Distribution of Acetic and Propionic Acids Between Furfural and Water

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MANY FACTORS are important in determining the characteristic of a given solvent for extraction purposes. Among these are the specificity of the solvent toward different solute species, the effect of commonly encountered solvent impurities, and the effects of temperature.

This work is concerned with the systems furfural-water-acetic acid and furfural-water-propionic acid. The two systems thus differ only with respect to the solute species, both of which are members of a homologous series of compounds. The effects of a temperature increase from 25° to 35° C. on each of these systems are described. A brief investigation has also been made of the effect on the first system resulting from the substitution of commercial grade furfural for purified furfural. The nature of the products found in unpurified furfural has been described (*2*).

In spite of the wide interest in the solvent properties of furfural, relatively few precise data are available concerning phase equilibrium in ternary systems containing it (*8, 9*). A contributing factor might have been the instability of pure furfural (*2*). The distribution of acetic acid between furfural and water has been briefly studied by Leonard and others (*4*). Skrzec and Murphy (*10*) examined this system more throughly at 26.70° C. using furfural marked 99 to 100% as aldehyde, which was not further purified before use. Pegoraro and Guglielmi (*6*) also studied it using freshly distilled furfural, but neglecting the control of temperature, which varied from 18.6° to 23.4° C. A plot of these latter two sets of data on a large scale shows varying degrees of agreement over different parts of the binodal curve, with neither set consistently higher or lower than the other. This presents the problem of determining which factor is more pronounced in its effect on the solvent properties of furfural: temperature variation or impurities. The work presented here may be of some value in answering this question, because both the temperature and purity of the furfural were varied in turn.

MATERIALS AND EQUIPMENT

The furfural (Quaker Oats Co.) used in this study was commercial grade. It was distilled under 5 mm. of mercury pressure through a Vigreux column, and only the middle third was recovered for use. The refractive index of this colorless fraction was n_D^{25}, 1.5235. The accepted value is 1.5235 (*7*). After distillation, the furfural was stored in a closed container at −10° C. until used. It could thus be stored for several days with no detectable deterioration. Deterioration was checked by titration of the acid products known to form as the result of furfural autoxidation (*2*). The deterioration may also be followed qualitatively by means of color change, because some of the resinous products formed impart a definite darkening to the furfural. When used, furfural was still colorless, with an acid content of less than 3×10^{-3} equivalent per liter. Expressed in terms of acetic acid, it contained less than 0.02% acid by weight. In the phase studies, during the time required for mixtures of furfural and the other components to reach equilibrium, however, a slight yellowing was usually observed. The effect was more pronounced at 35° than at 25° C. The catalytic effects of acids on furfural decomposition have been described (*12*). Furfural alone, when allowed to stand at room temperature for the same period of time, showed no color change.

Acetic acid (Baker and Adamson, reagent grade) minimum assay 99.7% by weight, was not further purified.

Propionic acid (Matheson, Coleman, and Bell) assay 99%, was distilled through the Vigreux column at atmospheric pressure, and the middle third recovered for use [refractive index, n_D^{25}, 1.3841, accepted value, 1.38430 (*1*)]. The water, singly distilled from an ordinary laboratory still, was protected from carbon dioxide during storage.

All analytical equipment was calibrated against certified standards. The systems were studied in a thermostated bath, constant to ±0.05° C.

EXPERIMENTAL PROCEDURE

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

Binodal Curve Determination. Heterogeneous synthetic samples of known composition were titrated by the addition of acid to the disappearance of turbidity. The titrations were carried out in 125-ml. glass-stoppered bottles. After the addition of each acid increment, the samples were stirred vigorously with a magnetic stirrer until it was apparent that the sample had not yet reached homogeneity. With the use of this type of stirrer, allowing a high degree of agitation with an intimate mixing of the two phases, little time was required for achieving equilibrium. Duplicate determinations of the mutual solubilities of furfural and water established that 1 hour was sufficient to allow for the complete titration of a sample to homogeneity. No more than two points on the binodal curve were established with a single sample of furfural.

Tie-Line Determination. Tie lines were determined by titrating the acid in each of the two phases formed from synthetic samples of known composition in the two-phase region. The samples, contained in 125-ml. glass-stoppered bottles, were vigorously agitated with the magnetic stirrer for 1/2 hour, and allowed to stand 1/2 hour for complete separation into two phases. Weighed fractions of each phase were titrated quickly using a sodium hydroxide solution containing 50 weight % of ethyl alcohol. The alcohol was to keep the furfural-rich phase homogeneous during titration and had no effect upon the end point (*10*). Room temperatures varied from about 27° to 35° C. Thus, at 35° C. the pipet used to withdraw fractions of each phase had to be warmed to prevent separation of the fractions in the pipet.

