Liquid–Liquid Equilibria of the Ternary Systems 3-Methyl-1-butanol + Ethanol + Water and 2-Methyl-1-propanol + Ethanol + Water at 293.15 K

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Liquid–liquid equilibrium (LLE) data for the ternary systems 3-methyl-1-butanol + ethanol + water and 2-methyl-1-propanol + ethanol + water were measured at 293.15 K and atmospheric pressure. The NRTL and UNIQUAC models were used to correlate the experimental data. Good agreement was obtained with both models.

Introduction

The production of neutral spirit with multistage distillation columns requires the removal of all ethanol fermentation congeners. Fusel oils (mixture of higher alcohols such as propyl, butyl, and amyl alcohols and their isomers) are the more important congeners. The relative volatility to ethanol of higher alcohols in aqueous ethanol solutions depends on ethanol mole fraction in the liquid, and it falls from more than 1 at lower mole fractions to less than 1 at high mole fractions. Due to the reversal of the relative volatility, these compounds have a tendency to concentrate on the trays where their relative volatility to ethanol is equal to 1.[1] To avoid a build-up of these impurities into the column, it is necessary to withdraw them from where they accumulate: on the tray where the ethanol mole fraction is around 0.34 for amyls and butyl alcohols and around 0.54 for propanol.[2] It is possible for the lower extraction rich in amyl alcohols to recover the ethanol using the fact that these compounds have a low miscibility in water. Indeed, water is added to the extraction, and the separation of an organic phase rich in isoamyl alcohol (3-methyl-1-butanol) and isobutyl alcohol (2-methyl-1-propanol) from the aqueous phase rich in water is made in a simple stage decanter.[3] Design of this extraction operation requires quantitative estimates of the liquid–liquid equilibrium properties of the fluid mixture.[4] Such estimates should be based on reliable experimental data for the mixture.

Examination of the literature on the liquid–liquid equilibrium (LLE) gives few data. For the ternary system 3-methyl-1-butanol + ethanol + water, Aznar et al.[5] gives three tie-lines at 298.15 K; Bonner[6] gives three tie-lines at 273.15 K; and Tegtmeier and Misselhorn[7] give only the solubility curve at 303.15 K without tie lines. For the system 2-methyl-1-propanol + ethanol + water, only Bonner[6] gives data for tie lines at 273.15 K. These data are insufficient for understanding the extraction process.

In this work, liquid–liquid equilibrium data have been measured for the two ternary systems 3-methyl-1-butanol + ethanol + water and 2-methyl-1-propanol + ethanol + water at 293.15 K and atmospheric pressure. Experimental results have been correlated using the NRTL[8] and UNIQUAC[9] models. The results are also compared with the data of the literature and presented on rectangular diagrams.

Experimental

Chemicals. All chemicals used in this work are analytical grade. The purities were checked with gas chromatography, and the chemicals were used without any other purification. Suppliers and mass percent purities were as follows: ethanol (Carlo Erba Reagenti, 99.8 %), 1-butanol (Carlo Erba Reagenti, 99.5 %), 1-propanol (Carlo Erba Reagenti, 99.5 %), 2-methyl-1-propanol (Fisher Chemicals, 99.9 %), and 3-methyl-1-butanol (VWR, 99.7 %). The water used was ultrapure (Millipore, Elix3, resistivity 15 MΩ·cm).

Apparatus and Procedure

The measurement of LLE data can be divided in two steps.

First, the solubility curves were obtained using the cloud-point method.[10] The end point was determined by observing the transition from a clear liquid to a cloudy liquid. The transition was determined visually using a source of light. Due to the large inaccuracies of this method the curves obtained in this way are not reliable, and they are only used to calibrate the gas chromatograph and to prepare the mixtures for the determination of the tie lines.[11]

Second, the tie lines were obtained by preparing mass ternary mixtures of known overall composition included in the immiscible region of the solubility curves determined previously. Weighing was carried out with a Mettler AE160 balance with a precision of 10^{-4} g. Mixtures were prepared in test tube of 75 cm^3. After being stirred vigorously with a magnetic stirrer for at least 1 h, the mixtures were settled for 20 h at constant temperature, (293.15 ± 0.1) K. After equilibrium was reached, samples from lower and upper phases were withdrawn using a syringe and transferred into vials for weighing and analysis.

