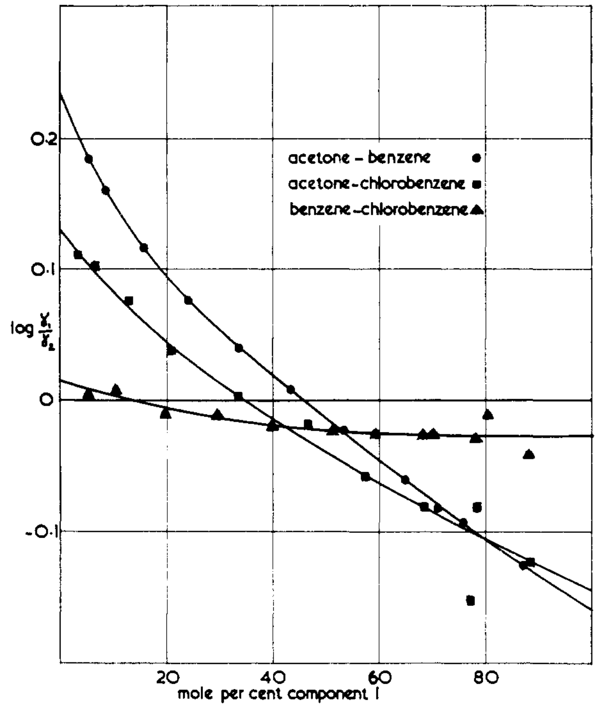

Figure 3. Activity coefficient plots for the three binary systems

The integrals in Equation 13 have been evaluated for the ternary from the chlorobenzene point to the acetone point along the path defined by the lines $x_B = x_A$ and $x_C = 0$, and are given in Table IV.

The small difference term indicates the consistency of the results and demonstrates the practicality of the method, but a drawback is that smoothed data must be used, giving no indication of the magnitude of random errors in the data.

NOMENCLATURE

F^E = excess free energy per mole of solution
d_4^{25} = specific gravity at 25° C. with respect to water at 4° C.
n_D^{25} = refractive index for sodium D line at 25° C.
p_M = property (either d_4^{25} or n_D^{25}) of a mixture as recorded in this work
p_M' = property of mixture as determined in other situations
Δp = $10^4(p_M - \Sigma x_i p_i)$
x = mole fraction in liquid
y = mole fraction in vapor in equilibrium with liquid of composition x
γ = activity coefficient
ΔH_m = isobaric and isothermal heat of mixing

SUBSCRIPTS

A = acetone
B = benzene
C = chlorobenzene

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Phase Equilibria in 1-Butanol–Water–Lactic Acid System

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Purification of lactic acid by liquid-liquid extraction has been investigated by several investigators, and the results have been summarized recently by Weiser and Geankoplis (*8*). They found that 3-methyl-1-butanol appeared to be the best selective solvent to extract lactic acid from aqueous solutions. They obtained a complete ternary equilibrium and phase diagram for the system 3-methyl-1-butanol–water–lactic acid at 25.0° C. and some data at 49.5° C.

However, they found that the butyl alcohols were also good extracting agents for lactic acid. The amyl alcohols are somewhat less soluble in dilute lactic acid–water solutions than the butyl alcohols and should give lower solvent losses in an extraction process.

To make a more complete study of extraction of lactic acid it was felt that ternary data using a butyl alcohol would be useful. As a result complete solubility and tie line data were obtained for the system 1-butanol–water–lactic acid at 25.0° C. Also the tie line data for the 3-methyl-1-butanol and 1-butanol systems were correlated by two methods.

EXPERIMENTAL PROCEDURES

The lactic acid and 1-butanol used in the experiments were Baker analyzed reagent grade. The lactic acid solution was 85% lactic acid and contained a mixture of free lactic acid and the self-polymer. To break up the mixture into the simple monomeric lactic acid, solutions containing about 20% acid were prepared and refluxed for 24 hours. This was analyzed by

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the methods outlined by others (*1, 4, 8*) and no polymer remained in the solution.

The solubility curve for the ternary phase diagram was determined by titrating known lactic acid–water solutions to the cloud point with 1-butanol. The solution was agitated in the constant temperature bath during the titration. Two solubility points using 3-methyl-1-butanol were also obtained as a check and to supplement the data on that system.

To determine the tie lines a procedure similar to that used by others (*8*) was used. Known weights of the three components were added to a flask and equilibrated for several hours at 25.0° C. Then, after settling, samples of each phase were removed, weighed, and analyzed for lactic acid by titration with 0.2*N* sodium hydroxide. The data are given in Table I.

Table I. Solubility and Tie-Line Data for System

(1-Butanol–water–lactic acid at 25.0° C.)

