
| furfural (1) + 5-methylfurfural (2) | 2.0247 | −998.5178 | 1.8907 | −434.5114 |
| 5-methylfurfural (2) + water (3) | −1.8452 | 493.2926 | 4.6579 | 57.5461 |
| Furfural (1) + Acetic acid (2) + Water (3) | | | | |
| furfural (1) + acetic acid (2) | 0 | −782.8670 | 0 | 1292.1934 |
| furfural (1) + water (3) | −3.1078 | 964.0374 | 4.4233 | −95.0897 |
| acetic acid (2) + water (3) | 0 | −654.5973 | 0 | 1056.3549 |

**Table 8. Root-Mean-Square Deviations Calculated for the Furfural (1) + 5-Methylfurfural (2) + Water (3) System and the Binary Systems (UNIQUAC Model)**

| data set[a] | comp | $N$[b] | $\sigma T$[c]/K | $\sigma P$/kPa | $\sigma x_1$(L1) | $\sigma x_2$(L1) | $\sigma x_3$(L1) | $\sigma x_1$(L2) | $\sigma x_2$(L2) | $\sigma x_3$(L2) | $\sigma y_1$ | $\sigma y_2$ | $\sigma y_3$ | $P$/kPa | $T$/K |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| UNIQUAC Temperature Dependent Parameters | | | | | | | | | | | | | | | |
| BIVLE | 1, 2 | 12 | 0.240 | 0.11 | 0.0052 | 0.0052 | | | | | 0.0018 | 0.0018 | | 3.49 | |
| BIVLE | 1, 2 | 12 | 0.164 | 0.17 | 0.0041 | 0.0041 | | | | | 0.0035 | 0.0035 | | 4.98 | |
| TRILLE | 1, 2, 3 | 7 | 0.021 | | 0.0202 | 0.0154 | 0.0211 | 0.0003 | 0.0002 | 0.0004 | | | | | 298.15 |
| BILLE[7] | 2, 3 | 9 | 0.129 | | | 0.0228 | 0.0228 | | 0.0009 | 0.0009 | | | | | 293.15−413.15 |
| AZ1[10] | 1, 3 | 9 | 0.786 | 0.042 | 0.0000 | | 0.0000 | | | | 0.0340 | | 0.0340 | 3.32−101.32 | |
| AZ2[10] | 2, 3 | 1 | 0.224 | 0.020 | | 0.0000 | 0.0000 | | | | | 0.0083 | 0.0083 | 13.33 | |
| BILLE[7] | 1, 3 | 6 | 2.720 | | 0.0193 | | 0.0193 | 0.0010 | | 0.0010 | | | | | 293.15−373.15 |
| BIVLE[8] | 1, 3 | 11 | 1.191 | 1.04 | 0.0388 | | 0.0388 | | | | 0.0174 | | 0.0174 | 101.3 | |
| BIVLE[8] | 1, 3 | 6 | 0.124 | 0.88 | 0.0047 | | 0.0047 | | | | 0.0268 | | 0.0268 | 7.3 | |
| BIVLE[8] | 1, 3 | 7 | 0.374 | 0.69 | 0.0084 | | 0.0084 | | | | 0.0434 | | 0.0434 | 40 | |
| BIVLE[8] | 1, 3 | 9 | 0.393 | 0.396 | 0.0076 | | 0.0076 | | | | 0.0304 | | 0.0304 | 80 | |

[a] AZ1, AZ2 = azeotropic data; BILLE = solubility data; BIVLE = binary VLE data; TRILLE = ternary LLE data. [b] $N$ = number of data. [c] $\sigma$ = root-mean-square deviation.

