



Experimental and calculated liquid–liquid equilibrium data for water + furfural + solvents

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ABSTRACT

Liquid–liquid equilibrium data for water + furfural + ethyl or propyl acetate are reported at 288.2, 303.2 and 318.2 and atmospheric pressure (≈ 95 kPa). The systems present type II phase diagrams, since water is partially miscible with furfural and esters. In order to obtain more general water + furfural interaction parameters, NRTL and UNIQUAC models were utilized to correlate data determined in this work and data for 13 systems previously reported. The models correlate well the obtained tie lines and NRTL presents better performance than UNIQUAC.

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1. Introduction

Furfural is an important chemical in petroleum industry and in several chemical processes, where it is used as extraction solvent for lube oil refining, in pharmaceuticals, in the manufacture of phenolic resins, as intermediate in the manufacture of nylon, lubricants, adhesives, solvents and plastics [1–4]. Also, furfural is one of the byproducts of cellulose industry, which concentrated liquor contains amounts of furfural together with water [5].

Furfural is prepared by biomass digestion, forming a dilute aqueous solution [1,6]. Separation of furfural from this solution can be performed by distillation, adsorption or liquid extraction. However, since an azeotrope is formed at 0.35 furfural mass fraction, distillation is rather expensive; besides, there are some difficulties to desorb furfural from the adsorbents [7]. In this way, liquid extraction can be an economically attractive option.

Up to date, tie lines and binodal curves for water + furfural + solvent were reported with a few solvents: trichloroethylene, perchloroethylene, 1,2-dichloroethane, 1,1,1-trichloroethane and 1,1,2-trichloroethane at 298.15 K [6]; 2-methyl-2-butanol and 2-ethyl-1-hexanol at 298.15 K [1]; and 1-butanol between 298.15 and 398.15 K [11]. Some articles

reported only binodal curves using ethyl acetate at 298.15 K [13], methyl-isobutyl-ketone at 298.15 K [8]; acetic acid at 299.85 K [9]; methyl-isobutyl-ketone, toluene and isobutyl acetate at 303.15 K [10]. Other work reported only tie lines using 5-methylfurfural as solvent at 298.15 K [12]. The extraction of furfural from aqueous acetic acid solutions with ionic liquids $[C_4mim][PF_6]$, $[C_6mim][PF_6]$, and $[C_8mim][PF_6]$ was also published [4]. Quaternary systems employing two solvents are also presented in literature [14].

In this work, experimental liquid–liquid equilibrium data were determined for water + furfural + ethyl acetate at 288.2, 303.2 and 318.2 K, and water + furfural + propyl acetate at 288.2 and 303.2 K. Water + furfural + 1-butanol at 298.2 K was employed as validation system. Density and refractive index measurements were performed to quantify the composition of equilibrium phases. In the theoretical section, tie line data determined in this work and in previously published articles were used as input to estimate general parameters for NRTL and UNIQUAC models.

2. Experimental

2.1. Materials

The physical properties of the utilized compounds are shown in Table 1. The chemicals were used as received and distilled water was produced in our laboratory. The properties of furfural and propyl acetate were not found in the open literature, except for the density of propyl acetate at 303.2 K.

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Table 1
Properties of the compounds.^a

			Compound				
			Water	Furfural	1-Butanol	Ethyl acetate	Propyl acetate
Supplier				Fluka	Merck	Sigma–Aldrich	Sigma–Aldrich
Purity mass fraction				>0.99	>0.995	>0.995	>0.998
M (g mol ⁻¹)			18.01	96.08	74.12	88.11	102.13
ρ (kg m ⁻³)	$T=288.2$ K	exp	999.105	1165.243	813.820	906.89	894.325
		lit	999.1 ^b		813.373 ^d	906.48 ^e	
	$T=303.2$ K	exp	995.661	1149.766	802.407	888.196	877.529
		lit	995.647 ^b		801.923 ^d	887.5 ^f	876.7 ^g
	$T=318.2$ K	exp	990.170	1133.829	790.724	869.522	860.512
		lit	990.21 ^b		790.231 ^d	869.52 ^e	
n	$T=288.2$ K	exp	1.3334	1.5280	1.4013	1.3749	1.3866
		lit	1.33334 ^c		1.40135 ^d	1.37519 ^e	
	$T=303.2$ K	exp	1.3319	1.5206	1.3952	1.3672	1.3792
		lit	1.33196 ^c		1.39523 ^d	1.3671 ^f	
	$T=318.2$ K	exp	1.3298	1.5133	1.3892	1.3594	1.3717
		lit	1.32993 ^c		1.38901 ^d	1.35919 ^e	1.3807 ^g

^a Maximum standard and combined standard uncertainties, u and u_c , are: $u(T)=0.1$ K, $u(\rho)=0.04$ kg m⁻³, $u(n)=0.0002$.

