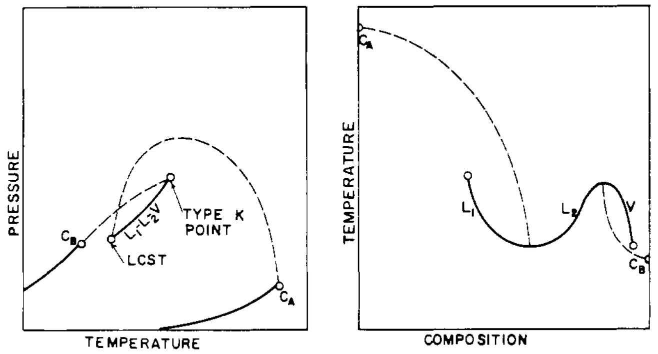

Figure 1. Phase behavior in the three-phase regions

were done on the vapor phase, since it was the most difficult phase upon which to obtain reproducible molar volume information. For all practical purposes, the vapor phases coexisting with the two liquid phases for both systems may be regarded as pure ethane gas.

Figure 1 shows schematic sketches of the phase behavior in the three-phase region. The dashed lines are vapor-liquid critical loci. Actually only one vapor-liquid critical point was experimentally determined. The critical phase was at a temperature of 37.51° C. and a pressure of 55.96 atm. and had a composition of 0.9668 mole fraction ethane and a molar volume of 93.79 ml. per gram mole. From the figure, it is apparent that there is a discontinuity in the vapor-liquid critical locus.

Three-phase behavior of the type presented here has been discussed at some length by Rowlinson (*7*). The results obtained here further confirm Rowlinson's observation that this type of miscibility is found in mixtures of nonpolar molecules of the same chemical type if the molecular sizes and energies of interaction of the components are sufficiently different. The data definitely prove, however, that these two systems do not follow the Bronsted and Koefoed "principle of congruence" (*1*) nor do they follow regular solution theory even when the compositions are expressed in volume fractions.

## NOMENCLATURE

$C_A$ = vapor-liquid critical point of pure high boiling hydrocarbon
$C_B$ = vapor-liquid critical point of pure ethane
$L_1$ = liquid phase less rich in ethane (higher density)
$L_2$ = liquid phase richest in ethane
LCST = lower critical solution temperature ($L_1$ is in critical identity with $L_2$ in presence of vapor phase)
Type K = singular point ($L_2$ is in critical identity with $V$ in presence of $L_1$ phase)
$V$ = vapor phase

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# Ternary Liquid Equilibria

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**Phase equilibrium data for the ternary liquid-liquid systems acetic acid–water–methyl butyrate, propionic acid–water–methyl butyrate, and *n*-butyric acid–water–methyl butyrate at 30° C. are presented. The tie line data are well correlated by the methods of Hand and Othmer and Tobias.**

IN CONTINUATION of studies on liquid-liquid equilibria of fatty acid-water-solvent systems (*5*), the systems acetic acid-water-methyl butyrate, propionic acid-water-methyl butyrate, and *n*-butyric acid-water-methyl butyrate have been studied at 30° C. and atmospheric pressure and the data are presented here.

Acetic acid (British Drug Houses, Analar grade, 99.8%), propionic acid (Eastman Kodak Co., 99.9%), butyric acid (Narden Co., 99.8%), and methyl butyrate (Narden Co., $d^{30^\circ}$ 0.8821, $n_D^{30^\circ}$ 1.3822) with negligible free acidity were used. The method suggested by Othmer, White, and Truegar (*3*) was followed for the determination of saturation isotherm and tie-line data. The acid content of aqueous and ester layers was determined by titration.

The experimental data for the saturation isotherms and tie lines are given in Table I. The accuracy of the experimental data is within ± 0.5%. The binodal curves for the systems are plotted in Figures 1, 2, and 3. The equilibrium distribution of the acids between water and ester is shown in Figure 4, which also contains distribution data of formic acid between water and methyl butyrate, determined at 28° C. by Rao, Murty, and Rao (*5*), for comparison.

The tie line data are correlated satisfactorily by the methods of Othmer and Tobias (*2*) and Hand (*1*) (Table II). The plait points for the systems were located by the method of Treybal, Weber, and Daley (*6*) and their compositions are given in Table I, and indicated by arrows in the figures.

Table I. Mutual Solubility and Tie Line Data

Acetic acid-water-methyl butyrate, propionic acid-water-methyl butyrate, and butyric acid-water-methyl butyrate at 30° C. systems. Proportions expressed in wt. %.

