Liquid–liquid equilibria for the extraction of furfural from aqueous solution using different solvents

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A B S T R A C T

Liquid-liquid equilibria data are reported for the furfural-water system with p-xylene and also toluene as solvents at 298.15 and 323.15 K. Other solvents including methyl iso-butyl carbinol (MIBC) at 298.15 K, benzyl alcohol and acetophenone at 323.15 K have been investigated as well. The distribution coefficient and selectivity were calculated according to the LLE data. Both the NRTL and the UNIQUAC models were successfully applied to fit the data for these five ternary systems. All the root mean square deviation (RMSD) values of the two models were less 0.01.

1. Introduction

Furfural is a highly versatile and key derivative used in the manufacture of a wide range of important chemicals where it is used as a solvent for extractive refining of lubricating oils, as a raw material for pharmaceuticals and phenolic resins, as well as an intermediate in the manufacture of lubricants, nylon, adhesives, plastics and solvents [1–3].

Furfural can be produced by digestion of cellulose wastes with steam and sulfuric acid in the range of temperatures between 413.15 and 458.15 K, pressure between 3.5 and 10 atm, forming a dilute aqueous solution [4]. Solubility of furfural in water is limited to less than 8.3 wt % at 293.15 K. Separation of furfural from this solution can be performed by azeotropic distillation, supercritical CO_2 extraction, adsorption, organic solvent extraction, and membrane separation. However, separation of furfural from aqueous mixtures by azeotropic distillation is of large investment and high energy consumption [5]. The supercritical CO_2 extraction technology is still in the experimental stage due to its high equipment

investment and operating cost [6]. Besides, the adsorption separation and the membrane separation technology are limited to a certain concentration of the solution and difficult to realize mass production [7,8]. In this way, liquid–liquid extraction of furfural appears as the most convenient choice for furfural upgrading at the moment. To facilitate development of furfural extraction units, many different solvents including chlorinated hydrocarbons, various aliphatic alcohols and aliphatic ketones have been studied for their ternary liquid–liquid equilibria with water and furfural [9,10].

As a result of the limited solubility of furfural in water, phase splitting occurs easily at high content of furfural in aqueous solution. In this work, low concentration of furfural in aqueous solution is studied which is practical and meaningful. Experimental liquid-–liquid equilibrium data were determined for five systems, including water + furfural + p-xylene and also toluene at 298.15 and 323.15 K, water + furfural + methyl iso-butyl carbinol (MIBC) at 298.15 K, water + furfural + benzyl alcohol and acetophenone at 323.15 K as well. Considering the similar density of benzyl alcohol and acetophenone with water, a higher temperature of 323.15 K was used to speed up the molecular motion which greatly shortened the time to reach the equilibrium. To the best of our knowledge, all the LLE data determined in this paper have not been

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List of symbols

g, u	interaction parameters
D	the distribution coefficient
S	the separation factor
M	number of tie lines
OF	objective function
RMSD	root mean square deviation
R	volume parameter in UNIQUAC equation
Q	area parameter in UNIQUAC equation or randomly varying quantity described by a probability distribution
$\bar{q}$	arithmetic mean of n independent repeated observations q_k of randomly-varying quantity q
q_k	kth independent repeated observation of randomly-varying quantity q
$s(\bar{q})$	experimental standard deviation of the mean q, equal to the positive square root of $s^2(\bar{q})$
$s(q_k)$	experimental standard deviation, equal to the positive square root of $s^2(q_k)$
$s(\bar{X}_i)$	experimental standard deviation of input mean X_i, equal to the positive square root of $s^2(\bar{X}_i)$
$u(x_i)$	standard uncertainty of input estimate x_i that estimates input quantity X_i
x_i	mole fraction composition of liquid phase or estimate input quantity Xi in u(xi)
X_i	i th input quantity on which the measurand depends
$\bar{X}$	$_i$ estimate of the value of input quantity X_i

Greek letter

A	non-randomness factor in NRTL equation

Superscripts

ˆ	calculated

Subscript

i, j	component identification: 1 pertains to water, 2 to furfural, and 3 to the organic solvent
α, β	component identification: α for the aqueous phase, β for the organic phase
k	number of the tie line

reported up to now. Tie-lines were determined for the ternary systems according to the LLE data. The distribution coefficient and separation factor were calculated and were used as the standard to evaluate the separation efficiency. The experimental data were also correlated with Non-Random Two Liquids (NRTL) [11] and Universal Quasi-Chemical (UNIQUAC) [12] activity coefficient models.

2. Experimental

2.1. Materials

Materials such as furfural, p-xylene, toluene, methyl iso-butyl carbinol, benzyl alcohol and acetophenone were purchased from Sinopharm Chemical Reagent. Double distilled water was employed throughout. All the chemicals were used without further purifications. The major information of the used chemicals were displayed in Table 1.

2.2. Apparatus and procedure

LLE data for the studied ternary system were obtained at desired temperature under atmospheric pressure. The details about experimental equipment have been presented in our previous work and the reliability of the experimental system has been evaluated [13]. The agitation and settling time were investigated, demonstrating that 3 h was enough for furfural in water and solvents to reach liquid−liquid equilibrium. Therefore, this mixture was agitated vigorously for at least 1 h and left for at least 4 h before GC

measurements. Moreover, the air in the still was replaced by N_2 in order to prevent the oxidation of furfural. The evaporated compounds were completely condensed by the condenser to ensure the mass balance.

In each measurement, the samples were carefully withdrawn by syringes from the organic phase and the aqueous phase, respectively. The internal standard method was used to obtain quantitative results in the analysis, and isopropanol was chosen as the internal standard substance. The Agilent GC6820 gas chromatograph equipped with a thermal conductivity detector and Porapak N column (3 mm × 3 m) was used to analyze the composition of both phases. Hydrogen was used as the carrier gas at the rate of 60 mL/min. The temperatures of the injector and the detector were maintained at 523.15 K. After 1 min of holding at 373.15 K, the column temperature was raised to 376.15 K at a rate of 0.5 K/min, afterwards raised to 523.15 K and maintained at this temperature

Table 2
UNIQUAC structural parameters (r and q).

Component	r	q
Deionized water	0.9200	1.3997
Furfural	3.1681	2.4840
p-Xylene	4.6579	3.5360
Toluene	3.9228	2.9700
Benzyl alcohol	4.4832	3.4864
Acetophenone	4.6941	3.6080
Methyl iso-butyl carbinol	4.8016	4.1240

Table 1
Materials description.

Component	CAS	Source	Reported GC purity (mass%)	GC Purity (mass%)
Double-distilled water	7732-18-5	Self-made		99.91
Furfural	98-01-1	Sinopharm	≥99.0	99.46
p-Xylene	106-42-3	Sinopharm	≥99.0	99.53
Toluene	108-88-3	Sinopharm	≥99.5	99.91
Methyl iso-butyl carbinol	108-11-2	Sinopharm	≥99.0	99.49
Benzyl alcohol	100-51-6	Sinopharm	≥99.0	99.57
Acetophenone	98-86-2	Sinopharm	≥99.5	99.85