^b Ref. [15].

^c Ref. [16]; n at 288.2 K was estimated by a quadratic extrapolation.

^d Ref. [17].

^e Ref. [18].

^f Ref. [19].

^g Ref. [20].

2.2. Binodal curves

Experiments for determination of binodal curves and tie line data were carried out as shown in previous articles [21,22]. Equipment used in this work: analytical balance (Shimadzu AS200, ± 0.1 kg precision), glass equilibrium cells, stirrers (Fisatom 152 A) thermostatic bath (Tecnal TE-184, ± 0.1 K precision), circulating fluid (water), septa, and sample syringes (Braun Injekt, 3 mL).

Two binodal curves were determined, one for organic and another for aqueous-rich side of immiscibility region. For the organic side, water was added to a furfural+solvent mixture until a constant, faint turbidity is reached; for the aqueous side, solvent was added to a furfural+water mixture. Using the analytical balance, a densimeter (U-tube Anton-Paar DMA 5000, $\pm 5 \times 10^{-3}$ kg m⁻³ precision) and a refractometer (Mettler Toledo RE40D, $\pm 1 \times 10^{-4}$ precision), the mass of each component, the density ρ and the refractive index n of the turbid mixture were measured. This method gives the profile (equations) of one physical property (ρ or n) as a function of composition. We adjusted simple plane equations of the type $z = a + bx + cy$ with these data, where z is the physical property; a , b and c are constants; x and y are compositions (mass or molar fractions). These equations are shown in Section 4.1.

2.3. Liquid–liquid equilibria

Systems treated in this work present the same mechanical behavior of those previously reported [21,22]. Agitation and separation times were of 6 and 12 h, respectively, in order to achieve equilibrium.

Tie line compositions were determined by equations obtained from binodal curve data treatment, as cited above. Densimetry and refractometry were used to determine water and furfural concentration simultaneously. The solvent concentration was determined by difference.

3. Thermodynamic modeling

Two well-known models were used to correlate the obtained data and data already published in literature concerning LLE for water + furfural + solvents [1,6,11–13]. These data were added in order to obtain more general binary parameters for water + furfural, which are common for these systems.

The non-random two-liquid model (NRTL) [23], based on the local composition concept, was used to correlate experimental data. NRTL equations are given by:

$$\ln \gamma_i = \frac{\sum_j \tau_{ji} G_{ji} x_j}{\sum_k G_{ki} x_k} + \sum_j \frac{x_j G_{ij}}{\sum_k G_{kj} x_k} \left[\tau_{ij} - \frac{\sum_k x_k \tau_{kj} G_{ki}}{\sum_k G_{kj} x_k} \right] \quad (1)$$

$$\tau_{ij} = \frac{\Delta g_{ij}}{RT} = A_{ij} + \frac{B_{ij}}{T} (\tau_{ij} \neq \tau_{ji}) \quad (2)$$

$$G_{ij} = \exp(-\alpha_{ij} \tau_{ij}) (\alpha_{ij} = \alpha_{ji}) \quad (3)$$

The universal quasi-chemical model (UNIQUAC) [24], an extension of the quasi-chemical theory from Guggenheim [25] for non-random mixtures of different size components, was also used to correlate experimental data. UNIQUAC equations are given by:

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \quad (4)$$

$$\ln \gamma_i^C = \ln \left(\frac{\Phi_i}{x_i} \right) + \frac{z}{2} q_i \ln \left(\frac{\theta_i}{\Phi_i} \right) + l_i - \frac{\Phi_i}{x_i} \sum_{j=1}^c x_j l_j \quad (5)$$

$$\ln \gamma_i^R = q_i' \left[1 - \ln \left(\sum_{j=1}^c \theta_j' \tau_{ji} \right) - \sum_{j=1}^c \left(\frac{\theta_j' \tau_{ij}}{\sum_{k=1}^c \theta_k' \tau_{kj}} \right) \right] \quad (6)$$

$$\Phi_i = \frac{x_i r_i}{\sum_{i=1}^c x_i r_i} \quad (7)$$

$$\theta_i = \frac{x_i q_i}{\sum_{i=1}^c x_i q_i}; \quad \theta_i' = \frac{x_i q_i'}{\sum_{i=1}^c x_i q_i'} \quad (8)$$

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