The analysis of the composition of the two phases was carried out with a Varian 3800 series gas chromatograph with the following specifications: capillary column, CP-WAX 57 CB, 50 m × 0.32 mm × 0.2 μm; injection port temperature was held at 483.15 K; injections were performed on the split 1/80 mode; the volume injected was 1 μL; the carrier used was hydrogen at a rate of 1.2 mL·min^{-1}; oven temperature program was 1 min at 313.15 K, 5 K·min^{-1} to 373.15 K, 40 K·min^{-1} to 433.15 K; detector FID at 513.15 K. To obtain quantitative

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Table 1. Experimental Tie Line Data for 3-Methyl-1-butanol (1) + Ethanol (2) + Water (3) at 293.15 K

organic-rich phase			aqueous-rich phase		
x_1	x_2	x_3	x_1	x_2	x_3
0.662	0.000	0.338	0.006	0.000	0.994
0.606	0.038	0.356	0.006	0.014	0.980
0.534	0.079	0.387	0.006	0.027	0.968
0.477	0.121	0.403	0.006	0.040	0.954
0.393	0.145	0.463	0.006	0.056	0.938
0.339	0.175	0.486	0.007	0.071	0.921
0.274	0.207	0.520	0.008	0.082	0.910
0.199	0.215	0.587	0.015	0.105	0.881

Table 2. Experimental Tie Line Data for 2-Methyl-1-propanol (1) + Ethanol (2) + Water (3) at 293.15 K

organic-rich phase			aqueous-rich phase		
x_1	x_2	x_3	x_1	x_2	x_3
0.517	0.000	0.483	0.022	0.000	0.978
0.455	0.027	0.518	0.027	0.011	0.962
0.430	0.055	0.515	0.022	0.017	0.961
0.369	0.076	0.555	0.027	0.025	0.948
0.322	0.088	0.590	0.024	0.035	0.942
0.249	0.112	0.639	0.033	0.046	0.921
0.201	0.117	0.682	0.044	0.063	0.893

results, the internal standard method was applied[12] with 1-butanol as the internal standard. Seven calibration mixtures of ethanol, 3-methyl-1-butanol, 2-methyl-1-propanol, and internal standard were prepared by weighing, diluted with 1-propanol, and analyzed by the GC. The plot of alcohols to internal standard peak area ratios against corresponding mass ratios showed a linear function with a fit correlation factor of at least 0.999 for all compounds. To estimate the uncertainty of the GC analysis, a solution of quality control (QC) was prepared with known masses of each compound and analyzed by the GC. The uncertainties were calculated using eq 1. Results obtained are 0.0068 for ethanol, 0.0019 for 3-methyl-1-butanol, and 0.0004 for 2-methyl-1-propanol.

$$\epsilon_{\text{rel}} = \left|\frac{w_{i,\text{meas}} - w_{i,\text{known}}}{w_{i,\text{known}}}\right| \tag{1}$$

where $w_{i,\text{meas}}$ is measured mass fraction of compound i by GC and $w_{i,\text{known}}$ is the known mass fraction of compound i.

Results

Experimental tie line data for ternary systems 3-methyl-1-butanol (1) + ethanol (2) + water (3) and 2-methyl-1-propanol (1) + ethanol (2) + water (3) at 293.15 K and atmospheric pressure are reported, respectively, in Table 1 and Table 2, and all the concentrations are expressed in mole fraction. The representations of LLE data on rectangular diagrams for the two systems are shown, respectively, in Figure 1 and Figure 2. The ternary systems studied belong to the type I liquid–liquid phase diagram.

