Ternary Liquid Equilibria

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Phase equilibrium data for the ternary liquid-liquid systems acetic acid–water–ethyl butyrate and n-butyric acid–water–ethyl butyrate at 28° C. are presented. The tie-line data are well correlated by the methods of Hand and of Othmer and Tobias.

THE SYSTEMS acetic acid-water-ethyl butyrate and butyric acid-water-ethyl butyrate have been studied at 28° C. and at atmospheric pressure as part of an investigation of liquid-liquid equilibria of fatty acid-water-solvent systems (*6*). The data are presented here.

Acetic acid (B.D.H. Analar grade, 99.8%), butyric acid (Naarden Co., 99.8%), and ethyl butyrate (Naarden Co., $d^{30°}$, 0.8685, n_D^{30}, 1.3880) with negligible free acidity were used. The method suggested by Othmer and coworkers (*3*) was followed for the determination of saturation iso-

Table I. Mutual Solubility and Tie Line Data at 28° C.
(Proportions expressed in wt. %)

Mutual Solubility Data

Water	Acid	Ester	Water	Acid	Ester
Acetic acid–water–ethyl butyrate			Butyric acid–water–ethyl butyrate		
89.0	10.1	0.9	95.6	3.9	0.5
82.2	16.8	1.0	91.4	8.1	0.5
87.9	20.5	1.6	87.3	12.2	0.5
72.0	26.2	1.8	83.2	16.3	0.5
67.3	30.1	2.6	78.6	20.7	0.7
60.9	35.5	3.6	73.9	25.0	1.1
56.3	39.1	4.6	70.0	28.6	1.4
48.9	42.9	8.2	65.7	32.8	1.5
43.2	44.9	11.9	60.4	37.6	2.0
38.6	45.0	16.4	55.6	42.1	2.3
34.7	44.9	20.4	48.9	47.9	3.2
31.3	43.8	24.9	44.5	51.3	4.2
28.0	42.7	29.3	36.9	57.0	6.1
18.1	36.5	45.4	27.2	61.5	11.3
14.6	33.7	51.7	21.9	62.3	15.8
11.5	29.9	58.6	20.1	59.8	20.1
9.0	26.1	64.9	13.4	59.0	27.6
7.2	21.3	71.5	10.0	50.0	40.0
5.3	17.1	77.6	8.3	46.3	45.4
3.7	10.8	85.5	7.2	41.9	50.9
2.8	5.8	91.4	6.4	37.2	56.4
			5.7	32.8	61.5
			4.7	24.8	70.5
			3.1	16.9	80.0
			2.5	13.5	84.0
			2.5	8.7	88.8
			2.5	6.0	91.5

Tie Line Data

Ester layer			Water layer		
Water	Acid	Ester	Water	Acid	Ester
Acetic acid–water–ethyl butyrate					
3.3	7.3	89.4	82.7	16.3	1.0
4.0	11.1	84.9	76.1	22.4	1.5
5.1	14.7	80.2	70.8	27.5	1.7
6.1	17.4	76.5	64.2	33.0	2.8
7.1	21.2	71.7	54.5	40.1	5.4
Butyric acid–water–ethyl butyrate					
3.3	18.9	77.8	96.5	3.0	0.5
4.5	25.8	69.7	95.0	4.0	1.0
5.3	31.5	63.2	94.2	4.7	1.1
6.7	36.7	56.6	93.5	5.5	1.0
7.3	40.8	51.9	93.0	6.1	0.9
8.0	43.3	48.7	92.5	6.5	1.0

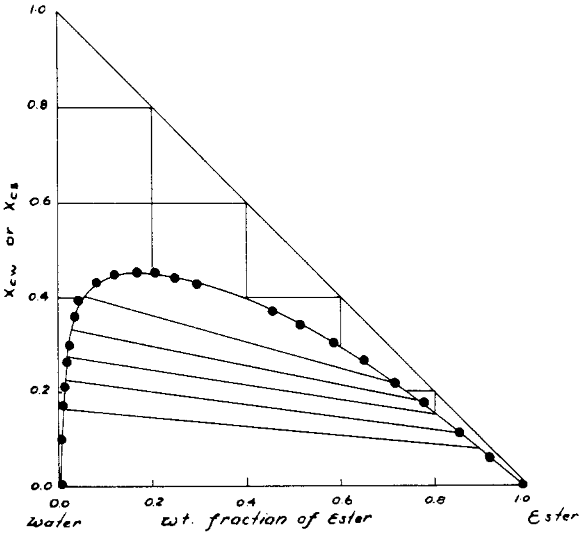

Figure 1. Ternary phase equilibrium diagram
System: water–acetic acid–ethyl butyrate

