System Furfural–Water–Valeric Acid at 25° and 35°C

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The binodal curves and tie lines of the system furfural–water–valeric acid have been determined at 25° and 35° C. The results are compared with those of previous studies of the lower *n*-alkanoic acids distributed between furfural and water at the same temperatures.

The distributions of formic (*6*), acetic (*5*), propionic (*5*), and butyric (*4*) acids between furfural and water at 25° and 35°C have been reported previously. In the present work the study is extended to valeric acid, the lowest member of the *n*-alkanoic acids which is not completely miscible with water at ambient temperatures. Thus the enhanced furfural–water miscibility resulting from the addition of acid in the previous systems is moderated here by the opposing tendency for phase separation at high acid concentration.

For brevity, in the text below, the various furfural–water–acid systems will be indicated by identifying the acid.

MATERIALS AND EQUIPMENT

The furfural used in the present work is the same as that previously described (*6*). The starting material (Fisher, reagent grade) was distilled under 5-torr pressure with a Vigreux column. The middle third was recovered. After distillation, the furfural was stored in a closed container at −20°C until used. Decomposition under these conditions was previously found to be negligible (*5*). Furfural decomposition during the time required for the synthesized mixtures to reach equilibrium also has, within the stated uncertainty of the data, negligible effect on the results (*4*).

Purified furfural was prepared in batches, and for the various batches the refractive index at 25°C using the sodium-D line varied by no more than 0.0007 unit from the accepted value of 1.5235 (*8*). There was no measurable effect on solubility from this variation in the batch-to-batch purity of the distilled furfural.

Valeric acid (Eastman, manufacturer's assay, 98% min by titration) was purified the same way as furfural. The refractive index of the purified product (25°C, sodium-D line) was 1.4066 (lit., 1.4064 (*2*)]. Assay of the purified product with standardized NaOH solution indicated a wt % purity of 99.15 ±0.03 std dev.

The water was singly distilled from an ordinary laboratory still.

All analytical equipment was calibrated against certified standards. Thermostat temperature (constant to ±0.01°C) was monitored with a Beckman thermometer set with another thermometer calibrated against an NBS-certified standard.

EXPERIMENTAL PROCEDURE

The methods used in determining the equilibrium data followed established techniques.

Binodal Curve Determination. Homogeneous synthetic samples of known concentration were titrated in thermostated glass-stoppered bottles to the onset of turbidity. The titrant was that component, the addition of which rendered the mixture immiscible. After the addition of each increment of titrant, the mixture was stirred vigorously with a magnetic stirrer to expedite equilibrium. No more than three points on a binodal curve were established with a single sample of furfural so that errors from furfural decomposition could be kept negligible.

Tie-Line Determination. Tie lines were determined by titrating the acid in each of the two immiscible phases formed by separation of stirred known synthetic mixtures in the two-phase region. Weighed fractions of each phase were removed and titrated with aqueous NaOH. Weighed amounts of ethanol were added to the acid-rich fractions prior to titration so that the mixture remained homogeneous during titration. The ethanol has negligible effect upon the end points of the titrations (*9*). As a check on the reliability of the tie lines, they were constructed in the phase diagram, and the closest approaches to the known synthetic mixture concentrations were measured. The agreement indicated no significant decomposition of the furfural in the time required for phase separation.

RESULTS AND DISCUSSION

The experimental binodal curve data for the valeric acid system are given in Table I, and the smoothed curves are given in Figure 1 for 25°C. The tie lines are given in Table II and in Figure 1 for 25°C.

Repeated determinations of the mutual solubilities of the two partially miscible component pairs show a precision of about ±0.05 wt % for these binary regions. From a plot of the smoothed ternary curves on a large scale, a precision of ±0.1% by weight is indicated there.

As for the other four acid systems (*4*–*6*), temperature increase reduces the region of immiscibility to a small extent. It has little effect on the slope of the tie lines.

