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Extraction of Furfural from Aqueous Solutions Using Alcohols

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Liquid–liquid equilibrium data are reported for the furfural–water system with 2-methyl-2-butanol and also 2-ethyl-1-hexanol as solvents at 25 °C. Selectivities for the extraction of furfural from aqueous solution are compared with alcohols and chlorinated hydrocarbons. Predictions of the ternary equilibria for the alcohol systems using the UNIFAC method showed the greatest deviations for the 2-methyl-2-butanol–furfural–water system. These deviations were reduced by considering the alcohol as one propanol group plus two methylene groups.

Furfural is used as a solvent for extractive refining of lubricating oils, as it is very effective in removing compounds containing oxygen or sulfur. Furfural is also a feedstock for producing furfuryl alcohol, which is used for making resins and tetrahydrofuran, an excellent solvent.

Furfural can be produced by digestion of cellulose wastes with steam and sulfuric acid at 153 °C and 400 kPa. Furfural is recovered from the reaction mixture by steam distillation. Upon condensation, the organic phase contains 84.1 wt % furfural and the aqueous phase 18.4 wt %, at a temperature close to 100 °C (*1*). The solubility of furfural in water is 8.3 wt % at 20 °C (*2*). The aqueous stream can be further distilled or an effective extraction process may be used.

A variety of different solvents have been tested for the extraction of furfural from aqueous solutions (*3–5*), including chlorinated hydrocarbons (*6*, *7*), various aliphatic primary alcohols, and 2-propanol (*8–12*).

Because alcohol selectivities increase when the hydrocarbon content increases, it seems reasonable to test an alcohol with a higher hydrocarbon content, and data are reported here for the 2-ethyl-1-hexanol–furfural–water system at 25 °C. The UNIFAC group interaction parameters technique (*13*, *14*) with the parameter set derived from liquid–liquid equilibrium data (*15*) was used to predict the ternary equilibria. In order to evaluate further the reliability of UNIFAC, a tertiary alcohol was studied as solvent and data for the 2-methyl-2-butanol–furfural–water system are also reported.

Experimental Section

Chemicals. All chemicals used in this work, furfural, 2-methyl-2-butanol, and 2-ethyl-1-hexanol, were of reagent grade and were purified by distillation in a packed column with automatic regulation of the reflux ratio. A nitrogen atmosphere was used to protect the furfural from oxidation, both in distillation and in storage in a closed automatic brown buret. In one set of experiments, carried out over a period of 5 days, the furfural developed a light yellowish color and the refractive index varied from 1.5237 to 1.5233; however, no noticeable impurity was detected by gas chromatography. The physical properties of the chemicals are listed in Table I.

Table I. Physical Properties of the Chemicals at 25 °C

chemical	refractive index exptl	refractive index lit. (*16*)	density exptl	density lit. (*16*)
furfural	1.5237	1.52345	1.1533	1.1545
2-methyl-2-butanol	1.4027	1.4024	0.8037	0.8050
2-ethyl-1-hexanol	1.4294	1.4292	0.8287	0.8291

Procedure and Analysis. The liquid–liquid contacting and sampling procedures were similar to those of previous publications (*7*, *17*). For each system, refractive indexes and densities determined at the turbidity point compositions enabled the binodal curves to be defined and provided the calibration curves for obtaining phase equilibrium data. Densities and refractive indices were measured at either 24 or 26 °C, to avoid turbidity and phase separation. Densities were measured with a calibrated U-pycnometer and refractive indexes with a PZO-RL2 Abbe refractometer.

Both binodal curve and tie line composition data in each phase were checked by using a Perkin-Elmer 990 gas chromatograph, with a flame-ionization detector at a hydrogen flow rate of 30 mL/min and an air flow rate of 240 mL/min. For the 2-methyl-2-butanol–furfural–water system, a 300 × 0.3 cm stainless steel column with 15% Carbowax on Chromosorb W/AW 50/80 mesh was used at 108 °C with a nitrogen carrier gas flow rate of 32 mL/min. For the 2-ethyl-1-hexanol–furfural–water system, a 200 × 0.3 cm column with 5% OV-17 on Chromosorb W/AW 80/100 mesh was used at 73 °C with a nitrogen flow rate of 15 mL/min.