Acetic Acid-Water-Methyl Butyrate

Mutual Solubility Data

| Ester | Acid | Water |
|---|---|---|
| 89.5 | 6.4 | 4.1 |
| 83.4 | 10.5 | 6.1 |
| 77.1 | 16.0 | 6.9 |
| 72.7 | 18.8 | 8.5 |
| 70.1 | 20.2 | 9.7 |
| 65.5 | 23.0 | 11.5 |
| 59.3 | 26.2 | 14.5 |
| 55.2 | 28.5 | 16.3 |
| 53.7 | 28.9 | 17.4 |
| 46.8 | 31.7 | 21.5 |
| 45.0 | 32.5 | 22.5 |
| 37.0 | 34.3 | 28.7 |
| 30.4 | 35.3 | 34.3 |
| 26.5 | 35.5 | 38.0 |
| 23.0 | 36.0 | 41.0 |
| 22.0 | 36.2 | 41.8 |
| 18.0 | 36.0 | 46.0 |
| 15.9 | 35.5 | 48.6 |
| 13.0 | 34.4 | 52.6 |
| 9.6 | 32.6 | 57.8 |
| 7.6 | 30.9 | 61.5 |
| 5.9 | 28.1 | 66.0 |
| 4.1 | 22.8 | 73.1 |
| 3.7 | 18.4 | 77.9 |
| 3.1 | 13.7 | 83.2 |
| 2.7 | 8.7 | 88.6 |

Tie Line Data

Ester Layer

| | | |
|---|---|---|
| 84.2 | 10.5 | 5.3 |
| 80.0 | 14.1 | 5.9 |
| 73.2 | 18.2 | 8.6 |
| 67.6 | 21.5 | 10.9 |
| 64.2 | 23.5 | 12.3 |
| 57.8 | 27.5 | 14.7 |

Water Layer

| | | |
|---|---|---|
| 2.9 | 15.2 | 81.9 |
| 3.9 | 21.2 | 74.9 |
| 5.0 | 25.5 | 69.5 |
| 7.0 | 28.8 | 64.2 |
| 8.2 | 31.6 | 60.2 |
| 15.0 | 35.2 | 49.8 |
| 28.1[a] | 35.4[a] | 36.5[a] |

Propionic Acid-Water-Methyl Butyrate

Mutual Solubility Data

| | | |
|---|---|---|
| 91.0 | 5.9 | 3.1 |
| 86.4 | 9.7 | 3.9 |
| 81.0 | 14.1 | 4.9 |
| 75.6 | 18.5 | 5.9 |
| 69.0 | 23.5 | 7.5 |
| 62.0 | 28.5 | 9.5 |
| 57.6 | 30.3 | 12.1 |
| 53.9 | 33.7 | 12.4 |
| 48.3 | 36.5 | 15.2 |
| 42.5 | 39.2 | 18.3 |
| 40.2 | 40.0 | 19.8 |
| 30.9 | 41.2 | 27.9 |
| 25.6 | 40.1 | 34.3 |
| 22.2 | 39.0 | 38.8 |
| 19.2 | 38.0 | 42.8 |
| 17.1 | 37.0 | 45.9 |
| 13.7 | 35.6 | 50.7 |
| 11.2 | 32.1 | 56.7 |
| 10.7 | 31.8 | 57.5 |
| 7.9 | 28.9 | 63.2 |
| 6.0 | 25.7 | 68.3 |
| 5.0 | 21.4 | 73.6 |
| 4.0 | 17.0 | 79.0 |
| 3.6 | 13.0 | 83.4 |
| 2.9 | 8.2 | 88.9 |

Tie Line Data

Ester Layer

| | | |
|---|---|---|
| 81.8 | 13.3 | 4.9 |
| 75.9 | 18.3 | 5.8 |
| 70.9 | 21.9 | 7.2 |
| 65.5 | 25.7 | 8.8 |
| 62.5 | 27.9 | 9.6 |
| 59.2 | 30.0 | 10.8 |

Water Layer

| | | |
|---|---|---|
| 2.5 | 6.2 | 91.3 |
| 2.7 | 8.4 | 88.9 |
| 2.9 | 10.3 | 86.8 |
| 3.0 | 11.8 | 85.2 |
| 3.0 | 13.2 | 83.8 |
| 3.2 | 14.6 | 82.2 |
| 14.2[a] | 36.2[a] | 49.6[a] |