Correlation

The NRTL[8] and UNIQUAC[9] equations were used to fit the experimental data of the ternary systems studied here. The nonrandomness parameter (α_{ij}) of the NRTL equation was set to 0.1, 0.2, and 0.3. The structural parameters r_i and q_i for the UNIQUAC equation are obtained from atomic and molecular structure data, the van der Waals group volumes, and surface areas $V_{\omega i}$ and $A_{\omega i}$ of the molecules given by Bondi[13]

$$r_i = V_{\omega i}/15.17 \text{ and } q_i = A_{\omega i}/(2.5 \cdot 10^9)$$

The normalization factors 15.17 and $2.5 \cdot 10^9$ are those used by Abrams and Prausnitz.[9] The parameters are listed in Table 3.

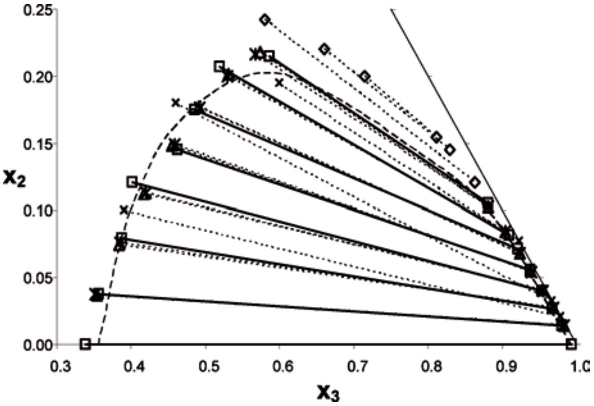

Figure 1. LLE of system 3-methyl-1-butanol (1) + ethanol (2) + water (3) (□–, this work, 293.15 K; ×---, Aznar et al.,[5] 298.15 K; ◇---, Bonner,[6] 273.15 K; Δ---, NRTL; *---, UNIQUAC; solubility curve of Tegtmeier and Misselhorn,[7] 303.15 K).

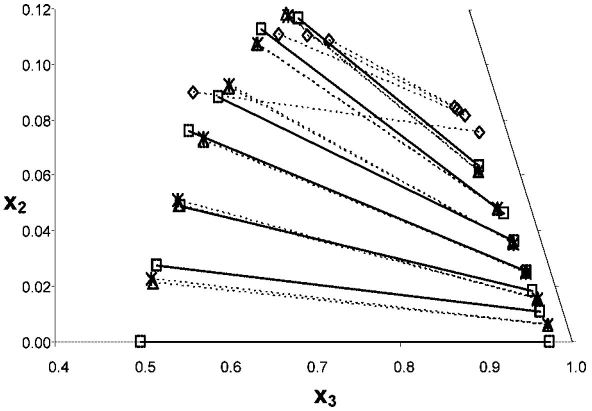

Figure 2. LLE of system 2-methyl-1-propanol (1) + ethanol (2) + water (3) (□–, this work, 293.15 K; ◇---, Bonner,[6] 273.15 K; Δ---, NRTL; *---, UNIQUAC).

Table 3. UNIQUAC Structural Parameters[9,13]

component	r_i	q_i
water	0.92	1.4
ethanol	2.1055	1.972
2-methyl-1-propanol	3.4535	3.048
3-methyl-1-butanol	4.1279	3.588

So, for both NRTL and UNIQUAC equations, six effective binary interaction parameters are needed for a ternary system. The binary interaction parameters were obtained by minimizing the difference between the experimental and calculated mole fractions for each of the components over all the tie lines with two defining objective functions (Fa and Fx).[14,15]

The activity objective function Fa

$$\text{Fa} = \sum_{k=1}^{M}\sum_{i=1}^{3}\left(\frac{(a_{ik}^{I} - a_{ik}^{II})}{a_{ik}^{I} + a_{ik}^{II}}\right)^2 + Q\sum_{n} P_n^2 \tag{2}$$

and the concentration objective function FX

$$\text{Fx} = \sum_{k=1}^{M} \min \sum_{j=1}^{2}\sum_{i=1}^{3} (x_{ijk} - \hat{x}_{ijk})^2 + Q\sum_{n} P_n^2 \tag{3}$$

where a is activity obtained directly from the NRTL or UNIQUAC model using the experimental mole fractions; Q is a constant; P_n are the NRTL or UNIQUAC parameters; x is experimental mole fraction; $\hat{x}$ is the calculated mole fraction; i represents the components of the mixture; j represents the phases and; k represents the tie lines.