Compositions determined either by refractive index or by density agreed to within 0.1 wt % for 63 out of the 72 line compositions. Compositions determined by gas chromatography agreed with results obtained by density and refractive index to within 0.4% for the organic phase, but deviations were higher for low concentrations of furfural in the aqueous phase: 0.4 wt % for the system with 2-methyl-2-butanol and 0.9 wt % for the system with 2-ethyl-1-hexanol.

Results and Discussion

Solubility and liquid–liquid equilibrium data for the furfural–water systems with 2-methyl-2-butanol and 2-ethyl-1-hexanol as solvents at 25 °C are shown in Tables II and III, respectively. Water composition can be easily obtained by difference. the binodal curves for these alcohols are shown in Figure 1, together with some available data for other alcohols. The binodal curves for ethanol (*9*) and 2-propanol (*10*) are not shown but are similar to those of 1-propanol. It can be observed that the heterogeneity region increases as the molecular weight of the alcohol increases in straight-chain primary alcohols. It can also be seen in Figure 1 that branching has little effect for

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Table II. Solubility and Liquid–Liquid Equilibrium Data for the Furfural (F)–Water (W)–2-Methyl-2-butanol (MB) System at 25 °C (Concentration in weight percent)

Solubility Data

organic phase				aqueous phase			
concn F	concn MB	d^{24-26}	n^{24-26}_{D}	concn F	concn MB	d^{24-26}	n^{24-26}_{D}
0.00	76.72	0.8550	1.3950	0.00	10.90	0.9829[a]	1.3452[a]
7.46	67.45	0.8793	1.4009	2.95	10.96	0.9872[a]	1.3507[a]
14.76	59.24	0.9024	1.4152	6.01	10.06	0.9929[a]	1.3552[a]
23.03	51.17	0.9506	1.4246	7.83	7.72	0.9994[a]	1.3558[a]
31.47	44.31	0.9506[a]	1.4246[a]	8.53	4.67	1.0040	1.3532
40.04	38.07	0.9737[a]	1.4351[a]	8.54	1.70	1.0086	1.3502
52.12	30.30	1.0058[a]	1.4509[a]	8.54	0.00	1.0112	1.3480
59.82	25.11	1.0259	1.4607				
68.22	19.43	1.0509	1.4730				
76.89	13.35	1.0790	1.4852				
85.77	6.84	1.1100	1.4991				
94.93	0.00	1.1460	1.5410				

Liquid–Liquid Equilibrium Data

organic phase		aqueous phase		
concn F	concn MB	concn F	concn MB	*K*
82.9	8.9	8.54	3.5	9.7
63.4	22.7	8.3	6.0	7.6
59.4	25.5	8.0	7.4	7.4
42.9	36.1	7.4	8.6	5.8
25.8	48.8	5.7	10.2	4.5
10.3	64.3	2.6	11.0	4.0

[a] Measurements at 24 °C.

Table III. Solubility and Liquid–Liquid Equilibrium Data for the Furfural (F)–Water (W)–2-Ethyl-1-hexanol (EH) System at 25 °C (Concentrations in weight percent)

Solubility Data

organic phase				aqueous phase			
concn F	concn EH	d^{26}	n^{26}_{D}	concn F	concn EH	d^{26}	n^{26}_{D}
0.00	97.73	0.8313	1.4273	0.00	0.07	0.9965	1.3325
12.09	84.93	0.8608	1.4353	2.54	0.07	1.0007	1.3371
22.52	73.93	0.8888	1.4424	4.51	0.05	1.0044	1.3409
31.48	64.43	0.9143	1.4491	6.33	0.03	1.0075	1.3442
39.81	55.79	0.9399	1.4560	8.54	0.00	1.0112	1.3480
48.12	47.14	0.9661	1.4630				
57.03	38.06	0.9966	1.4714				
67.05	27.65	1.0326	1.4813				
75.32	19.31	1.0641	1.4901				
86.24	8.35	1.1086	1.5029				
94.93	0.00	1.1460	1.5140				