Butyric Acid-Water-Methyl Butyrate

Mutual Solubility Data

| | | |
|---|---|---|
| 92.8 | 5.2 | 2.0 |
| 87.2 | 9.6 | 3.2 |
| 85.8 | 10.6 | 3.6 |
| 80.3 | 15.1 | 4.8 |
| 77.0 | 18.8 | 4.2 |
| 66.7 | 27.0 | 6.3 |
| 57.5 | 34.7 | 7.8 |
| 53.8 | 38.2 | 8.0 |
| 47.1 | 42.9 | 10.0 |
| 37.7 | 49.6 | 12.7 |
| 29.9 | 54.7 | 15.4 |
| 20.6 | 59.0 | 20.4 |
| 15.3 | 60.0 | 24.7 |
| 12.4 | 59.6 | 28.0 |
| 7.9 | 56.4 | 35.7 |
| 4.9 | 50.2 | 44.9 |
| 3.6 | 43.3 | 53.1 |
| 3.2 | 34.2 | 62.6 |
| 1.4 | 26.0 | 72.6 |
| 0.8 | 17.5 | 81.7 |
| 0.7 | 13.7 | 85.6 |
| 0.6 | 13.4 | 86.0 |
| 0.8 | 11.1 | 88.1 |
| 1.0 | 8.1 | 90.9 |

Tie Line Data

Ester Layer

| | | |
|---|---|---|
| 85.7 | 10.8 | 3.5 |
| 75.8 | 19.1 | 5.1 |
| 68.5 | 25.2 | 6.3 |
| 61.6 | 31.0 | 7.4 |
| 50.5 | 40.5 | 9.0 |
| 47.0 | 43.5 | 9.5 |
| 44.0 | 46.0 | 10.0 |

Water Layer

| | | |
|---|---|---|
| 1.5 | 1.6 | 96.9 |
| 1.3 | 3.1 | 95.6 |
| 1.3 | 3.5 | 95.2 |
| 1.2 | 4.3 | 94.5 |
| 1.1 | 5.7 | 93.2 |
| 1.1 | 6.3 | 92.6 |
| 1.1 | 6.8 | 92.1 |
| 1.8[a] | 30.4[a] | 67.8[a] |

[a] Plait point data at 30° C.

Table II. Tie Line Correlations

| System | Hand, $\frac{X_{cs}}{X_{ss}} = K\left(\frac{X_{cw}}{X_{ww}}\right)^n$ | | Othmer-Tobias, $\frac{1-X_{ss}}{X_{ss}} = K\left(\frac{1-X_{ww}}{X_{ww}}\right)^n$ | |
|---|---|---|---|---|
| Acetic acid-water-methyl butyrate | $K = 0.725$ | $n = 1.04$ | $K = 0.92$ | $n = 1.033$ |
| Propionic acid-water-methyl butyrate | $K = 4.35$ | $n = 1.227$ | $K = 10.0$ | $n = 1.666$ |
| Butyric acid-water-methyl butyrate | $K = 51.03$ | $n = 1.50$ | $K = 116.2$ | $n = 1.835$ |