Solubility Data

1-Butanol, wt. %	Water, wt. %	Lactic acid, wt. %
7.0	93.0	0
79.3	20.7	0
26.4	60.5	13.1
67.3	26.9	5.8
7.9	86.3	5.8
8.3	83.4	8.3
35.3	51.5	13.2
64.2	28.5	7.3
14.8	72.5	12.7
10.7	78.1	11.2
21.2	65.5	13.3
43.8	43.7	12.5
74.2	23.0	2.8
30.4	56.0	13.6
87.4^a	10.2^a	2.4^a
3.6^a	78.2^a	18.2^a

Equilibrium Tie-Line Data

Lactic acid in water-rich layer, wt. %	Lactic acid in 1-butanol-rich layer, wt. %
12.5	11.9
10.3	9.60
8.50	7.80
2.50	2.14
0.52	0.43
7.04	6.36
8.91	8.12
9.60	8.87

^{a} Data obtained using 3-methyl-1-butanol–water–lactic acid.

DISCUSSION OF DATA

Figure 1 gives the complete ternary diagram for the 1-butanol–water–lactic acid system. The area of immiscibility is much smaller in comparison to that of the 3-methyl-1-butanol–water–lactic acid system (*8*). The solubility of 1-butanol in water is 7.0 weight %, which is considerably greater than the solubility of 3-methyl-1-butanol in water of 2.5%. This greater loss of the extracting solvent 1-butanol in the water is somewhat counterbalanced by the high distribution coefficient (concentration of lactic acid in the organic phase in grams per 100 ml. over the concentration of lactic acid in the water phase in grams per 100 ml.) of about 0.73 compared to a value of 0.45 for 3-methyl-1-butanol alcohol (*7*).

The tie line data were correlated using the methods of Othmer and Tobias (*5*) and of Treybal (*3, 6*). No significant difference was found between the ability of the two methods to correlate the data and give reasonably straight lines. The Treybal type plot is shown in Figure 2 and X_{CB}/X_{BB} is plotted versus X_{CA}/X_{AA} on log-log scales where X_{CB} is the weight fraction of lactic acid, C, in the water layer, B, X_{BB} the weight fraction of water, B, in the water layer, B, X_{CA} the weight fraction of lactic acid, C, in the alcohol layer, A, and X_{AA} the weight fraction of alcohol, A, in the alcohol layer, A.

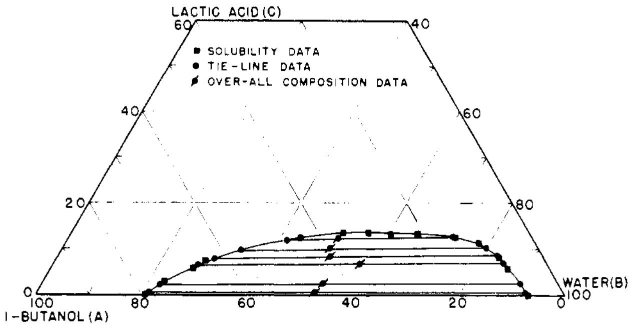

Figure 1. Phase diagram at 25.0° C. for the system 1-butanol–water–lactic acid

The straight lines can be represented by

$$X_{CB}/X_{BB} = k(X_{CA}/X_{AA})^n \qquad (1)$$

where k is a constant and the exponent n accounts for the mutual solubility of the solvents (*7*). For the 1-butanol system $k = 0.60$ and $n = 0.88$, and for the 3-methyl-1-butanol system $k = 0.86$ and $n = 0.76$.

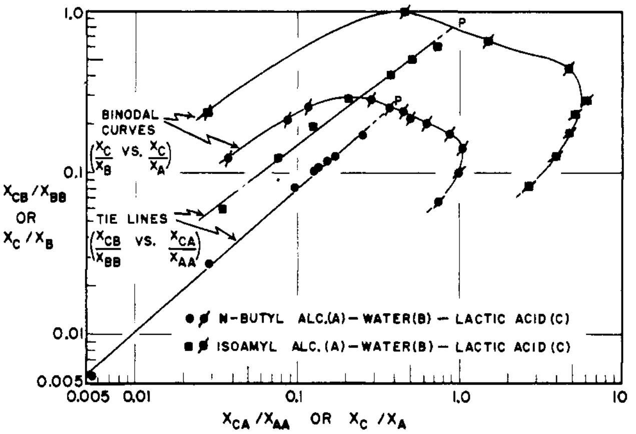

Figure 2. Treybal tie-line correlation and estimation of plait point

1-butanol(A)–water(B)–lactic acid(C)
3-methyl-1-butanol(A)–water(B)–lactic acid(C)

Using the method of Treybal (*7*) the binodal curves were also plotted on Figure 2, and the plait point, *P*, was determined as the intersection of the straight tie-line correlation and the binodal curve. The plait point for the 1-butanol system was $X_A = 35.0$ weight %, $X_B = 51.8\%$, and $X_C = 13.2\%$. For the 3-methyl-1-butanol system $X_A = 33.0\%$, $X_B = 37.2\%$, and $X_C = 29.8\%$.

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