**Table 9. Root-Mean-Square Deviations Calculated for the Furfural (1) + 5-Methylfurfural (2) + Water (3) System and the Binary Systems (NRTL Model)**

| data set[a] | comp | $N$[b] | $\sigma T$[c]/K | $\sigma P$/kPa | $\sigma x_1$(L1) | $\sigma x_2$(L1) | $\sigma x_3$(L1) | $\sigma x_1$(L2) | $\sigma x_2$(L2) | $\sigma x_3$(L2) | $\sigma y_1$ | $\sigma y_2$ | $\sigma y_3$ | $P$/kPa | $T$/K |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| NRTL Temperature Dependent Parameters | | | | | | | | | | | | | | | |
| BIVLE | 1, 2 | 12 | 0.171 | 0.11 | 0.0024 | 0.0024 | | | | | 0.0014 | 0.00138 | | 3.49 | |
| BIVLE | 1, 2 | 12 | 0.260 | 0.16 | 0.0023 | 0.0023 | | | | | 0.0015 | 0.00152 | | 4.98 | |
| TRILLE | 1, 2, 3 | 7 | 0.400 | | 0.0353 | 0.0417 | 0.0331 | 0.0011 | 0.0004 | 0.0016 | | | | | 298.15 |
| BILLE[7] | 2, 3 | 9 | 0.180 | | | 0.0953 | 0.0953 | | 0.0034 | 0.0034 | | | | | 293.15−413.15 |
| AZ1[10] | 1, 3 | 9 | 0.157 | 0.35 | 0.0000 | | 0.0000 | | | | 0.038 | | 0.038 | 3.32−101.32 | |
| AZ2[10] | 2, 3 | 1 | 0.373 | 0.02 | | 0.0000 | 0.0000 | | | | | 0.0032 | 0.0032 | 13.33 | |
| BILLE[7] | 1, 3 | 6 | 0.038 | | 0.0288 | | 0.0288 | 0.0007 | | 0.0007 | | | | | 293.15−373.15 |
| BIVLE[8] | 1, 3 | 11 | 1.120 | 0.97 | 0.0395 | | 0.0395 | | | | 0.0180 | | 0.0180 | 101.3 | |
| BIVLE[8] | 1, 3 | 6 | 0.129 | 0.92 | 0.00515 | | 0.00515 | | | | 0.0277 | | 0.0277 | 7.3 | |
| BIVLE[8] | 1, 3 | 7 | 0.403 | 0.74 | 0.0098 | | 0.0098 | | | | 0.04367 | | 0.0436 | 40 | |
| BIVLE[8] | 1, 3 | 9 | 0.499 | 0.49 | 0.0069 | | 0.0069 | | | | 0.0308 | | 0.0308 | 80 | |

[a] AZ1, AZ2 = azeotropic data; BILLE = solubility data; BIVLE = binary VLE data; TRILLE = ternary LLE data. [b] $N$ = number of data. [c] $\sigma$ = root-mean-square deviation.

where

$$\Delta J_i = J_i^{\text{calc}} - J_i^{\text{meas}} \quad (J = x, y, T, P) \tag{3}$$

The UNIQUAC and NRTL temperature dependent binary interaction parameters are expressed as follows:

$$\text{UNIQUAC} \qquad \tau_{ij} = \exp(a_{ij} + b_{ij}/T) = \exp(-\Delta u_{ij}/RT) \tag{4}$$

and

$$\text{NRTL} \qquad G_{ij} = \exp(-\alpha_{ij}\tau_{ij}), \quad \tau_{ij} = a_{ij} + b_{ij}/T \tag{5}$$

and are given in the Tables 6 and 7, respectively.

The NRTL $g^{\text{E}}$ model describes binary vapor−liquid equilibria for the furfural + 5-methylfurfural system better than the UNIQUAC model, as can be seen in Figure 2 and Tables 8 and 9, which list the root-mean-square deviations of the measured variables for all binary and ternary data. On the other hand, the UNIQUAC activity coefficient model was more effective in describing the ternary LLE data at 298.15 K. Using UNIQUAC model, good agreement was observed between experimental and calculated binodal curves as well as the tie lines in the triangular diagram (Figure 3).