Table 4. NRTL and UNIQUAC Parameters for the System 3-Methyl-1-butanol (1) + Ethanol (2) + Water (3) at 293.15 K

	UNIQUAC			NRTL			
component $i-j$	A_{ij} $(\mathrm{J \cdot mol^{-1}})$	A_{ji} $(\mathrm{J \cdot mol^{-1}})$	rmsd	A_{ij} $(\mathrm{J \cdot mol^{-1}})$	A_{ji} $(\mathrm{J \cdot mol^{-1}})$	α	rmsd
1–2	3991.36	−1707.78	0.0062	5116.92	−1801.16	0.2	0.0053
1–3	421.64	2781.30		−1318.50	16246.41	0.2	
2–3	−191.01	460.84		−665.70	4070.99	0.2	

Table 5. NRTL and UNIQUAC Parameters for the System 2-Methyl-1-propanol (1) + Ethanol (2) + Water (3) at 293.15 K

	UNIQUAC			NRTL			
component $i-j$	A_{ij} $(\mathrm{J \cdot mol^{-1}})$	A_{ji} $(\mathrm{J \cdot mol^{-1}})$	rmsd	A_{ij} $(\mathrm{J \cdot mol^{-1}})$	A_{ji} $(\mathrm{J \cdot mol^{-1}})$	α	rmsd
1–2	2322.76	−1615.76	0.0071	3633.81	−2154.72	0.2	0.0071
1–3	128.79	1957.79		−2400.17	12146.78	0.2	
2–3	−191.01	460.84		−665.70	4070.99	0.2	

The second term on the right-hand side of eqs 2 and 3, designated by the "penalty term", is added to the objective functions to reduce the risk of multiple solutions associated with high parameter values.[16]

Minimization of the objective functions was implemented with the commercial Simulis thermodynamics software[17] developed by ProSim SA which is a thermophysical properties calculation server available as an MS-Excel add-in.

The parameters estimation was started using the activity objective function eq 2 since this requires no qualified guess at the parameters. After convergence, the parameters obtained are used in the concentration objective function eq 3 to fit the experimental concentrations. In this work, parameter estimation was carried out in a way to obtain the same set of parameters for the binary ethanol + water in both systems studied. The parameter fitting is first done for the system 3-methyl-1-butanol + ethanol + water, and the parameters obtained for the binary ethanol + water were fixed in the system 2-methyl-1-propanol + ethanol + water.

The NRTL and UNIQUAC binary interaction parameters for the two systems studied are shown respectively in Tables 4 and 5. The comparison between experimental, calculated, and literature tie lines is shown in Figure 1 for the system 3-methyl-1-butanol + ethanol + water and in Figure 2 for the system 2-methyl-1-propanol + ethanol + water.

The quality of the correlation was measured by the root-mean-square deviation calculated as following

$$\mathrm{rmsd} = \left(\sum_k \sum_j \sum_j \frac{(x_{ijk} - \hat{x}_{ijk})^2}{6M} \right)^{1/2} \tag{4}$$

where M is the number of tie lines. The values of rmsd are reported in Table 5 and Table 6. As can be seen, both NRTL and UNIQUAC models give good representation of the LLE data of the systems studied here. However, the NRTL model with the parameter α optimized at 0.2 was slightly more accurate than the UNIQUAC model.

Conclusion

Liquid–liquid equilibrium data for 3-methyl-1-butanol + ethanol + water and 2-methyl-1-propanol + ethanol + water were measured at 293.15 K and atmospheric pressure. The NRTL and UNIQUAC models were used to correlate the experimental data. The NRTL equation with setting the non-randomness parameter α = 0.2 gives better results. The UNIQUAC equation also gives good results.

As mentioned in the Introduction, the aim of this work was essentially the determination of equilibrium data in view of understanding and improving the separation of fusel oils in the decanter. In addition, the determination of the NRTL and UNIQUAC parameters was carried out to help us in the choice of the thermodynamic model that will be more appropriate in the calculation of the operation of extraction with the ProSim Plus software.

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