ness can be employed to obtain the diffusion coefficient of an unknown substance.

With average concentrations of 40.71 and 44.68 wt % HMT and employing disc no. 2, we determined the diffusion coefficients at several temperatures in the range of 15–45°C. These data are plotted in Figure 3 as logarithm of D against the inverse of absolute temperature T. The activation energies of 4.34 and 4.44 kcal/g mol are obtained for 40.71 and 44.68 wt % HMT solutions, respectively. The activation energy calculated from the data of Costantino et al. (*1*) reported at only two temperatures, namely 3.66° and 24.72°C, is about 4.9 kcal/g mol for the various average concentrations ranging from 0.55–28.85 wt % HMT. Here again the agreement between the data of this work and that of Costantino is good. It appears that the activation energy of diffusion for HMT remains constant for the entire concentration range from 0.5 wt % to the saturation limit.

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

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The system furfural–water–formic 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 those of previous studies of acetic, propionic, and butyric acids distributed between furfural and water at the same temperatures.

Although one of the major autoxidation products of furfural is formic acid (*2*), the distribution of the latter between furfural and water has not previously been reported. The effects of acids on furfural-water miscibility become increasingly significant in light of recent work on the extraction of metal ions with furfural (*6, 9*). The system furfural–water–formic acid at 25° and 35°C is described here, including binodal curves, tie lines, and plait points. Furfural–water–acetic acid, furfural–water–propionic acid, and furfural–water–butyric acid at 25° and 35°C have been reported previously (*3, 4*). This provides four homologous *n*-alkanoic acid solutes for comparison of behavior, indicating the effect on distribution equilibrium of varying the length of the hydrocarbon chain of the solutes. The present system completes those of the type where the *n*-alkanoic acid is completely miscible with water at ambient temperatures.

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

MATERIALS AND EQUIPMENT

Furfural (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. Deterioration under these conditions was previously found to be negligible (*4*). 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 (*3*).

As previously (*3*), for the various batches of purified furfural, the refractive index at 25°C using the sodium-D line ranged from 1.5228 to 1.5237. The accepted value is 1.5235 (*7*). There was no measurable effect on solubility from this variation in the purity of the distilled furfural.

Formic acid (Fisher, certified ACS, mfgr. assay: wt % formic acid 90.5, acetic acid 0.2) was used without additional purification. By titration against standardized aqueous NaOH solution, 90.1 (±0.1 std dev) wt % acid was found. The equilibrium concentrations reported below have been corrected for the water in the acid.

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 which had been 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, either furfural or water, the addition of which rendered the system immiscible. After the addition of each increment of titrant, the mixture was stirred vigorously with a magnetic stirrer to expedite equilibrium. To minimize errors from furfural decomposition, no more than three points on a 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 immiscible phases formed from known synthetic mixtures in the two-phase region.

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Weighed fractions of each phase were removed and titrated with aqueous NaOH. Weighed amounts of ethanol were added to the furfural-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 (*8*).

When stirred, heterogeneous mixtures in the formic acid system formed emulsions of such instability that phase separation occurred within 30 min after agitation was stopped. 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 was satisfactory, indicating no significant decomposition of the furfural in the time required for phase separation.

RESULTS AND DISCUSSION

The experimental binodal curve data for the formic acid system are given in Table I, and the smoothed curve is given in Figure 1 for 25°C. Repeated determinations of the mutual solubilities of furfural and water and an examination of the smoothed curves plotted on a large scale indicate a precision of ±0.1% by weight. Included in Figure 1 for comparison are the binodal curves for the three other acid systems. The effect of decreasing the chain length of the acid is a decrease in the region of immiscibility. The extent of this decrease in immiscibility itself decreases from one acid to the next as the acid chain lengths decrease. As for the other three acid systems, temperature increase reduces the region of immiscibility to a small extent. In terms of the change in the maximum wt % acid in the immiscible region, the effect of an increase from 25° to 35°C is −3.9 for the butyric acid, −1.9 for the propionic acid, and −1.5 for both the acetic and formic acid systems.