Because of the scarce azeotropic data available in the literature for the binary system 5-methylfurfural + water, both activity coefficient models were used to predict the azeotropic composition of this system as a function of

**Table 10. Predicted Azeotropic Information for the System 5-Methylfurfural (2) + Water (3)**

| | UNIQUAC temp dep | | | | NRTL temp dep | | | |
|---|---|---|---|---|---|---|---|---|
| $P$/kPa | $T$/K | $y_3$ | $x_3{}^1$ | $x_3{}^2$ | $T$/K | $y_3$ | $x_3{}^1$ | $x_3{}^2$ |
| 13.33 | 324.47 | 0.9820 | 0.9919 | 0.2966 | 324.52 | 0.9822 | 0.9891 | 0.3003 |
| 13.33[a] | 324.05[a] | 0.9720[a] | | | | | | |
| 20 | 332.90 | 0.9785 | 0.9916 | 0.3224 | 332.96 | 0.9784 | 0.9886 | 0.3108 |
| 40 | 348.54 | 0.9725 | 0.9908 | 0.3735 | 348.58 | 0.9713 | 0.9876 | 0.3294 |
| 60 | 358.52 | 0.9693 | 0.9899 | 0.4081 | 358.53 | 0.9670 | 0.9869 | 0.3407 |
| 80 | 366.02 | 0.9672 | 0.9891 | 0.4351 | 365.99 | 0.9640 | 0.9865 | 0.3489 |
| 100 | 372.09 | 0.9657 | 0.9884 | 0.4577 | 372.03 | 0.9616 | 0.9861 | 0.3555 |

[a] Literature data: $x_i{}^i$ = mole fraction of component $i$ in the $i$-th liquid phase; $y_i$ = mole fraction of component $i$ in the vapor phase.

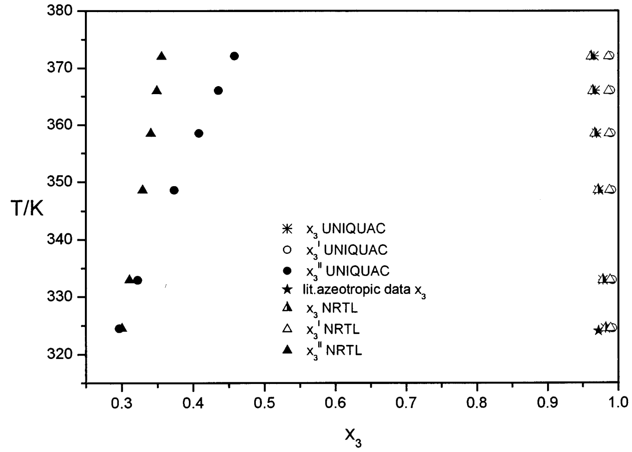

**Figure 5.** Predicted azeotropic composition of the system 5-methylfurfural (2) + water (3) as a function of temperature.

temperature. The azeotrope of the subject binary system is located in the heterogeneous part of the phase diagram with a maximum pressure. The composition of the vapor phase in equilibrium with two liquid phases at different temperatures was calculated by UNIQUAC and NRTL models (Table 10) and shown in Figure 5. It is evident from this figure that both the UNIQUAC and the NRTL models satisfactorily predict a vapor-phase azeotropic composition. Larger discrepancies between the two models were observed for the composition of the organic phase that is rich in 5-methylfurfural at temperatures above 333.15 K. The composition of the aqueous phase is equivalently described by both $g^E$ models.

The NRTL activity coefficient model represents binary vapor–liquid equilibria for the furfural + acetic acid system better than the UNIQUAC model, shown in Figure 4. A thermodynamic consistency area test[17,18] was passed for the subject binary system for both thermodynamic phase equilibria models, but the point test proposed by Van Ness[19] and Fredenslund[20] was not. In Table 6, the UNIQUAC binary interaction parameters of other constituent binary pairs are missing, since the regression performed in the way described above did not give satisfactory results for phase splitting of the ternary system furfural + acetic acid + water or binary vapor–liquid equilibria for acetic acid + water.

Residue curve maps that are a very effective tool for the design of separation processes were determined for both ternary systems at 101.32 kPa using ASPEN PLUS software release 10.2 and are shown in Figure 6. It is evident from Figure 6 that the binary azeotrope furfural + water is the top product at infinite reflux and with infinite number of stages of the rectification column in both cases.