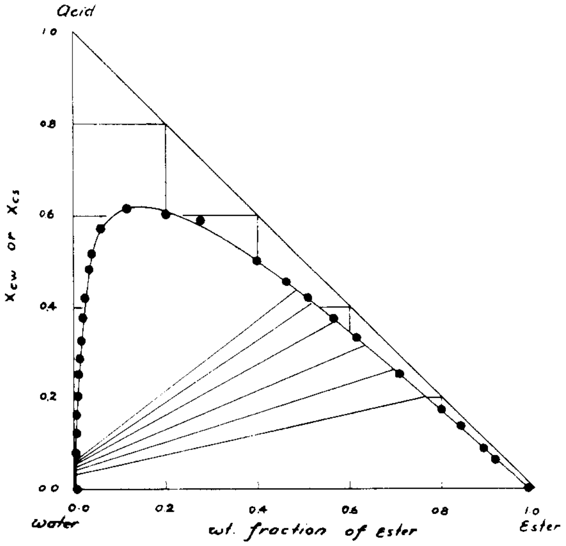

Figure 2. Ternary phase equilibrium diagram
System: water–n-butyric acid–ethyl butyrate

Table II. Plait Point Data at 28° C.

System	Water	Acid	Ester
Acetic acid-water-ethyl butyrate	13.89	30.97	55.11
Butyric acid-water-ethyl butyrate	6.30	36.54	57.09

Table III. Tie-line Data Correlations

System	Hand $\left[\frac{X_{cs}}{X_{ss}}\right] = K\left[\frac{X_{cw}}{X_{ww}}\right]^n$	
Acetic acid-water-ethyl butyrate	$K = 0.368$	$n = 0.775$
Butyric acid-water-ethyl butyrate	$K = 64.4$	$n = 1.62$
	Othmer-Tobias $\left[\frac{1-X_{ss}}{X_{ss}}\right] = K\left[\frac{1-X_{ww}}{X_{ww}}\right]^n$	
Acetic acid-water-ethyl butyrate	$K = 0.51$	$n = 1.15$
Butyric acid-water-ethyl butyrate	$K = 44.0$	$n = 1.52$

therm and the 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 and 2. The equilibrium distribution of the acids between water and ester is shown in Figure 3. Also, in the same diagram, the distribution data of propionic acid between water and ethyl butyrate, as determined by Jaya Rama Rao (*4*) are plotted for comparison.

The tie-line data are correlated satisfactorily by the method of Othmer and Tobias (*2*) and Hand (*1*) (Table III). The plait points for the systems, located by the method of Treybal and coworkers (*7*), and their compositions are given in Table II.

Figures 1 and 2 on comparison show that the region of heterogeneity increases as the solute is changed from acetic to butyric acid. The distribution curves of Figure 3 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 the earlier results (*4*, *5*).

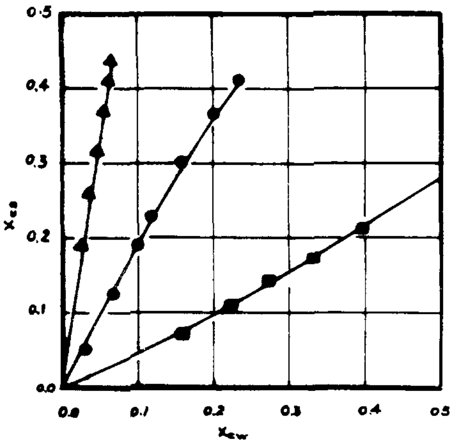

Figure 3. Distribution curves

▲ Butyric acid
● Propionic acid
■ Acetic acid

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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