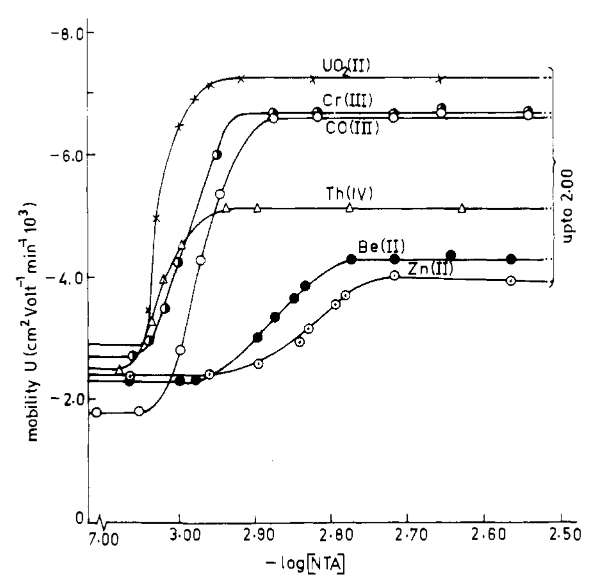

Figure 1. Metal-oxalic acid-NTA system: - log [NTA] vs. mobility.

exists as $C_2O_4^{2-}$ and the unprotonated ions, e.g., $C_2O_4^{2-}$, form complexes with the metal ions.[4] It has been found previously (*4*) that, around pH 10.00, NTA^{3-} is the principal complexing species with the above-mentioned metal ions; therefore, it will take part in the formation of mixed-ligand complexes. Hence, the present study carried out at pH 10.00 is actually the study of interconversion of pure complexes wherein mixed complex is formed in an intermediate stage.

The mobilities were plotted against the logarithms of the concentration of NTA (Figure 1). The graphs for various metal ions had two plateaus. The first plateau corresponds to the formation of $[M(C_2O_4)_p{}^{(2p-n)-}]$ and the second plateau to the formation of the formation of the mixed-ligand species $[M(C_2O_4)_{p-1}NTA^{(2p+1-n)-}]$. Further reaction between the last-mentioned complex species and NTA^{3-} is not possible, as evidenced by two (and not three) plateaus in the mobility graphs (Figure 1). The second plateau gave mobilities of -6.60×10^3, -3.95×10^3, -4.30×10^3, -7.30×10^3, -6.60×10^3, and -5.20×10^3 cm^2 V^{-1} min^{-1} for Co^{II}, Zn^{II}, Be^{II}, U^{II}O$_2$, Cr^{III}, and Th^{IV}, respectively. In the presence of only NTA^{3-} the mobilities of the above-mentioned ions in the form of complex with NTA^{3-} are -3.60×10^3, -5.00×10^3, -1.20×10^3, -3.60×10^3, -0.60×10^3, and -3.80×10^3 cm^2 V^{-1} min^{-1}, respectively (*5*). As the latter mobilities are different from the former, formation of mixed-ligand complexes is inferred in each case.

Various types of complexes formed with metal-oxalic acid and mixed complexes have been reported (*5*) in Table I. The values of log $K_{ML_{p-1}L^1}$ and log $\beta_{ML_{p-1}L^1}$ have been obtained at different - log [NTA] by employing eq 7 and they have been reported in Table II.

Acknowledgment

I thank Dr. K. L. Yadava, Chemistry Department, Allahabad University, Allahabad, India, for supplying the electrophoresis apparatus and for encouragement.

Literature Cited

(1) Biernat, J. *Rocz. Chem.* **1964**, *38*, 343; *Chem. Abstr.* **1964**, *61*, 6456*b*.
(2) Jokl, V. *J. Chromatogr.* **1964**, *14*, 71.
(3) Hurnik, B. *Rocz. Chem.* **1965**, *39*, 137; *Chem. Abstr.* **1965**, *63*, 1256*b*.
(4) Sircar, J. K. *J. Chem. Eng. Data* **1982**, *27*, 231.
(5) Sircar, J. K. Doctoral Thesis, University of Allahabad, Allahabad, India, 1980.
(6) Sulikowska, M. C. *Zesz. Nauk.—Politech. Lodz., Chem.* **1967**, *6*, 2038.

Received for review February 22, 1983. Accepted August 26, 1983.