RESULTS

Furfural-Water–Acetic Acid. The points determined on the binodal curves at 25° and 35° C. 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, indicate a precision of slightly better than ±0.10% by weight. The precision is best near the top of the curve, where the higher concentrations of acid result in a sharper transition from heterogeneity to homogeneity during titration. Tie-line data for this system are given in Table II, and the phase diagram is shown in Figure 1.

Only the 25° C. isotherm is given in Figure 1 because the two isotherms are essentially coincident on the reduced scale. The tie lines at the two temperatures are virtually

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parallel. The effect of the temperature increase, as indicated in Table I, is to decrease the area of immiscibility.

As a check on the reliability of the tie-line data, the tie lines were constructed in the phase diagram, and their distances of closest approach to the points representing the two-phase samples utilized in determining the tie lines were measured. The agreement was satisfactory.

An Othmer-Tobias plot of the data was made to determine the plait points (*5*). Figure 2 shows the plot using the data at 25° C. Again the 35° C. data are omitted because of the small scale of the figure. The equation of the straight line at 25° C. by the method of least squares is

$$\log\left(\frac{100-B_2}{B_2}\right) = 0.8422\log\left(\frac{100-A_1}{A_1}\right) - 0.0028 \quad (1)$$

where A_1 is the weight per cent of furfural in the furfural-rich phase and B_2 is the weight per cent of water in the water-rich phase. When the binodal curve at 25° C. is also plotted in terms of the Othmer-Tobias function, the intersection of that curve with the extrapolated straight line of Equation 1 fixes the plait point at the value given in Table I. At 35° C. the equation of the straight line, again by the method of least squares, is

$$\log\left(\frac{100-B_2}{B_2}\right) = 0.8461\log\left(\frac{100-A_1}{A_1}\right) + 0.0077 \quad (2)$$

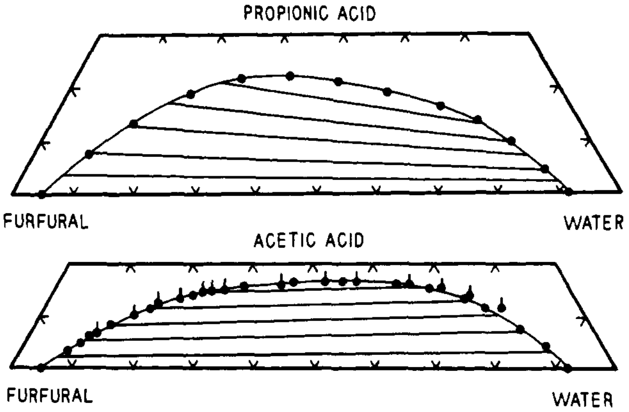

Figure 1. Ternary furfural system at 25° C.

● Purified furfural ♦ Commercial

Table I. Binodal Curve for the System Furfural-Water–Acetic Acid

(Per cent by weight, at equilibrium)

25° C.			35° C.		
Furfural	Acetic acid	Water	Furfural	Acetic acid	Water
95.07	0.00	4.93	94.15	0.00	5.85
88.6	3.6	7.8	85.2	4.8	10.0
86.1	4.8	9.0	79.9	7.3	12.8
83.8	6.0	10.2	78.1	8.0	13.9
79.2	8.1	12.7	74.4	9.3	16.3
70.9	11.3	17.8	68.1	11.4	20.5
62.7	13.8	23.5	56.7	13.8	29.5
53.5	15.3	31.2	46.0	14.6	39.4
44.9	16.0	39.1	34.9	14.8	50.3
36.8	16.3	46.9	25.8	13.8	60.3
28.4	15.8	55.8	18.6	11.2	70.2
23.1	14.8	62.1	13.1	6.7	80.2
18.4	12.9	68.7	10.6	3.3	86.2
16.0	11.1	72.9	8.87	0.00	91.13
12.1	7.7	80.2			
9.5	4.2	86.3			
8.06	0.00	91.94			
Estd. Plait Point			Estd. Plait Point		
41.2	16.2	42.6	42.3	14.7	43.0

Table II. Tie-line Data for the System Furfural-Water–Acetic Acid

(Per cent by weight)

