Distribution of Butyric Acid between Furfural and Water at 25° and 35° C.

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The system furfural–water–butyric acid has been studied at 25° and 35° C. The binodal curves, tie lines, and plait points have been determined. The results are compared with a previous study of acetic and propionic acids distributed between furfural and water at the same temperatures.

A STUDY of the systems furfural-water-acetic acid and furural-water-propionic acid at 25° and 35° C. has previously been reported (*3*). The present work is an extension to include the system furfural-water-butyric acid at those same temperatures. This provides three homologous acid solutes for comparison of behavior, indicating the effect on distribution equilibrium resulting from an increasing hydrocarbon nature of the solutes. The present system represents an upper solute limit for such systems at the selected temperatures, because higher aliphatic acids are only partially miscible with water.

MATERIALS AND EQUIPMENT

The furfural (Fisher, reagent grade) was purified and stored in batches as described previously (*3*). Furfural deterioration during storage, checked by titration of the acid decomposition products (*2*), amounted to about 5 × 10^{-3} equivalents of acid per liter of furfural. The extent of furfural decomposition during the time required for the synthesized mixtures to reach equilibrium has, within the stated uncertainty of the data, negligible effect on the results.

For the various batches of purified furfural, n_D^{25} ranged between 1.5228 and 1.5237. The accepted value is 1.5235 (*5*). There was no measurable effect on solubility behavior caused by this variation in the purity of the distilled furfural.

Butyric acid (Fisher, reagent grade) was distilled at atmospheric pressure [refractive index, n_D^{25} 1.3958, accepted value, 1.39581 (*1*)]. The water was singly distilled from an ordinary laboratory still.

All analytical equipment was calibrated against certified standards. The systems were studied in a thermostated bath, constant to ± 0. 1° C.

EXPERIMENTAL PROCEDURE

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

Binodal Curve Determination. Homogeneous synthetic samples of known composition were titrated in glass-stoppered bottles to the appearance of turbidity. In order to minimize errors from furfural deterioration, no more than three points on a binodal curve were established with a single sample of furfural.

Tie-Line Determination. Tie lines were determined as described previously (*3*). The present butyric acid system formed emulsions of considerably greater stability than the acetic and propionic acid systems, where phase separation occurred within about one-half hour after agitation was stopped. Usually several hours were required for complete phase separation. As a check on the reliability of the tie-line data, the tie lines were constructed in the phase diagram, and the closest approach to the gross composition of the samples synthesized for the determination of the tie lines was measured. The agreement was satisfactory, indicating that during the several hours required for phase separation no significant deterioration of furfural occurred.

Weighed fractions of each phase were titrated with aqueous sodium hydroxide. Weighed amounts of ethanol were added to each phase fraction prior to titration with base so that the fraction would remain homogeneous during titration. The ethanol has no effect upon the end point of the titrations (*6*).

RESULTS

The experimental points on the binodal curves are given in Table I. Repeated determinations of the mutual solubilities of furfural and water, and an examination of the smoothed binodal curve plotted on a large scale, indicated a precision of about ±0.1% by weight. The precision is best near the top of the curve, where the higher concentrations of acid result in a sharper transition to heterogeneity during titration. Tie-line data for this system are given in Table II, and the phase diagram is shown in Figure 1. Also shown in Figure 1, for comparison, is the same solvent-solvent system with acetic and propionic acids as solutes (*3*). Only the 25° C. isotherms are given in

Table I. Binodal Curve

Per cent by weight, at equilibrium

25° C.			35° C.		
Furfural	Butyric acid	Water	Furfural	Butyric acid	Water
95.0	0.0	5.0	94.3	0.0	5.7
83.6	8.2	8.2	83.6	7.1	9.3
71.4	16.7	11.9	80.0	9.7	10.3
48.8	31.4	19.8	69.3	17.1	13.6
43.1	34.7	22.2	60.6	22.7	16.6
36.8	38.4	24.8	52.9	27.4	19.7
28.6	41.0	30.3	52.1	27.9	20.0
27.5	41.3	31.2	47.0	30.9	22.2
20.3	41.9	37.8	45.9	31.5	22.6
15.4	39.9	44.7	42.6	33.3	24.1
11.8	35.6	52.7	35.9	36.2	27.8
11.0	33.8	55.2	30.5	37.9	31.6
10.8	33.1	56.0	20.9	38.0	41.2
8.4	27.6	64.1	16.1	34.0	49.9
6.0	18.3	75.7	13.9	31.4	54.7
5.8	13.9	80.3	12.9	29.8	57.3
5.7	12.8	81.5	10.9	25.0	64.1
6.0	8.8	85.2	10.5	24.4	64.9
8.3	0.0	91.7	9.3	21.7	68.8
			7.0	13.6	79.3
			7.3	13.5	79.2
			7.1	12.1	80.8
			7.2	9.6	83.3
			8.8	0.0	91.2
Estd. Plait Point			Estd. Plait Point		
6.6	21.3	72.1	8.6	19.6	71.8

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Figure 1 in order to avoid crowding. Both isotherms and tie lines are virtually parallel at the two temperatures for each system. The effect of the temperature increase in all three systems is to decrease the area of immiscibility.