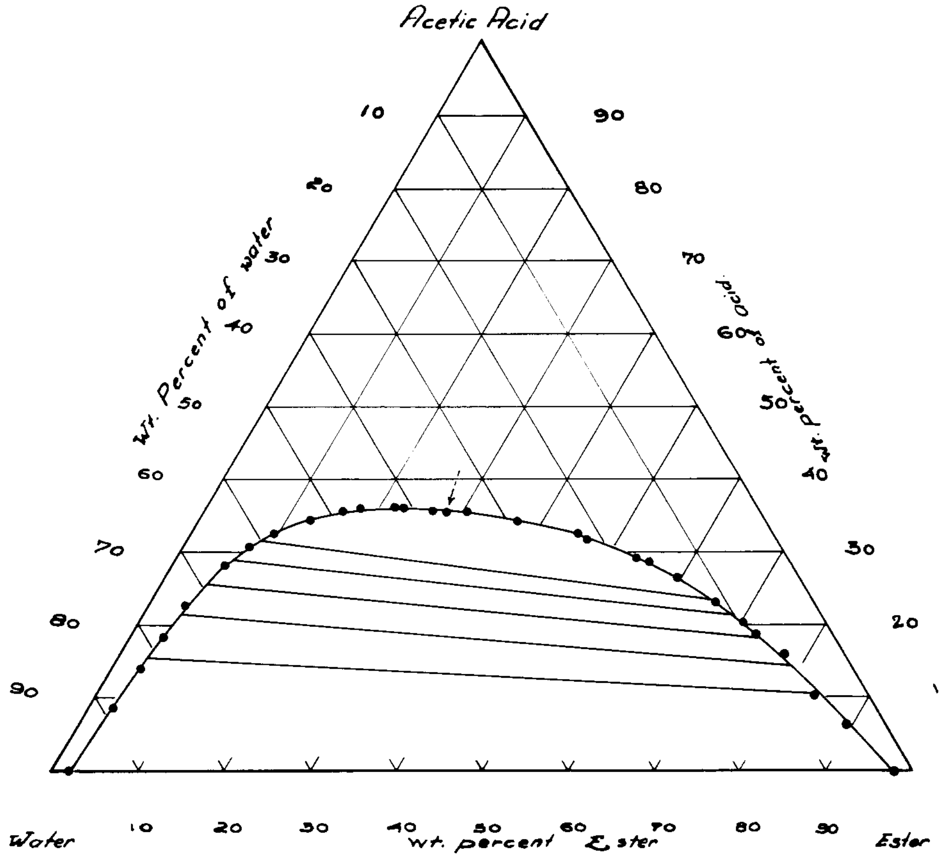

Figure 1. Ternary phase equilibrium diagram for system water–acetic acid–methyl butyrate

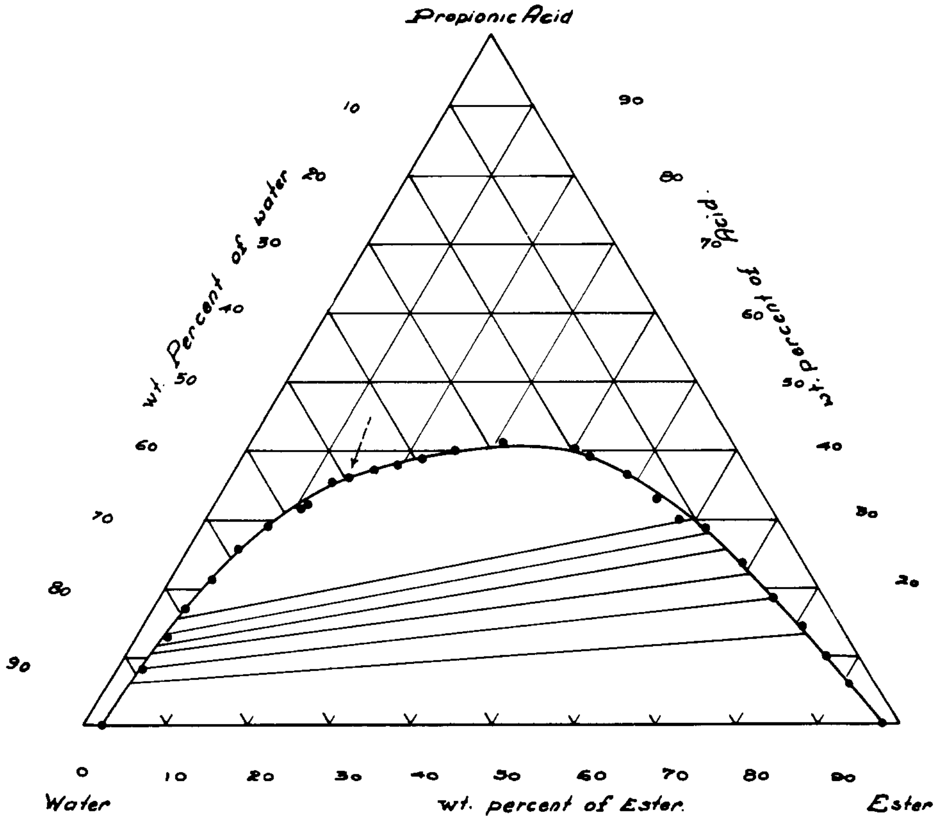

Figure 2. Ternary phase equilibrium diagram for system water–propionic acid–methyl butyrate