The NRTL binary interaction parameters given in Table 7 were used to study the feasibility of the rectification process for the separation of furfural from the aqueous stream containing both furfural and a small amount of either 5-methylfurfural or acetic acid. The ASPEN PLUS process simulator was adopted, using the Redlich–Kwong method to describe nonidealities in the vapor phase and the NRTL $g^E$ model with temperature dependent binary interaction parameters for the description of the behavior of the liquid phase.

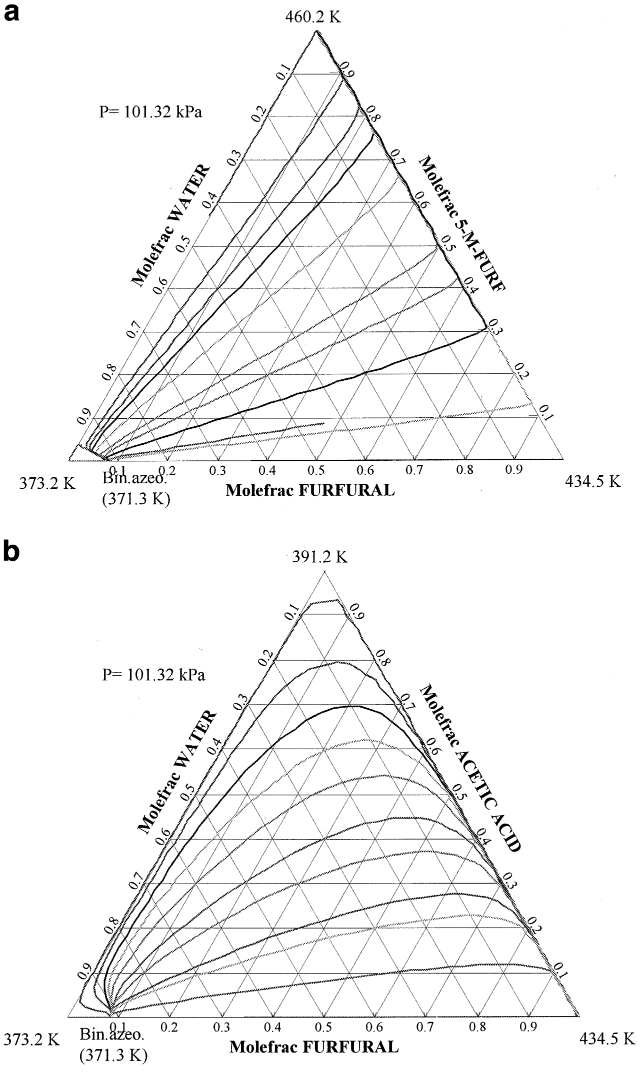

**Figure 6.** Residue curves for both ternary mixtures at 101.32 kPa: (a) NRTL model, furfural + 5-methylfurfural + water system; (b) NRTL model, furfural + acetic acid + water system.

The steady-state simulation of the distillation process was performed in order to demonstrate the applicability of the model parameters given above to meet separation requirements. For this case, the top product contained no 5-methylfurfural or acetic acid and there was a negligible amount of furfural in the bottom product.

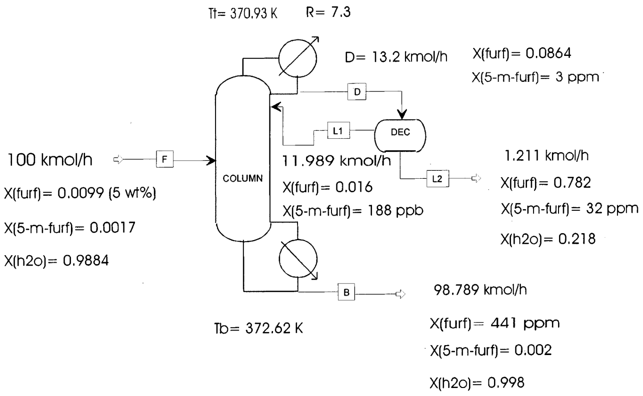

**Figure 7.** Distillation scheme used in the simulation procedure for furfural + 5-methylfurfural + water mixtures ($P = 100$ kPa; $N_t = 29$; $n_{feed} = 12$; model, NRTL-RK; $N_t$ = total number of theoretical stages; $n_{feed}$ = feed location counting upside down).