Othmer-Tobias plots of the present data were made to determine the plait points (*4*):

$$\log\left(\frac{100 - b_2}{b_2}\right) = m \log\left(\frac{100 - a_1}{a_1}\right) + n$$

where a_1 is the weight % of furfural in the furfural-rich phase and b_2 is the weight % of water in the water-rich phase. The plots are clearly linear, and the constants by least-squares treatment of the data at 25° and 35° C. respectively, are: $m = 0.2957$, $n = -1.6406$; $m = 0.3073$, $n = -1.6205$. The plait points obtained with these equations are also included in Table I.

An index of the suitability of a given solvent for the extraction of a solute is the selectivity (*7*). This may be defined as x/y, where x is the ratio of acid concentration in the furfural-rich phase to that in the water-rich phase, and y is the ratio of water concentration in the furfural-rich phase to that in the water-rich phase. Selectivities for the present system at 25° and 35° C. are plotted *vs.* the per cent by weight of acid in the furfural-rich phase in Figure 2. Included there, for comparison, are the selectivities of the systems where acetic and propionic acids are distributed between furfural and water (*3*).

DISCUSSION

As Figure 1 shows, the effect of increasing the length of the aliphatic chain in the solute acid is an increase in the extent of the region of immiscibility. The effect in passing from propionic to butyric acid is considerably greater than that found in passing from acetic to propionic acid. Butyric acid represents the upper limit of chain length of the normal aliphatic acids which are totally water-soluble at ambient temperatures.

The effect of the nature of the acid on the position of maximum acid solubility is variable. Thus, on a weight % basis, for acetic acid the maximum on the binodal curve is near a 1 to 1 ratio of water-furfural, for propionic acid it is toward the furfural-rich side, and for butyric acid it has shifted to the water-rich side.

Unlike the other acid solutes, the butyric acid system exhibits a minimum in the solubility of furfural in the water-rich phase. This occurs at 25° C. in the region on the binodal curve between 10 and 15 weight % acid. Expressed in mole %, it is 2 to 3% acid; and as volume %, it is 10 to 15% acid. The solubility minimum indicates that at this butyric acid-water ratio, the activity coefficient of furfural has become relatively large as a result of acid-water attractive forces.

Another difference in behavior among the three acid solutes is evident from the selectivity plots (Figure 2) and the plait points (Figure 1). Butyric acid shows a considerably greater tendency to concentrate in the organic phase than does either acetic or propionic acids. Again the effect is probably related to the length of the aliphatic chain on the acid.

For all three acids, the effect of increasing the temperature from 25° to 35° C. is to lower the acid concentration at maximum solubility by about ten % of the value at 25°.

The effect of this temperature change on the plait points is uniformly small, lowering the acid content by about 1.5% acid, and leaving the percentage of water almost unchanged.

As to the effect of temperature on the ratio of acid concentrations in the two immiscible phases, that the tie lines for each individual system are essentially parallel at the two temperatures shows that the ratio is little dependent upon temperature. A similar conclusion regarding selectivities is apparent from Figure 2.

Table II. Tie Line Data

Per cent by weight

Furfural-Rich Phase			Water-Rich Phase		
Furfural	Butyric acid	Water	Furfural	Butyric acid	Water
		25° C.			
83.3	8.4	8.3	7.7	1.9	90.4
82.5	8.9	8.6	7.7	2.0	90.3
67.0	19.7	13.3	7.1	4.2	88.7
54.9	27.7	17.4	6.6	6.1	87.3
44.8	33.7	21.5	6.1	8.3	85.6
30.6	40.4	29.0	5.8	11.0	83.2
		35° C.			
83.0	7.8	9.3	8.6	1.7	89.8
67.1	18.5	14.4	8.0	4.0	87.9
53.5	27.2	19.4	7.8	5.8	86.4
48.9	29.8	21.3	7.6	7.1	85.3
38.0	35.4	26.7	7.3	9.4	83.2

