NOMENCLATURE

a = interfacial surface area, sq. ft./cu. ft. of volume
c = concentration of solute, lb. moles/cu. ft. of solution in the phase indicated by the subscript
E_A = stage efficiency, dimensionless
H.E.T.S. = height equivalent to a theoretical stage, ft.
H.T.U. = individual film height of a transfer unit based on the phase indicated by the subscript, ft.
H.T.U.$_O$ = over-all height of a transfer unit based on the phase indicated by the subscript, ft.
Ka = over-all mass transfer coefficient, based on the phase indicated by the subscripts, lb. moles/hr., cu. ft., ΔC
K' = constant
M.I.B.C. = methyl isobutyl carbinol
m = slope of the equilibrium curve = dC_W^*/dC_S
M.B.E. = material balance error for the solute, %.
N' = rate of mass transfer, lb. moles/sq. ft., hr.
N_a = number of actual stages
N_t = number of theoretical stages
V = superficial velocity, cu. ft./hr., sq. ft., of the phase indicated by the subscript
Z = effective extraction height, ft.
Δ = difference
γ' = constant
θ = time

Subscripts

C or W = continuous phase (water)
D or S = dispersed phase (solvent)
T = toluene phase
1 = conditions at the top of the column
2 = conditions at the bottom of the column

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Ternary Liquid Equilibria: 1-Hexanol–Water–Fatty Acids

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LIQUID EXTRACTION has lately received considerable attention as an important separation process, especially in view of its applicability in such processes where vaporization methods are not practicable. For the successful development of liquid extraction processes and the design of extraction equipment, it is necessary to have a knowledge of the phase equilibrium relations of ternary liquid systems.

The present work, part of a study of fatty acid extraction and investigations of liquid phase equilibria in search of potential solvents, was undertaken to find out the applicability of higher alcohols as solvents for the extraction of fatty acids from dilute aqueous solutions.

MATERIALS

Propionic Acid. Propionic acid of reagent grade from E. Merck Co. was used. Chemical analysis, as determined by titration with standard alkali, shows it to be 99.0% pure. Density at 30° C. = 0.9829 gram per cc.

Butyric Acid. Butyric acid of reagent grade from Naarden Chemical Co. (Holland) was used. The purity as determined by titration with standard alkali is 99.3%. Density at 30° C. = 0.9508 gram per cc.

n-Hexanol. *n*-Hexanol of Jean A. du Crocq, Jr., Ltd., (Holland) was subjected to fractionation in an all-glass fractionating column and the fraction, boiling between 156° and 156.5° C. was collected and used.

Distilled water, free from carbon dioxide, was used in all the cases.

EXPERIMENTAL PROCEDURE

Solubility and tie-line data were determined by the method of Othmer and others (*2*). The binodal curve was determined by the appearance and disappearance of turbidity, the former being used for building up the end wings; the latter, for establishing the middle portion of the curve.

For the determination of the tie-line data, ternary liquid mixtures of known composition within the two-phase region were prepared in separating funnels, shaken vigorously for

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about 15 minutes, and then allowed to settle for nearly 3 hours with intermittent shaking in a constant temperature bath, which was maintained at 30° C. After further settling for 3 hours, which was found to be adequate for the attainment of equilibrium, the two layers were separated, and the acid content of each layer was titrated with a standard alkali (0.1N NaOH).

By use of the mutual solubility curve and the acid compositions of the conjugate layers, the compositions of of the other two components in the equilibrium phases were estimated.

RESULTS AND CORRELATION

The mutual solubility and equilibrium distribution data for the two systems are recorded in Tables I and II. Saturation isotherms of the two systems are compared in Figure 1, and equilibrium distribution curves are shown in Figure 2.

Plait points for the systems were estimated by the method of Treybal, Weber, and Daley (*7*) (shown in Figure 3) and their compositions recorded in Tables I and II. Because of the distribution of the fatty acid in favor of the alcohol, the tie lines sloped towards the water-rich side of the binodal curve (the saturated isotherm) (Figure 1), and the estimated plait points also lay on this side of the curve.