Liquid–Liquid Equilibrium Data

organic phase		aqueous phase		
concn F	concn EH	concn F	concn EH	*K*
82.9	11.7	7.95	0.01	10.4
68.9	25.8	7.07	0.02	9.87
53.5	41.6	6.35	0.03	8.4
39.5	56.1	5.87	0.04	6.7
24.6	71.7	4.50	0.05	5.5
10.2	86.8	2.60	0.07	3.9

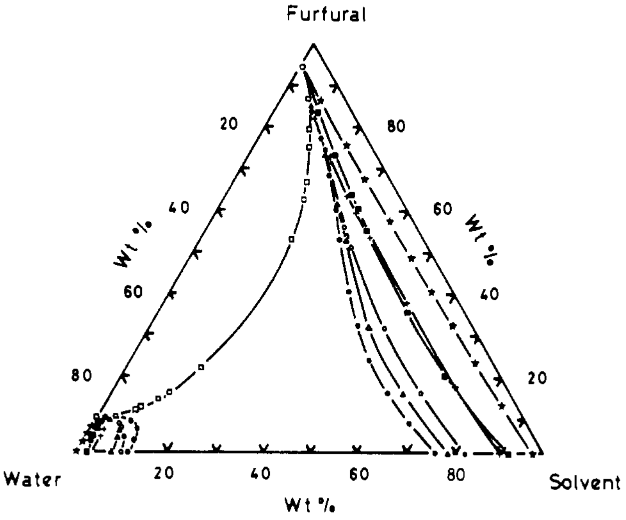

Figure 1. Liquid–liquid equilibrium diagram for the systems alcohol–furfural–water at 25 °C. Alcohols: □, 1-propanol (*10*), △, 1-butanol (*11*), ■, 1-pentanol (*12*), ○, 2-methyl-1-propanol (*11*), +, 3-methyl-1-butanol (*12*), ●, 2-methyl-2-butanol, ☆, 2-ethyl-1-hexanol.

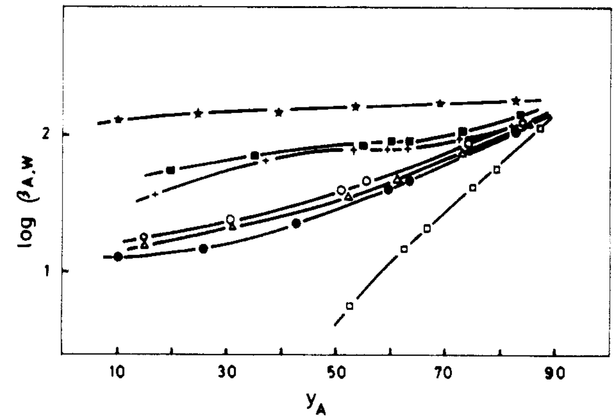

Figure 2. Solvent selectivity for the extraction of furfural from aqueous solution, plotted versus furfural concentration in the solvent phase (wt %), at 25 °C. Alcohol solvents: □, 1-propanol (*10*), △, 1-butanol (*11*), ■, 1-pentanol (*12*), ○, 2-methyl-1-propanol (*11*), +, 3-methyl-1-butanol (*12*), ●, 2-methyl-2-butanol, ★, 2-ethyl-1-hexanol.

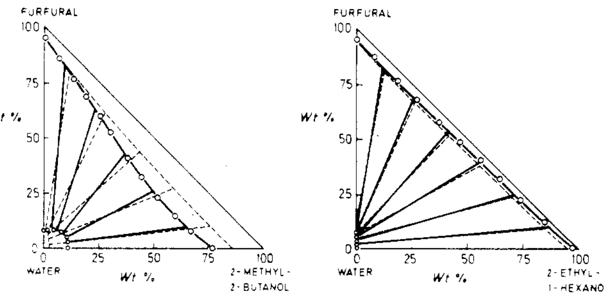

Figure 3. Experimental (solid lines) and UNIFAC predicted (dashed lines) liquid–liquid equilibrium data at 25 °C for the systems: (a) 2-methyl-2-butanol–furfural–water, and (b) 2-ethyl-1-hexanol–furfural–water.

alcohols of the same molecular weight: 1-butanol behaves similarly to 2-methyl-1-propanol and 3-methyl-1-butanol is similar to 1-pentanol. However, the tertiary alcohol 2-methyl-2-butanol has a very different behavior than the primary five-carbon alcohols and, in fact, has a smaller heterogeneity region than any of the four-carbon primary alcohols.