Furfural-Rich Phase			Water-Rich Phase		
Furfural	Acetic acid	Water	Furfural	Acetic acid	Water
		25° C.			
90.5	2.6	6.9	9.4	3.6	87.0
85.2	5.3	9.5	11.5	7.0	81.5
78.6	8.4	13.0	14.8	10.2	75.1
70.6	11.5	17.9	18.9	13.1	68.0
60.9	14.2	24.9	25.4	15.4	59.2
		35° C.			
91.3	1.6	7.1	10.0	2.3	87.7
86.3	4.3	9.4	12.0	5.5	82.4
82.3	6.2	11.5	14.0	7.7	78.3
76.5	8.6	14.8	17.1	10.2	72.7
69.0	11.2	19.8	21.6	12.5	65.9

Table III. Binodal Curve for the System Commercial Furfural-Water–Acetic Acid

(Per cent by weight at 25° C.)

Commercial Furfural	Acetic Acid	Water	Commercial Furfural	Acetic Acid	Water
95.15	0.00	4.85	57.1	14.9	28.0
89.2	3.3	7.5	46.9	16.1	37.0
82.1	7.0	10.9	39.9	16.4	43.7
79.8	8.0	12.3	34.4	16.5	48.1
74.5	10.2	15.4	26.0	16.1	57.9
69.6	12.0	18.5	21.2	15.3	63.5
65.4	13.2	21.4	21.1	15.2	63.7
61.0	14.2	24.8	17.2	13.7	69.1
59.4	14.7	25.9	13.1	11.6	75.3

The plait point at 35° C., determined as described above, is also included in Table I. A 10° increase in temperature lowers the acid composition at the plait point and renders it somewhat richer in furfural. It is evident that the system is only moderately sensitive to temperature change.

The binodal curve at 25° C. reported in the present work agrees qualitatively with those reported previously (*6, 10*), exhibiting in general, however, lower acid concentration. The plait point reported here falls between those of the above workers with respect to water and furfural content, and at a lower acid content. An unexplained disagreement exists between the mutual solubilities of furfural and water reported here, and those reported earlier by one of the authors, using a different method of determination (*3*).

In an attempt to determine the effect of furfural deterioration, the system commercial furfural-water-acetic acid was also studied at 25° C. The data are given in Table III.

On the furfural-rich side of the curve it appears that the effect of impurities is not large, the binodal curve with commercial furfural falling about 0.3% above the curve for purified furfural in terms of acetic acid composition. Upon extending the curve toward the water-rich side of the curve, it became evident that in this region the methods used in this work would not yield accurate results. As the water concentration was increased, the water-insoluble resinous impurities in the furfural effectively masked the transition to homogeneity of the bulk phases. Although it is questionable just how many of the points taken with commercial furfural are significant, these have been included in Figure 1 to show the effect encountered. No tie-line data were recorded for the commercial furfural system, nor was any additional work with this substance attempted.

Furfural-Water–Propionic Acid. Table IV contains the binodal curve data for this system at 25° and 35° C. The tie-line data at both temperatures are given in Table V, and the phase diagram at 25° C. is shown in Figure 1.

As for the acetic acid system, the 35° C. data are omitted here and in the Othmer-Tobias plot of Figure 2.

The two-phase region for propionic acid is of greater

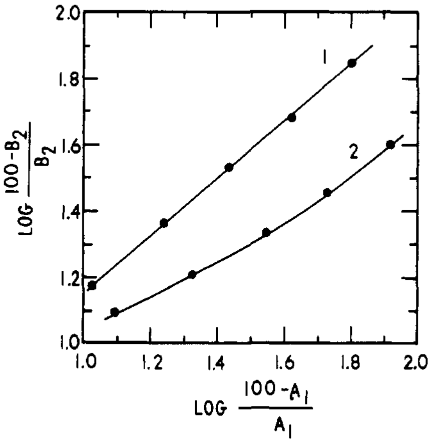

Figure 2. Othmer-Tobias plots of both systems at 25° C.
1. Acetic acid as solute
2. Propionic acid as solute