The tie-line data were correlated by the well-established method of Hand, (*1*), which resulted in single straight lines essentially parallel for the two systems. This shows that the exponent n of the Hand correlation, given below, is the same for the two systems and is independent of the concentration of the solute in the conjugate phases.

$$\frac{X_{CB}}{X_{BB}} = K \left(\frac{X_{CA}}{X_{AA}}\right)^n$$

An examination of the saturation isotherms in Figure 1 shows that for a given water-solvent pair, the area of heterogeneity increases with increasing molecular weight of the homologous series of fatty acids. With the increase in the molecular weight of the fatty acid, the acid shows less affinity toward water, as generally shown by a decrease in its solubility in water. The distribution ratio could, therefore, be expected to favor the solvent layer more than the water layer. The increase in the area of heterogeneity and the increased distribution of acid in favor of the solvent phase from propionic acid to butyric acid may be attributed to the increasing influence of the alkyl group in the fatty acid toward water and the organic solvent. This confirms our earlier observations on fatty acid–water–ester systems (*2*, *3*), fatty acid–water–hydrocarbon systems (*5*), and fatty acid–water–4-methyl-2-pentanol systems (*6*).

CONCLUSION

Mutual solubility and equilibrium tie-line data have been obtained at 30° C. for ternary systems of water–1-hexanol with propionic and butyric acids as the solute components. The area of heterogeneity was observed to increase, for the same solvent-water pair, with increase in molecular weight of the homologous series of the fatty acids. The distribution of the acid was found to be in favor of the solvent layer for both systems. Distribution ratio in favor of the solvent phase was greater in the case of the ternary system water–1-hexanol-butyric acid than with water–1-hexanol-propionic acid. This was explained in terms of the

Table I. Mutual Solubility and Tie-Line Data for the System Propionic Acid–Water–1-Hexanol at 30° C.

Mutual Solubility Data, Wt. %

No.	Propionic Acid	Water	1-Hexanol
1	0.0	99.35	0.65
2	15.7	83.6	0.7
3	22.1	76.3	1.6
4	25.3	71.7	3.0
5	31.4	60.6	8.0
6	35.2	52.0	12.8
7	38.6	43.5	17.9
8	40.8	35.7	23.5
9	41.4	30.8	27.8
10	41.2	27.0	31.8
11	41.1	26.8	32.1
12	38.7	21.0	40.3
13	33.9	16.3	49.8
14	27.7	12.8	60.5
15	19.5	10.8	69.7
16	6.8	8.3	84.9
17	0.0	7.0	93.0

Tie-Line Data at 30° C.

No.	Acid	Water	Solvent
	Wt. % in Solvent Layer		
1	7.6	8.8	83.6
2	14.0	9.5	76.5
3	19.7	10.4	69.9
4	32.9	15.7	51.4
5	40.6	24.0	35.4
6	35.0	52.0	13.0
	Wt. % in Water Layer		
1	2.5	96.85	0.65
2	4.8	94.5	0.7
3	7.4	91.8	0.8
4	14.1	84.9	1.0
5	21.2	76.7	2.1
6	Plait	Point	

Table II. Mutual Solubility and Tie-Line Data for the System Butyric Acid–Water–1-Hexanol at 30° C.

Mutual Solubility Data, Wt. %

No.	Butyric Acid	Water	1-Hexanol
1	0.0	99.35	0.65
2	23.5	75.7	0.8
3	29.8	68.8	1.4
4	43.4	53.7	2.9
5	48.4	47.7	3.9
6	53.9	40.3	5.8
7	57.0	35.1	7.9
8	58.6	31.2	10.2
9	59.5	25.7	14.8
10	57.9	21.1	21.0
11	53.3	16.6	30.1
12	48.1	13.9	38.0
13	37.2	11.0	51.8
14	21.1	8.6	70.3
15	0.0	7.0	93.0

Tie-Line Data at 30° C.

No.	Acid	Water	Solvent
	Wt. % in Solvent Layer		
1	9.0	8.0	83.0
2	16.2	8.2	75.6
3	23.0	9.0	68.0
4	39.0	11.4	49.6
5	46.4	13.2	40.4
6	54.1	16.9	29.0
7	39.6	58.1	2.3
	Wt. % in Water Layer		
1	0.9	98.5	0.6
2	1.7	97.7	0.6
3	2.6	96.8	0.6
4	5.1	94.25	0.65
5	6.5	92.85	0.65
6	8.3	91.0	0.7
7	Plait	Point	

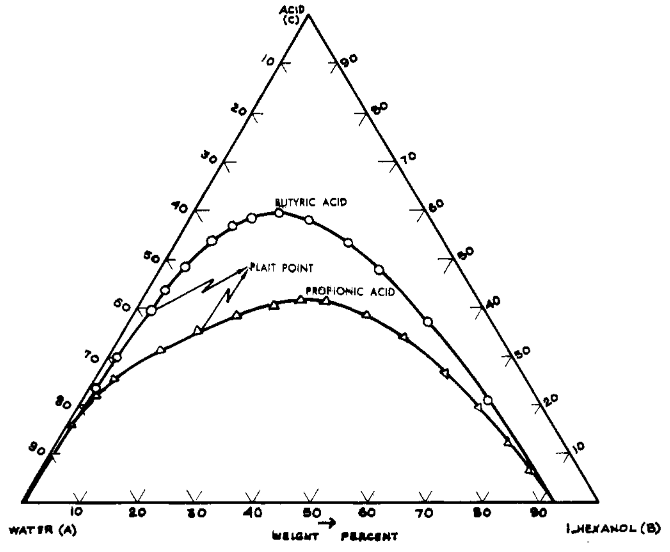

Figure 1. Phase equilibrium diagram for fatty acid–water–1-hexanol systems at 30° C.

