Quaternary and ternary LLE measurements for solvent (2-methyltetrahydrofuran and cyclopentyl methyl ether) + furfural + acetic acid + water between 298 and 343 K

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A B S T R A C T

The suitability of two promising solvents for the extraction of furfural from aqueous streams is assessed through novel quaternary and ternary liquid-liquid equilibria data for mixtures of solvent (2-methyltetrahydrofuran or cyclopentyl methyl ether) + acetic acid + furfural + water. The measured data between 298 and 343 K at atmospheric pressure are reported along with regressed binary interaction parameters for UNIQUAC-HOC activity coefficient model and further analyzed through distribution coefficients and selectivity for both acetic acid and furfural. Cyclopentyl methyl ether shows promising characteristics towards selective furfural extraction from a stream containing both studied solutes. Distribution coefficients below 1 are observed for acetic acid and as high as 9 for furfural in the quaternary mixtures.

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1. Introduction

There is a growing demand for more active use of bio-based materials and chemicals due to the increasing concerns for the environment and the increasing greenhouse gas emissions produced by the fossil-source based production methods. To facilitate this goal, various bioprocesses have been studied for the production of chemicals that could substitute fossil-based matter in synthesis of, for example, pharmaceuticals, solvents and even fuels. One bio-component that has received increasing attention is furfural, which can be produced from xylose via dehydration in bioreactors. Furfural production is hindered by decomposition [1–3] as well as the side-reactions furfural undertakes in reactor conditions [4]. Furfural is utilized in the industry as a solvent for lubrication oil production industry [5] and as a raw material for some pharmaceuticals [6]. There have also been suggestions for its potential in production of biofuels [7].

Additionally, an industrial furfural product streams consist mostly of water with circa 5–10 w-% furfural content with a similar weight of acids in the streams. To separate furfural from these streams, various unit operations like membrane separation, adsorption or liquid-liquid extraction have been suggested.

Majority of current industrial processes use steam distillation to separate furfural. However, this is energy intensive and limited by the minimum boiling azeotrope between furfural and water. Membrane processes have shown promise for the separation; however, their maturity is not yet at a stage where large scale industrial applications are reasonable. Adsorption is a promising technology as well; however, majority of the studies focus mostly on the absorption research, leaving the desorption research somewhat lacking. Liquid-liquid extraction has been proposed to be currently the most energy efficient method for furfural removal from aqueous streams through either biphasic reactors or extraction units.

To facilitate liquid-liquid extraction, the liquid-liquid equilibria of various solvents with furfural has been studied to determine their ability for selective furfural extraction. Various other solvents ranging from ionic liquids [8] to alcohols [9] and other solvents [10–12] have also been studied for the extraction of furfural from aqueous ternary mixtures. Such solvents as MTBE [13] (methyl tertbutyl ether), TAME [14] (*tert*-amyl methyl ether), MIBK [15] (methyl isobutyl ketone), 2-MTHF [16] (2-methyl tetrahydrofuran) and CPME [16] (cyclopentyl methyl ether) have shown great promise in our previous studies, however study of ternary systems involving furfural is not enough alone – the acid content of the feed needs to be addressed as well. To this end, ternary and quaternary measurements involving both furfural and acetic acid with the solvents and water provide necessary data for accurate solvent assessment. CPME has additionally been reported to have a low

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tendency for peroxide formation, an issue often met when dealing with ethers, and a relatively good stability in acidic conditions [17].

In our earlier work with TAME [14], the ternary system with acetic acid shows a tendency towards concentrating the acid in the aqueous phase, which is a desired feature for the solvent. Due to the high affinity of CPME for furfural shown in earlier work [16], determination of the behavior of the two solvents studied in that work (2-MTHF and CPME) towards acetic acid is paramount. This work provides novel quaternary and ternary LLE data and model parameters along with distribution factors and selectivities for studied solutes in 2-MTHF and CPME. The obtained data is compared to other solvents to assess the suitability of 2-MTHF and CPME to furfural extraction in ternary and quaternary mixtures.