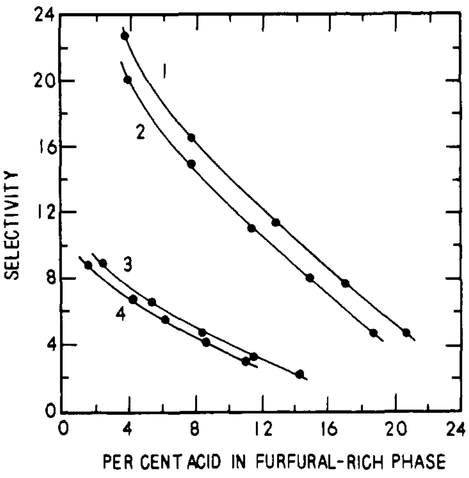

Figure 3. Selectivities in both systems
1. Propionic acid as solute at 25° C.
2. Propionic acid as solute at 25° C.
3. Acetic acid as solute at 25° C.
4. Acetic acid as solute at 35° C.

extent than that for acetic acid, and the propionic acid is more concentrated in the nonaqueous phase. The effect of temperature increase is to reduce the region of immiscibility.

The Othmer-Tobias correlation plot is nonlinear for this system when expressed in terms of the usual weight percentage variables, A_1 and B_2 (Equations 1 and 2). When these variables are replaced by the corresponding mole percentages, a_1 and b_2, the plot shows a definite linearity of the form, at 25° C.,

$$\log\left(\frac{100-b_2}{b_2}\right) = 0.6851 \log\left(\frac{100-a_1}{a_1}\right) - 1.4043 \tag{3}$$

At 35° C. the corresponding equation is

$$\log\left(\frac{100-b_2}{b_2}\right) = 0.6968 \log\left(\frac{100-a_1}{a_1}\right) - 1.4032 \tag{4}$$

The constants of Equations 3 and 4 were determined by the method of least squares. The plait points of this system at the two temperatures (Table IV) were determined by combining the Othmer-Tobias function as given here with the binodal curve expressed in mole per cent. It is apparent that the plait points for propionic acid occur at a considerably lower percentage of furfural than those of acetic acid. The effect of temperature on the plait point of the propionic acid system is similar to that encountered with acetic acid.

An index of the suitability of a given solvent for the extraction of a solute is the selectivity *(11)*. Let x be the ratio of acid concentration in the furfural-rich phase to that in the water-rich phase, and let y be the ratio of water concentration in the furfural-rich phase to that in the water-rich phase. Then the selectivity of the system may be defined as x/y. Thus a selectivity greater than unity indicates an enrichment of acid in the furfural-rich (solvent) phase, with a corresponding decrease in acid concentration in the water-rich (raffinate) phase.

The selectivities (Figure 3) are a function of per cent by weight of acid in the furfural-rich phase. The selectivity is much more pronounced with propionic than with acetic acid.

Table IV. Binodal Curve for the System Furfural-Water–Propionic Acid

(Per cent by weight, at equilibrium)

25° C.			35° C.		
Furfural	Propionic acid	Water	Furfural	Propionic acid	Water
95.07	0.00	4.93	94.15	0.00	5.85
83.3	7.2	9.4	84.7	5.8	9.5
73.0	12.9	14.0	75.2	11.0	13.8
60.9	18.5	20.6	61.3	17.1	21.6
50.9	21.5	27.6	51.8	19.5	28.7
42.8	21.8	35.3	43.0	19.9	37.0
35.6	20.8	43.7	35.7	18.8	45.5
28.3	19.0	52.7	28.2	16.9	55.0
20.9	16.4	62.7	21.9	14.8	63.4
16.3	13.6	70.1	18.4	12.9	68.7
12.6	9.7	77.7	14.4	9.8	75.8
9.6	4.4	86.0	11.3	5.9	82.8
8.06	0.00	91.94	8.87	0.00	91.13
Estd. Plait Point			Estd. Plait Point		
29.0	19.3	51.7	30.6	17.6	51.8

Table V. Tie-Line Data for the System Furfural-Water–Propionic Acid

(Per cent by weight)

Furfural-Rich Phase			Water-Rich Phase		
Furfural	Propionic acid	Water	Furfural	Propionic acid	Water
25° C.					
88.9	3.9	7.1	8.8	2.1	89.1
82.5	7.7	9.8	9.5	4.1	86.4
73.8	12.6	13.6	10.7	6.8	82.5
65.0	16.8	18.2	12.3	9.4	78.2
54.9	20.5	24.5	15.2	12.8	72.0
35° C.					
87.8	4.0	8.2	9.6	2.1	88.3
81.4	7.7	10.9	10.4	4.1	85.5
74.6	11.3	14.1	12.4	6.1	82.5
67.3	14.8	17.9	13.0	8.2	78.8
56.5	18.5	24.9	16.2	11.4	72.3

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