Table I. Binodal Curve
Percent by Weight, at Equilibrium

25°C			35°C		
Furfural	Formic acid	Water	Furfural	Formic acid	Water
95.1	0.0	4.9	94.2	0.0	5.8
84.9	5.0	10.1	89.4	2.3	8.3
75.5	8.9	15.6	78.1	7.2	14.7
71.4	10.1	18.5	66.2	10.6	23.2
69.2	11.1	19.7	57.1	12.5	30.4
60.4	13.0	26.6	49.5	13.5	37.0
53.0	14.4	32.6	44.3	13.8	41.9
45.5	15.1	39.4	37.1	13.8	49.1
43.4	15.2	41.4	28.4	13.2	58.4
38.8	15.3	45.9	23.0	12.2	64.8
33.7	15.1	51.2	18.1	9.8	72.1
24.9	14.0	61.2	14.8	7.3	78.0
18.9	12.0	69.2	12.2	4.6	83.2
16.2	9.9	74.0	11.3	3.7	85.1
13.0	7.0	80.0	8.9	0.0	91.1
11.0	4.5	84.5			
8.0	0.0	92.0			
Estd. plait point			Estd. plait point		
46.2	15.1	38.7	48.2	13.6	38.2

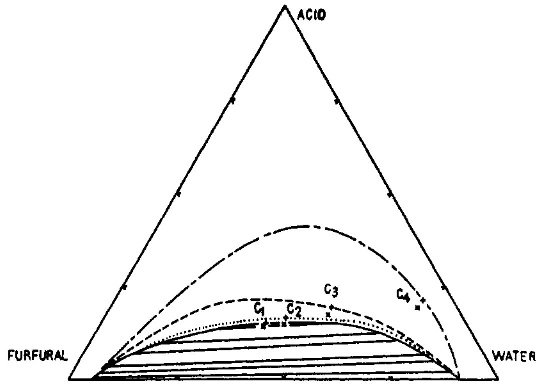

Figure 1. Furfural–water–acid systems, wt %

———— Formic acid, 25°C
.... Acetic acid, 25°C (4)
------ Propionic acid, 25°C (4)
—— —— Butyric acid, 25°C (3)

Plait points at 25° (+) and 35° C (×), with the number of carbon atoms in the acid given by n in C_n

The binodal curves for the formic acid system fall within those reported for 0° and 50°C graphically by Akopov and Voitko (*1*), who did not tabulate solubility data or report tie lines. The present formic acid system tie lines are given in Table II and in Figure 1. In addition to the tie line reliability test noted above, the synthetic heterogenous mixtures for the determination of the fourth and sixth tie lines at 25°C in Table II were duplicated. For each phase, the acid concentration agreed to the nearest 0.1 wt % between duplicates. Although it is not apparent from the wt % plot of Figure 1, the formic acid system exhibits a solutrope on a mol % basis. This occurs at low acid concentration.

The trend of tie lines through the four acid systems is an increasingly greater relative concentration of the acid in the furfural-rich phase with increasing acid chain length. For the formic and acetic acid systems, the water phase is richer in acid, and for the other two systems the furfural phase is richer

Table II. Tie Line Data
Percent by Weight

Furfural-rich phase			Water-rich phase		
Furfural	Formic acid	Water	Furfural	Formic acid	Water
25°C					
94.6	0.3	5.1	9.5	2.3	88.2
91.8	1.7	6.5	11.4	5.1	83.5
88.7	3.2	8.1	12.8	6.9	80.3
80.4	6.9	12.7	16.9	10.6	72.5
73.8	9.4	16.8	20.4	12.6	67.0
59.3	13.3	27.4	32.3	15.1	52.6
35°C					
93.0	0.6	6.4	10.7	2.5	86.8
79.7	6.3	14.0	17.5	9.4	73.1
74.6	8.2	17.2	19.9	10.8	69.3
64.8	11.0	24.2	30.4	13.4	56.2