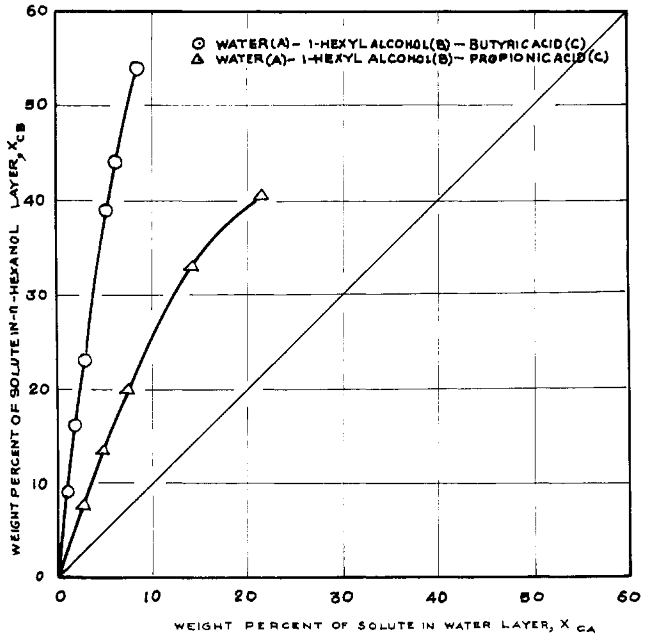

Figure 2. Equilibrium distribution diagram for fatty acid–water–1-hexanol systems at 30° C.

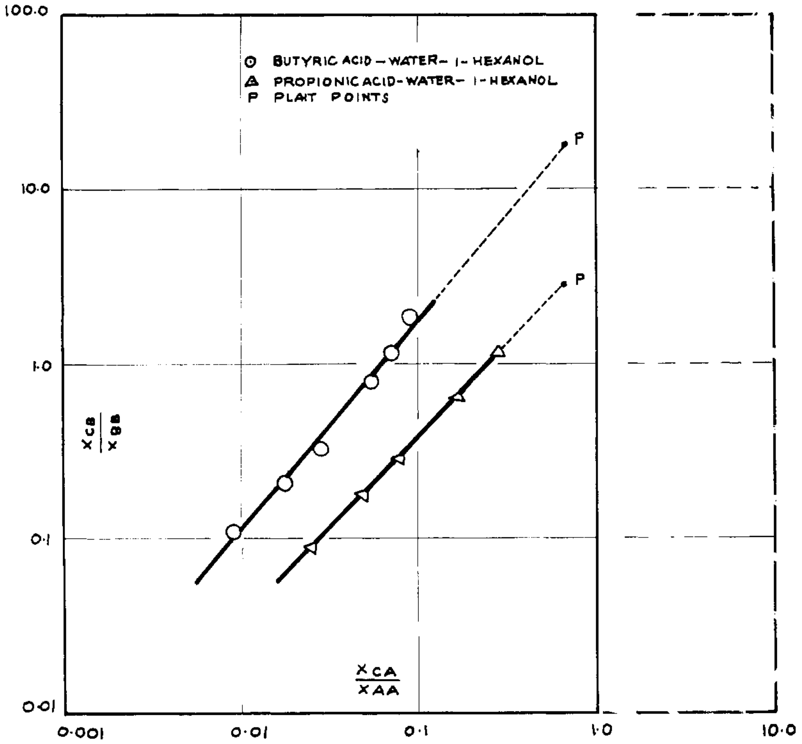

Figure 3. Hand tie-line correlation for fatty acid–water–1-hexanol systems

relative influences of the alkyl and carboxyl groups on water and the organic solvent. The equilibrium distribution data have been satisfactorily correlated by the method of Hand.

NOMENCLATURE

C = solute (acid)
A = water
B = solvent
X_{CB} = weight fraction of solute in the solvent layer
X_{CA} = weight fraction of solute in the aqueous layer
X_{BB} = weight fraction of solvent in the solvent layer
X_{AA} = weight fraction of water in the water layer
K, n = constants in the Hand correlation

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