2. Experimental section

2.1. Materials

All the chemicals used were purchased from Sigma-Aldrich, except for the analytical acetone, which was purchased from Merck and the water, which was purified in-house with a Millipore Milli-Q system. Manufacturer reported purities were checked with a gas chromatograph analysis. The manufacturer specified furfural (CAS: 98-01-1, MW: 96.08 g/mol) at a purity of 99 wt-%, and it was further distilled to obtain a purity of 99.90 wt-%. 2-MTHF (CAS: 96-47-9, MW: 86.13 g/mol) was specified at a purity of 99.5 w-%, CPME (CAS: 5614-37-9, MW: 100.16 g/mol) at 99.9 wt-% and acetic acid (CAS: 64-19-7, MW: 60.05 g/mol) at 99.8 wt-%. The analyzed purities for these components were 99.92 wt-%, 99.95 w-% and 99.58 wt-% respectively. The purity of the components was deemed appropriate and they were used as is. Karl Fischer titration was used to determine the water content of the components prior

to standard preparation. The purities of the components were additionally verified with a Dr. Kernchen Abbemat digital automatic refractometer. Sample and standard preparation was done gravimetrically with a Precisa 410AM-FR analytical balance with a reported uncertainty of 0.002 g. Purities and refractive indices of the components have been gathered to Table 1.

The refractive index for 2-MTHF is on the lower limit of the range of the available literature data, the nD for CPME is on the high limit of the range available in the literature data, both nD are however still within the literature range. For acetic acid, the nD differs somewhat from the literature. The difference in the refractive index for acetic acid can be explained with the moisture of acid. The moisture affects the response factor of acetic acid but not the aqueous LLE measurement because the both liquid phases are analyzed. The effect of moisture content on response factor is less than the uncertainty of response factor of acetic acid. The vapor pressures of both solvents were measured using a recirculation still [31] in the range of 320–380 K to verify the purity of the solvents and are presented in Table 2 and Fig. 1. The solvents were dried with 3 Å molecular sieve prior to the vapor pressure measurement. The effect of moisture of solvents in response factors is much less than in case of acetic acid and does not affect the LLE measurement of aqueous system.

2.2. Equipment and procedure

The ternary and quaternary liquid-liquid equilibria measurements were performed in a four-cell static thermostated apparatus with shaker-type mixer presented in our earlier work[13]. Various compositions of the mixtures were prepared within the cells in temperatures ranging from 298 to 343 K. The uncertainty for temperature in the apparatus has earlier been determined to be u(T/K) = 0.2 K. Fig. 2 presents a schematic diagram of the apparatus.

Table 1
Used Chemicals and Their Reported and Measured GC Purities (wt.%), Refractive Indices (nD^{25}) and Water Contents (wt.%) Measured at 101.3 kPa.[a]

chemical	reported GC purity	measured GC purity	n$_D^{25}$ measured	n$_D^{25}$ ref [18]	water content[c]
2-methyltetrahydrofuran	99.5	99.92	1.40299	1.4017–1.4102 [19–25]	0.032
cyclopentyl methyl ether	99.9	99.95	1.41833	1.4183–1.4206 [26]	0.017
acetic acid	99.8	99.58	1.37203	1.3698 [27]	0.193
furfural	99	–	–	1.52345 [28]	–
furfural (Distilled)	–	99.90	1.52364	1.52345 [28]	0.001
de-ionized water	–	–	1.3325	1.3325 [29]	–
analytical acetone	–	99.93	1.3555	1.35596 [30]	0.000

[a] Refractive indices measured in atmospheric pressure and room temperature, standard uncertainty (u) reported by the refractometer manufacturer u(n$_D$) = 0.0005 and u(T/K) = 0.03. Determined uncertainties are u(w) = 0.05, u(p/kPa) = 2.7. [b]Reference retrieved from DIPPR 801 project [18], except for CPME and acetone, which were obtained from Reaxys database [26] and direct literature respectively. [c]Water content was measured for the solvents with KF titration and the determined uncertainties were u(w$_{water, 2-MTHF}$-%) = 0.013, u(w$_{water, CPME}$-%) = 0.009, u(w$_{water, Furfural}$-%) = 0.001, u(w$_{water, HAc}$-%) = 0.004.

Table 2
Vapor Pressures for 2-Methyltetrahydrofuran and Cyclopentyl Methyl Ether.[a]

2-Methyltetrahydrofuran		Cyclopentyl methyl ether	
T/K	p$_{vapour}$/kPa	T/K	p$_{vapour}$/kPa
352.84	100.8	377.89	99.8
350.53	93.8	374.39	90.0
347.21	84.4	369.78	78.3
341.54	70.1	366.69	71.1
337.97	62.1	363.57	64.4
327.67	43.0	356.30	50.7
323.22	36.4	350.40	41.4
		345.38	34.6
		340.92	29.4

[a] The standard uncertainties are u(T) = 0.05 K, where calibration uncertainty is 0.02 K, the rest 0.03 K comes from fluctuation of the measurement. u(p) = 0.10 kPa, where reported uncertainty is 0.07 kPa, the rest comes from fluctuation.