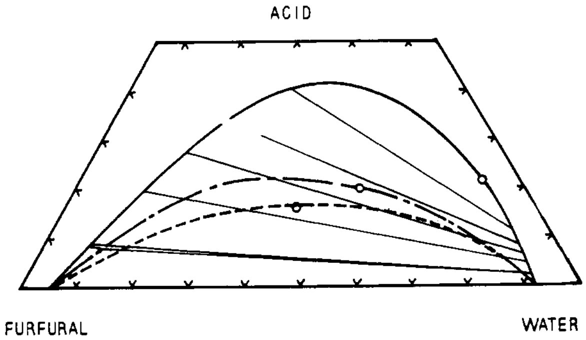

Figure 1. Furfural-acid-water systems at 25° C., weight %

——— Butyric acid
—— — Propionic acid
- - - - - Acetic acid
° Plait points

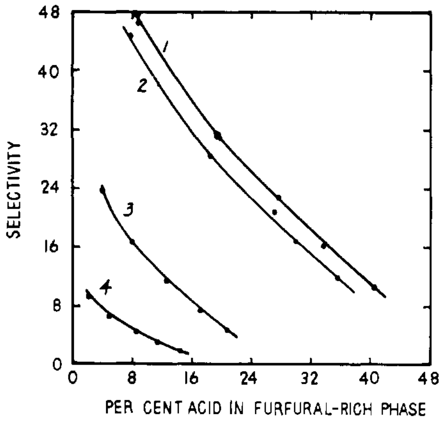

Figure 2. Selectivities in furfural-acid-water systems

1. Butyric acid at 25° C.
2. Butyric acid at 35° C.
3. Propionic acid at 25° C.
4. Acetic acid at 25° C.

The minimum in furfural solubility in the water-rich phase also occurs at 35° C. The minimum is less pronounced, however, probably owing to the greater thermal energy of the system at the higher temperature. The minimum appears to be shifted to a slightly lower acid-to-water ratio, but the effect is not pronounced.

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Endothermic Heats of Mixing by Isothermal Dilution Calorimetry

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An evaluation is presented of an isothermal dilution calorimeter for the measurement of endothermic heats of mixing. Results accurate to well within ±1% are obtained routinely and rapidly. Both integral and partial molal heats of mixing may be measured, and data may be taken at mole fractions as low as 0.001.

THE PRINCIPLE of operation of the heat-of-mixing calorimeter discussed here was first described by Mrazek and Van Ness (*4*) in 1961. Subsequent refinement of this calorimeter has led to the development of a highly versatile instrument which lends itself to the rapid and routine production of data.

For a truly isothermal calorimeter, the only data necessary from which to calculate heats of mixing of endothermic systems are the masses of the constituents mixed and the electrical energy added to the system for maintenance of isothermal conditions. Such measurements lend themselves to high precision. The temperature of the calorimeter and the temperature of its surroundings must not only be the same, but must be held constant within very close limits. The practicality of the basic idea was demonstrated by Mrazek and Van Ness (*4*) with their publication of data on alcohol-aromatic hydrocarbon systems. Because of hydrogen bonding between alcohol molecules, these systems exhibit wide departures from ideality. In particular, a large heat addition is necessary to maintain isothermal conditions when a small quantity of alcohol is mixed with a relatively large amount of pure hydrocarbon. The calorimeter design of Mrazek and Van Ness (*4*) did not permit accurate determination of this important measurement. The new design allows measurements of integral heats of mixing to be made to mole fractions as low as 0.001, and at the same time provides means for the direct determination of partial molal heats of mixing. Two recent papers (*5*) have reported extensive data taken with the newly designed calorimeter for alcohol–*n*-hydrocarbon systems, but its description and evaluation are reserved to this paper.

APPARATUS

The general mode of operation of the calorimeter can be visualized by reference to the schematic diagram of Figure 1. The primary element of the calorimeter is a 150-ml. Dewar flask, *A*. One of the components to be mixed is weighed into this flask and is then sealed by the plug, *B*; all air is vented in the process. The second component, to be added to the one contained in the Dewar flask, is stored in the feed bulb, *C*, of about 100-ml. capacity. Small-bore tubing leads from the top of the feed bulb, through plug *B*, into the interior of the Dewar flask, where its open end is submerged in mercury contained in a small cup, *E*. Mercury is initially drawn up into the tubing to a fiducial mark at *D*. The feed component in *C* is stored over mercury, which is introduced into the bottom of the feed bulb through a length of glass tubing leading upward to a 150-ml. mercury-storage reservoir, *G*. The mercury level is initially adjusted so that it just touches a probe in the neck at *H* as indicated by a neon bulb in a sensing system. This probe is located about 70 cm. above the bottom of the feed bulb, *C*. When the stopcock, *I*, is open, this head of mercury pressurizes the system.

The side-arm assembly, *J*, is used for loading and draining mercury from reservoir *G*. A rubber stopper, *K*, holding a line leading to a vacuum system, can be inserted into the top of reservoir *G*, allowing vacuum to be applied to draw mercury up into the reservoir from the feed bulb. This is used during the loading operation, as it is necessary to flush the feed bulb thoroughly and then fill it with the second component of the system to be studied. Flushing and loading are accomplished before the Dewar flask is placed on its closure plug. The cup, *E*, is removed from the end of the feed tube, and an extension is placed on the feed tube to allow it to dip into a beaker containing the second component. The feed bulb is flushed and then filled by appropriate use of the vacuum system. A small amount of mercury is then drawn into the end of the feed tube and the mercury-filled cup, *E*, is returned to position. The O-ring joints at *L* require no grease, nor does the stopcock, *I*, with its Teflon plug. Thus grease is never introduced into the system.

The entire apparatus shown in Figure 1 is mounted on a portable rack. For loading, this rack is fastened over a laboratory bench; for running, it is lowered into a constant-temperature bath, *F*, so that the Dewar flask and feed bulb are submerged. The plug, *B*, is held firmly in a fixed position, but the Dewar flask, *A*, is fastened to a movable frame that can be raised or lowered by turning a threaded rod. The mixing process is carried out by lowering the Dewar flask. This draws material from the feed bulb into the feed line so that it bubbles up through the mercury in cup *E* into the Dewar flask. The head of mercury from reservoir *G*, is the driving force for the process,