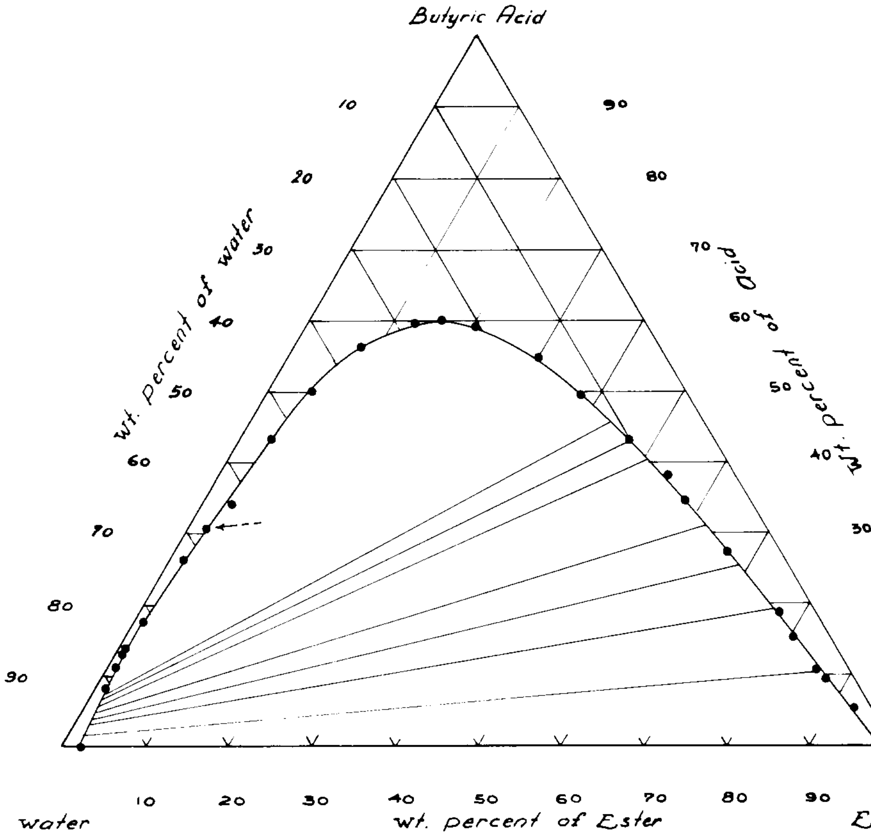

Figure 3. Ternary phase equilibrium diagram for system water–butyric acid–methyl butyrate

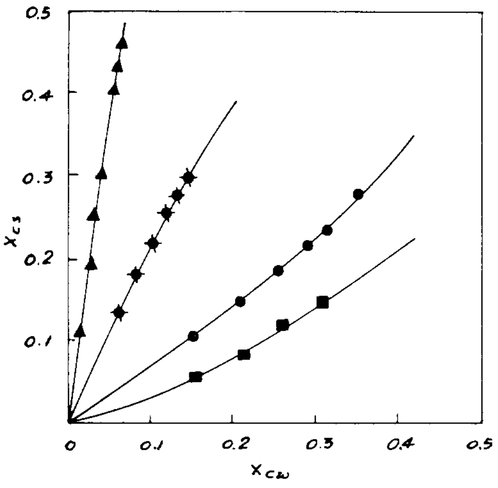

Figure 4. Distribution curves

■ Formic acid (5)
● Acetic acid
✦ Propionic acid
▲ Butyric acid

Figures 1, 2, and 3 show that the region of heterogeneity increases as the solute is changed from acetic to butyric acid. The distribution curves (Figure 4) show that the solute prefers the solvent phase rather than the water phase, when the solute is changed in a homologous series in the increasing order of molecular weight, thus confirming earlier results (*4*, *5*).

## NOMENCLATURE

C = solute
W = water
S = solvent
$X_{cw}$ = weight fraction of solute in water layer
$X_{cs}$ = weight fraction of solute in ester layer
$X_{ww}$ = weight fraction of water in water layer
$X_{ss}$ = Weight fraction of solvent in solvent layer

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# Pressure-Volume-Temperature Behavior of Pentafluoromonochloroethane

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FOR a number of years, this laboratory has investigated the physical and chemical properties of molecules containing fluorine. As a part of this continuing study, both a Benedict-Webb-Rubin and a Martin-Hou equation of state have been obtained for pentafluoromonochloroethane. Vapor pressure and liquid density data have been determined over a wide temperature range. Finally, the rectilinear diameter line has been computed.

## MATERIAL

The sample of $CF_3CF_2Cl$ originated from commercially available Genetron 115 (Allied Chemical) with a minimum purity of 98 mole %. Impurities detected by gas chromatography were removed from the sample by distillation in a 5 foot × ½ inch vacuum-jacketed column packed with Helipak. The distillate was collected until the concentra-