Solvent selectivity (weight fraction basis) for furfural relative to water as a function of furfural concentration in the organic phase is shown in Figure 2. As expected, trends for selectivity are similar to those for the region of heterogeneity: a larger heterogeneity region is associated with a higher value of selectivity. At low furfural concentrations, the selectivity of chlorinated hydrocarbons is at least one order of magnitude higher than that of alcohols. This is primarily due to the lower solubility of water in the chlorinated hydrocarbon phase. Distribution coefficients for furfural extraction are within the range *K* = 2–13 either for chlorinated hydrocarbons or the alcohol

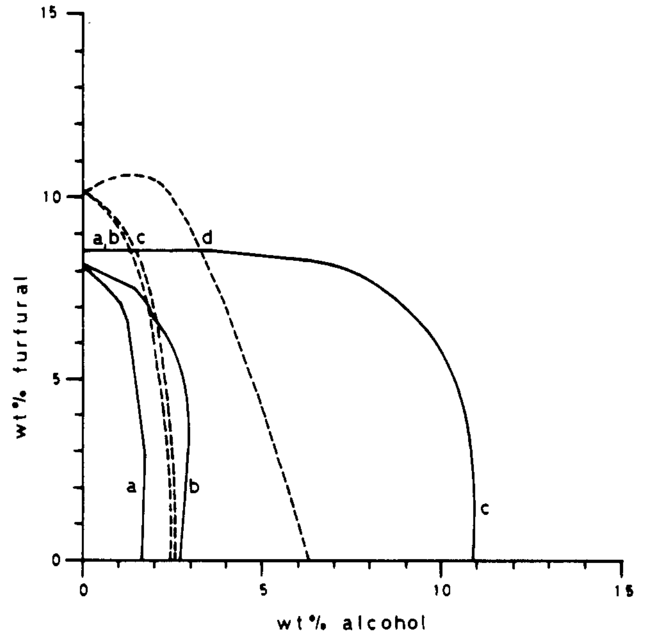

Figure 4. Detail of the aqueous phase experimental (solid lines) and UNIFAC predicted (dashed lines) liquid–liquid equilibrium data at 25 °C for five-carbon alcohols–furfural–water. Alcohols: (a) 1-pentanol, (b) 3-methyl-1-butanol, (c) 2-methyl-2-butanol modelled as one OH, one C, one CH_2 and three CH_3 groups, and (d) 2-methyl-2-butanol modelled as one (2-propanol) and two CH_2 groups.

solvents considered in this work.

Measured data and UNIFAC predictions of the two alcohols used as solvents in this work are plotted together in Figure 3. Tie-line predictions are very good for the 2-ethyl-1-hexanol system, but rather poor for the 2-methyl-2-butanol system. Experimental and predicted values of the water-rich corner of the ternary diagram for systems involving all three five-carbon alcohols are shown in detail in Figure 4. The UNIFAC predictions for the three alcohols using the UNIFAC parameter table for one OH group and appropriate C, CH, CH_2, and CH_3 groups are almost identical. This is because the additivity assumption of UNIFAC means that steric hindrance, inductive effects, and alcohol association effects are not accounted for. A UNIFAC prediction for the tertiary alcohol composed of one 2-propanol group ($CH_3CHOHCH_3$) and two CH_2 groups is also shown. This seems to be significantly better and suggests that adding secondary and tertiary alcohol groups to the UNIFAC parameter set may improve predictions. Thus, for the liquid-liquid parameter set, separate groups were required for 1-propanol and 2-propanol to obtain an adequate correlation.

Glossary

A	solute
S	solvent
W	water
d	density g cm^{-3}
n_D	refractive index
K	distribution coefficient ($K = y_A/x_A$)
x_i	weight percent of component i in the aqueous phase
y_i	weight percent of component i in the aqueous phase

Greek Letters

$\beta_{A,W}$	solvent selectivity ($\beta_{A,W} = y_A x_W / x_A y_W$)

Registry No. 2-Methyl-2-butanol, 75-85-4; 2-ethyl-1-hexanol, 104-76-7; furfural, 98-01-1.

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