The trend, on a wt % basis, of an increased region of furfural–water immiscibility with increasing acid chain length (*6*)

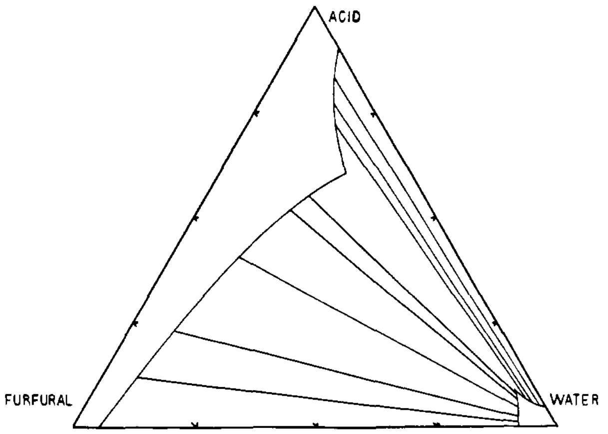

Figure 1. The system furfural–water–valeric acid at 25°C, wt %

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is continued through the present system. The effect is sufficient here to produce an intersection with the region of acid-water immiscibility, producing an indented band region. These indentations represent coexistent maxima, one as the maximum solubility of acid in the aqueous phase and the other as the maximum solubility of water in the acidic phase. The maximum in the acidic phase lies relatively closer to the acid-water than to the furfural-water binary axis, showing that furfural increases the acid-water miscibility more effectively than acid increases furfural-water miscibility.

Previously (*6*) the increased tendency of the acid to concentrate preferentially in the organic phase as the acid chain length increased was noted. That trend continues in the present system. Moreover, here the tendency of the acid (as solute) toward greater relative concentration in the organic phase of the furfural-water nonconsolute pair is significantly greater than that of the furfural (as solute) to concentrate preferentially in the organic phase of the acid-water nonconsolute pair at comparable solute concentrations.

Several tie-line correlation relationships are available. Considered here are those of Bachman (*1*), Hand (*3*), and Othmer and Tobias (*7*):

$$A_1 \text{ vs. } A_1/B_2\ (1) \tag{1}$$

$$\log (C_1/A_1) \text{ vs. } \log (C_2/B_2)\ (3) \tag{2}$$

$$\log [(b_1 + c_1)/a_1] \text{ vs. } \log [(a_2 + c_2)/b_2]\ (7) \tag{3}$$

In the above, A, B, C are, respectively, the wt % of furfural, water, and acid; a, b, c the corresponding mol %; and 1 and 2 are the organic (acidic) and aqueous phases.

Table I. Binodal Curves

(% by weight)

25°C			35°C		
Water	Valeric acid	Furfural	Water	Valeric acid	Furfural
		Acidic Phase			
4.91	0.00	95.09	5.80	0.00	94.20
6.3	8.9	84.8	7.1	5.0	87.9
7.2	14.4	78.4	8.3	10.0	81.7
9.4	23.2	67.4	10.1	18.0	71.9
11.4	30.6	58.0	13.7	32.0	54.3
14.9	42.8	42.3	16.5	41.2	42.3
19.8	54.6	25.6	18.8	45.6	35.6
23.3	59.2	17.5	20.3	49.4	30.3
25.7	60.6	14.7	24.1	55.1	20.8
23.3	63.8	12.9	24.6	55.5	19.8
22.0	66.1	11.9	27.2	57.8	15.0
15.9	76.6	7.5	25.9	62.1	12.0
10.12	89.88	0.00	23.4	66.0	10.6
			21.5	69.5	9.0
			18.0	75.8	6.2
			14.5	82.6	2.9
			12.90	87.10	0.00
		Aqueous Phase			
92.00	0.00	8.00	91.12	0.00	8.88
90.8	2.9	6.3	90.9	1.2	7.9
89.0	6.1	4.9	90.1	3.5	6.4
86.8	8.5	4.7	89.2	5.4	5.5
87.1	8.3	4.6	87.6	7.4	5.0
88.7	7.4	3.9	86.0	9.2	4.8
92.6	5.6	1.8	86.9	9.0	4.1
95.68	4.32	0.00	89.4	7.6	3.0
			91.9	6.5	1.6
			94.74	5.26	0.00