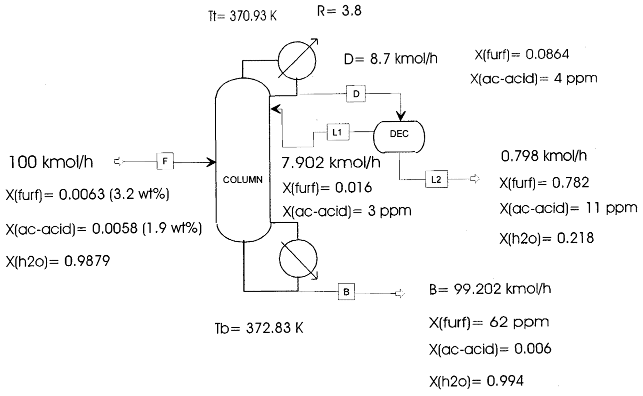

**Figure 8.** Distillation scheme used in the simulation procedure for furfural + acetic acid + water mixtures ($P = 100$ kPa; $N_t = 23$; $n_{feed} = 12$; model, NRTL-RK; $N_t$ = total number of theoretical stages; $n_{feed}$ = feed location counting upside down).

Figures 7 and 8 show that rectification of furfural from an aqueous mixture with a small amount of 5-methylfurfural or acetic acid can be an appropriate method from a separation point of view. Since the composition at the top of the column approaches the heterogeneous binary azeotrope furfural + water that splits into aqueous and furfural streams in the mole ratio of 9.9 to 1, this process may be a very expensive one and unjustified from an economical point of view.

## Conclusions

Pure-component vapor pressures for furfural and 5-methylfurfural were measured together with the following phase equilibrium data: VLE for the binary system furfural + 5-methylfurfural; VLE for the furfural + acetic acid system; and LLE for the ternary system furfural + 5-methylfurfural + water at 298 K. Activity coefficients at infinite dilution were determined for water in 5-methylfurfural by using an ebulliometric technique at the temperatures (360, 366, and 371) K. A very slight temperature dependence was observed.

Antoine constants for furfural and 5-methylfurfural were determined by using a maximum likelihood procedure with the experimental measured data. Furfural vapor pressure data were in good agreement with the DDB data with deviations in pressure less than 1.6%. UNIQUAC and NRTL temperature dependent binary interaction parameters were evaluated by fitting experimental measured data including the literature data. The NRTL model was found to better describe binary vapor−liquid equilibria for furfural + 5-methylfurfural and furfural + acetic acid than the UNIQUAC model. The UNIQUAC model was more effective to describe the ternary LLE data of the furfural + 5-methylfurfural + water system at 298.15 K.

Azeotropic information was derived for the binary system 5-methylfurfural + water on the basis of both activity coefficient models. The azeotrope is located in the heterogeneous part of the phase diagram with a maximum pressure. Satisfactory agreement was obtained between calculated azeotropic information and literature data. Larger discrepancies between the two models were observed for their descriptions of the composition of the organic phase that is rich in 5-methylfurfural at temperatures greater than 333.15 K. A simulation of the column was performed in order to demonstrate the applicability of the model parameters for separation of furfural from both ternary mixtures.

## Acknowledgment

The authors wish to express their gratitude to MŠZŠ (Ministry for Education, Science and Sport of Slovenia) for financial support.

## Literature Cited

(1) Ullmann's Encyclopedia of Industrial Chemistry, 5th Edition, VCH: Weinheim, 1989; Vol A12, pp 122−125.

(2) Cabezas, J. L.; Barcena, L. A.; Coca, J.; Cockrem, M. Extraction of Furfural from Aqueous Solutions Using Alcohols. *J. Chem. Eng. Data* **1988**, *33*, 435−437.