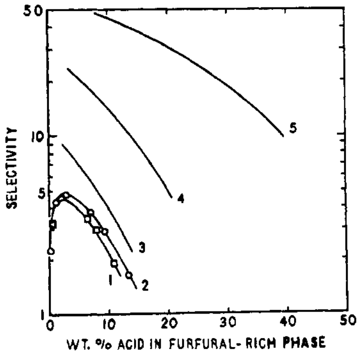

Figure 2. Selectivities in furfural–water–acid systems

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

in acid. The effect on the slope of the tie lines of the increase from 25–35°C is small in all of these furfural–water–acid systems.

Othmer and Tobias (*5*) have shown that binodal curve data may be conveniently correlated through the equation

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

where for the present system, a_1 is the mol % furfural in the furfural-rich phase and b_2 is the mol % water in the water-rich phase. The plots for the present system are linear, and the constants by least-squares treatment of the data at 25° and 35°C, respectively, are: $m = 0.8375$, $n = -1.0183$; $m = 0.9412$, $n = -1.0682$. The plait points have been obtained with the aid of these plots (*4*), and the results are included in Table I and Figure 1. Also included in Figure 1 for comparison are the plait points for the acetic, propionic, and butyric acid systems (*3*, *4*). The plait points in the formic acid system occur at a furfural-to-water ratio greater than unity. This ratio is less than unity for the plait points in the other three acid systems. In each acid system, the furfural-to-water ratio at the plait point increases as the temperature is increased.

The effectiveness of extraction of a solute by a solvent is given by the selectivity (*10*), which in the present work is a measure of the ability of furfural to separate water and acid.

Selectivity may be defined here as x/y, where x is the ratio of solute (acid) wt % concentration in the furfural-rich phase to that in the water-rich phase, and y is the ratio of water wt % concentration in the furfural-rich to that in the water-rich phase. The selectivities of the formic acid system at 25° and 35°C, and of the other acid systems at 25°C are given in Figure 2. The selectivity is lowest in the formic acid system, and this system exhibits maximum selectivity at about 3 wt % acid in the furfural-rich phase.

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Flammability Characteristics of Methylene Chloride (Dichloromethane)

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Studies have been made to determine the effects of temperature, pressure, and additives on the flammability of methylene chloride vapors in air. Flammability diagrams for methylene chloride and for methyl alcohol in oxygen-nitrogen atmospheres are presented, together with diagrams showing the effect of methyl alcohol and of tertiary butyl alcohol on the flammability diagram of methylene chloride in air. It was determined that methylene chloride becomes flammable at 80°F and 760 mm Hg at a vapor concentration of 17% (by volume) with the addition of less than 0.5% (by volume) of methyl alcohol. Pure methylene chloride vapors in air become flammable at approximately 217°F at 760 mm Hg and at 80°F at 1280 mm Hg absolute.

Dichloromethane, methylene chloride in more popular terminology, is a common solvent often considered to be nonflammable. Because of extensive use in large quantities by many companies, a thorough study of those conditions which contribute to flammability was in order.

An explosive limits apparatus was employed, adapted so that limits could be determined at a wide variety of pressures and temperatures. The primary aims were to determine upper and lower flammable limits at atmospheric pressure and the effects of pressure and temperature on those limits.

Changes in the flammable limits because of admixture with known flammable solvents were also to be explored since methylene chloride is commonly used in mixed solvent systems.

PROCEDURE

Flammability results were based on visual observations of upward and outward flame propagation from a 12-kV arc-ignition source centrally located in a 5-liter spherical flask (Figure 1). The flask was contained in a small oven equipped with a heavy duty hair-dryer type of heater which permitted variation and control of apparatus temperature. *Caution:* Tests should commence at concentrations known to be outside the flammable range, with limits being approached in small increments. Violent explosions are possible with stoichiometric and near-lower-limit mixtures, with tests run at elevated pressures, and with tests run in strong oxidizers. Thus, all testing of this nature in simple glass equipment should include the use