Table II. Tie-Line Data

(% by weight)

Acidic phase			Aqueous phase		
Water	Valeric acid	Furfural	Water	Valeric acid	Furfural
		25°C			
7.0	12.0	81.0	91.6	1.0	7.4
9.1	23.2	67.7	91.2	2.1	6.7
14.5	40.8	44.7	90.0	4.6	5.4
18.9	52.3	28.8	88.8	6.2	4.9
20.8	55.9	23.3	87.0	8.2	4.8
18.2	72.5	9.4	90.4	6.6	3.0
15.5	77.6	6.9	92.0	5.8	2.2
12.6	83.8	3.6	94.0	5.0	1.0
		35°C			
11.6	24.0	64.4	90.7	2.1	7.2
14.8	35.1	50.1	90.0	3.8	6.2
18.1	45.5	36.4	88.4	6.2	5.3
22.2	53.0	24.9	86.4	8.7	4.9
21.8	68.8	9.4	88.0	8.4	3.6
18.4	74.9	6.8	90.6	7.0	2.3
16.4	78.7	4.9	92.7	6.1	1.2

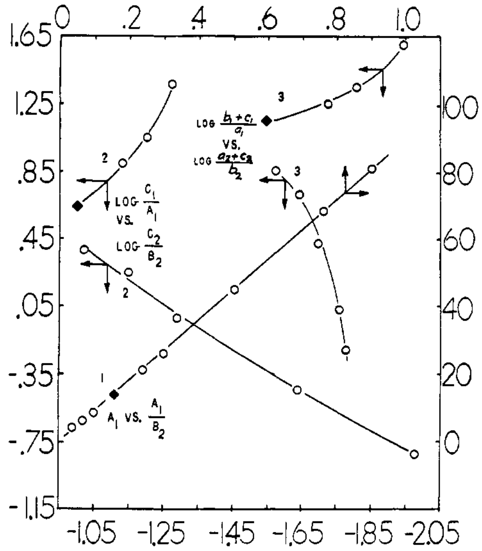

Figure 2. Tie-line correlation plots for the system furfural–water–valeric acid at 25°C

1. Bachman plot (*1*), Equation 1
2. Hand plot (*3*), Equation 2
3. Othmer-Tobias plot (*7*), Equation 3

(○) Tie-line data

(◆) Intersection of branches of binodal curves of Figure 1

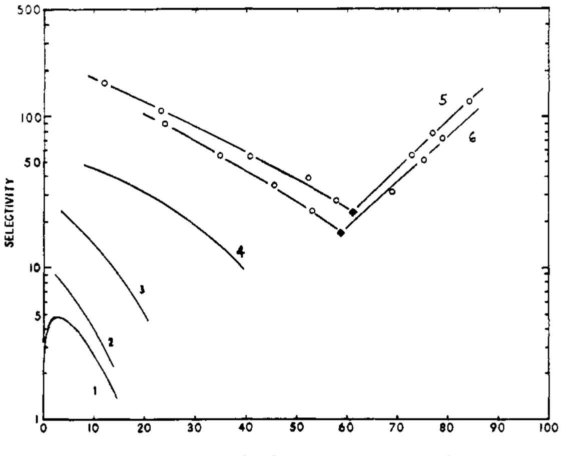

Figure 3. Selectivities in furfural–water–acid systems. Wt % acid in organic (acidic) phase

1. Formic acid, 25°C (*6*)
2. Acetic acid, 25°C (*5*)
3. Propionic acid, 25°C (*5*)
4. Butyric acid, 25°C (*4*)
5. Valeric acid, 25°C
6. Valeric acid, 35°C

(○) Tie-line data

(◆) Intersections of branches of binodal curves

The Othmer-Tobias relationship is frequently expressed in wt % rather than mol %, but in the systems of these acids with furfural and water the latter may be linear even though the former may not be (*5*). Figure 2 shows that for the valeric acid system, the latter is also nonlinear. Moreover it is branched and passes through an extreme abscissa. Data are insufficient to establish whether the extreme involves a continuous or discontinuous first derivative of the function. The Hand relationship in Figure 2 shows a similar behavior.