(3) Zeitsch, K. J. Extractive Condensation: A New Separation Process. *Ind. Eng. Chem. Research* **1999**, *38*(10), 4123−4124.

(4) Sako, T.; Sugeta, T.; Nakazawa, N.; Otake, K.; Sato, M.; Ishihara, K.; Kato, M. High-pressure vapor-liquid and liquid−liquid equilibria for systems containing supercritical carbon dioxide, water and furfural. *Fluid Phase Equilibria* **1995**, *108*, 293−303.

(5) Gautreaux, M. F.; Coates, J. Activity Coefficients at Infinite Dilution. *AIChE J.* **1955**, *1*, 496−500.

(6) Olsson, T. Activity Coefficients at Infinite Dilution. Thesis; Lund 1989.

(7) Soerensen, J. M.; Arlt, W. *Liquid−Liquid Equilibrium Data Collection, Binary Systems*; Chemistry Data Series; Dechema: Frankfurt, 1979; Vol. V, Part 1.

(8) Gmehling, J.; Onken, U. *Vapor-Liquid Equilibrium Data Collection, Aqueous − Organic Systems*; Chemistry Data Series; Dechema: Frankfurt, 1988; Vol. 1, Part 1.

(9) Gmehling, J.; Onken, U.; Rarey-Nies, J. R. *Vapor-Liquid Equilibrium Data Collection, Aqueous Systems*; Chemistry Data Series; Dechema: Frankfurt, 1988; Vol. 1, Part 1b.

(10) Gmehling, J.; Menke, J.; Krafczyk, J.; Fischer, K. *Azeotropic Data*; VCH Verlagsgesellschaft: Weinheim, 1994; Part 2.

(11) Soerensen, J. M.; Arlt, W. *Liquid−Liquid Equilibrium Data Collection, Ternary Systems*; Chemistry Data Series; Dechema: Frankfurt, 1980; Vol. V, Part 2.

(12) Redlich, O.; Kwong, J. N. S. On the Thermodynamics of Solutions V. An Equation-of-State. Fugacities of Gaseous Solutions. *Chem. Rev.* **1979**, *44*, 223−244.

(13) Hayden, J. G.; O'Connell, J. P. A Generalized Method for Predicting Second Virial Coefficients. *Ind. Eng. Chem. Process Des. Dev.* **1974**, *14*, 209−216.

(14) Abrams, D. S.; Prausnitz, J. M. Statistical Thermodynamics of liquid mixtures: A new expression for the Excess Gibbs Energy of Partly or Completely Miscible Systems. *AIChE J.* **1975**, *21*, 116−128.

(15) Renon, H.; Prausnitz, J. M. Local Compositions in Thermodynamic Excess Functions for Liquid Mixtures. *AIChE J.* **1968**, *14*, 135−144.

(16) Prausnitz, J. M.; Andersen, T. F. *Computer Calculations for Multicomponent Vapor Liquid and Liquid Liquid Equilibria*; Prentice Hall: Englewood Cliffs, NJ, 1980.

(17) Redlich, O.; Kister, A. T. Algebraic Representation of Thermodynamic Properties and the Classification of Solutions. *Ind. Eng. Chem.* **1948**, *40*, 345−348.

(18) Gmehling, J.; Onken, U. Vapor-Liquid Equilibrium Data Collection; Chemistry Data Series; DECHEMA: Frankfurt, 1977−1982.

(19) Van Ness, H. C.; Byer, S. M.; Gibbs, R. E. Vapor-Liquid Equilibrium: Part I. An Appraisal of Data Reduction Methods. *AIChE J*. **1973**, *19*, 238−244.
(20) Fredenslund, A.; Gmehling, J.; Rasmussen, P. *Vapor-Liquid Equilibria Using UNIFAC.*; *A Group-Contribution Method*; Elsevier: Amsterdam, 1977.
(21) Aspen Plus User Manual, Aspen Technology Inc., Cambridge, MA 1996.
(22) Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The Properties of Gases and Liquids*, 4th ed.; McGraw-Hill: New York, 1988.

Received for review June 19, 2002. Accepted January 15, 2003.

JE020117Y