The relationship of Bachman is linear in Figure 2, with a slope and intercept by a least-squares procedure of, respectively, 91.53 and −0.37. Clearly this relationship is the most useful of the three in that the maxima of the binodal curve, Figure 1, do not affect the continuity of the tie-line correlation.

For each of the three plots of Figure 2, the points corresponding to the maxima in Figure 1 have been added. That point is consistent with the linearity of the Bachman plot, and lies on one of the branches of each of the other two plots.

The effectiveness of the extraction of a solute by a solvent is given by the selectivity (*10*), which in the present work may be considered as the ability of furfural to separate water and acid. Then the selectivity may be defined here as either b_2c_1/b_1c_2 or the equivalent ratio B_2C_1/B_1C_2. The selectivities in the valeric acid system at 25° and 35°C, and of the other acid systems at 25°C are given in Figure 3. The selectivity is greatest in the valeric acid system, and this system exhibits a selectivity minimum at the coexistent maxima of the binodal curves. Figure 3 shows that the effect of temperature in the present system is relatively small.

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Examination of Ethanol–*n*-Heptane, Methanol–*n*-Hexane Systems Using New Vapor-Liquid Equilibrium Still

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Isobaric vapor-liquid equilibrium data are presented for the binary systems ethanol–*n*-heptane and methanol–*n*-hexane. Rigorous thermodynamic tests indicated excellent thermodynamic consistency. The data were obtained using a new dynamic vapor-liquid equilibrium still. A salient feature of the design is a two-phase vapor-liquid flow through an annular space surrounding the equilibrium chamber which permits accurate temperature measurement and ensures adiabatic operation of the inner chamber at thermal equilibrium.

The two binary systems examined were ethanol–*n*-heptane and methanol–*n*-hexane. Both systems are highly nonideal, and the relative volatilities, particularly in the hydrocarbon-rich regions, are very large. Accurate determination of vapor-liquid equilibrium data for such systems presents a stringent test of the experimental method. Also, the availability of heat of-mixing data permits rigorous testing of the data for thermodynamic consistency. Equilibrium data predicted by Van Ness et al. (*18*) from total pressure–composition measurements show a maximum in one of the activity coefficient–composition curves. Such a maximum was not detected (*9*).

Isobaric vapor-liquid equilibrium data were determined for the above two systems using a new dynamic vapor-liquid equilibrium still described in detail below.

EQUILIBRIUM STILL DESIGN

Among the more serious difficulties encountered with many of the equilibrium stills presented in the literature (*4*) are partial condensation of the equilibrium vapor (which may lead to considerable error), inadequate mixing and vapor-liquid contact in the equilibrium chamber, complete evaporation of liquid droplets, and imprecise temperature measurement.

An attractive feature of stills with vapor-phase circulation of the kind proposed by Jones-Colburn (*7*) is the excellent mixing and intimate contact of vapor bubbles with surrounding liquid in the equilibrium chamber. Drawbacks of this design (and its subsequent modifications) are the imprecise measurement of boiling temperature and the difficulties encountered in exactly balancing heat losses to maintain adiabatic operation of the equilibrium chamber. Also, vertical temperature gradients in the latter, such as may arise from uneven heating, may produce erroneous results.

The above drawbacks are largely eliminated in stills with circulation of both liquid and vapor phases of the type proposed by Gillespie (*3*) and subsequently modified by several investigators (*1, 2, 13*). The Cottrell pump feature of these stills permits very precise temperature measurement but provides less satisfactory mixing and vapor-liquid contact than the bubbling chamber of the Jones still. Partial condensation of equilibrium vapor, although very effectively reduced, probably is not completely eliminated particularly in the region of the thermocouple

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