Temperature Influence on the Ternary System 1-Butanol-Butanone-Water

Francisco Ruiz,* Maria I. Galan,[†] Daniel Prats, and Ana M. Ancheta
Departamento de Química Têcnica, Universidad de Alicante, Aptdo, 99 Alicante, Spain

Solubility and liquid-liquid phase equilibrium data have been measured for the ternary system 1-butanol-butanone-water at temperatures ranging from 15 to 20 °C. Data for the binodal curves have been determined by the cloud-point method. Data for the tie lines have been determined by gas-chromatographic analysis. Experimental results show the extreme phase sensitivity of this system to temperature. At 17 °C the ternary system has two separate biphasic regions, while at 18 °C the system has only one region of immiscibility. This rapid and unusual temperature dependence is not very common for ternary liquid systems.

Introduction

Mutual solubility of liquids usually increases with temperature (*1*). Although this behavior is the most common, there are cases where an increase in temperature causes a solubility decrease. Francis (*2*) has compiled some examples of this behavior in binary systems. However, the number of published studies relating to ternary systems with this temperature dependence is very small.

Galán (*3*) reported some binodal curves for the system 1-butanol-butanone-water, showing that at 15 °C this ternary system had two separate biphasic regions, while at 20 °C the system had only one biphasic region. In our paper, extensive data for this system have been determined. Binodal curves at 15, 16, 17, 18, 19, and 20 °C are reported in order to mark the temperature of overlapping of the two biphasic regions. Moreover, several tie lines have been determined for each temperature. The coordinates of the plait points are also reported.

Experimental Section

Materials. The contents of volatile impurities in 1-butanol and butanone (analytical reagent grade; Merck) were determined by

---

[†] Departamento de Química Têcnica, Universidad de Barcelona, Spain.

0021-9568/84/1729-0143$01.50/0

Table I. Ternary Solubility Data (Weight Percent) for 1-Butanol (1)-Butanone (2)-Water (3)

X_1	X_2	X_3	X_1	X_2	X_3	X_1	X_2	X_3
			1-Butanol-Rich Zone					
T = 15 °C			T = 16 °C			T = 17 °C		
7.9	2.4	89.7	7.6	5.1	87.3	7.7	5.1	87.2
8.0	7.3	84.7	8.2	11.9	79.9	7.8	5.1	87.1
8.5	11.3	80.2	8.6	13.3	78.2	7.9	8.1	84.0
9.4	15.5	75.1	10.2	19.9	69.9	8.2	12.0	79.8
10.1	19.4	70.5	10.5	19.6	69.9	8.3	13.2	78.5
12.1	22.9	65.0	11.6	23.1	65.3	9.1	15.8	75.1
12.8	22.2	65.0	13.3	27.3	59.4	10.0	21.4	68.6
13.4	26.5	60.1	15.4	29.6	55.0	12.8	28.4	58.8
14.4	26.1	59.5	17.9	32.1	50.0	14.6	32.1	53.3
15.4	29.5	55.2	17.9	32.5	49.6	15.6	34.0	50.5
16.4	28.7	54.9	21.0	34.1	44.9	17.2	36.0	46.8
18.2	31.8	50.0	25.2	34.8	40.0	20.1	36.6	43.3
18.8	31.2	50.0	25.9	34.1	40.0	25.1	35.7	39.2
21.2	33.8	45.0	31.9	32.2	35.9	28.3	34.4	37.3
21.8	33.2	45.0	32.5	31.9	35.6	32.3	32.6	35.1
25.2	34.4	40.4	33.4	31.5	35.1	34.3	31.4	34.3
26.0	33.8	40.2	38.1	29.2	32.7	34.1	31.8	34.1
32.7	31.6	35.7	43.8	25.9	30.3	40.1	28.2	31.7
40.2	27.9	31.9	46.0	24.4	29.6	39.9	28.6	31.5
48.0	23.0	29.0	50.3	21.8	27.9	40.2	28.4	31.4
58.2	16.3	25.5	52.4	20.6	27.0	44.0	25.8	30.2
72.7	6.1	21.2	58.0	16.9	25.1	54.8	19.1	26.1
73.7	5.0	21.3	66.2	10.7	23.1	57.4	17.0	25.6
			71.1	7.0	21.9	59.6	15.4	25.0
			74.7	4.5	20.8	64.5	11.7	23.8
						69.3	8.3	22.4
						71.2	6.9	21.9
						73.1	5.7	21.2
			Butanone-Rich Zone					
T = 15 °C			T = 16 °C			T = 17 °C		
2.4	31.2	66.4	0.9	29.2	69.9	0.9	28.6	70.5
5.2	33.9	60.9	4.4	30.4	65.2	1.9	28.6	69.5
5.4	33.8	60.8	4.4	30.6	65.0	5.5	30.3	64.2
5.3	34.8	59.9	6.2	32.1	61.7	10.0	34.8	55.2
7.8	36.0	56.2	7.0	33.5	59.5	11.2	36.4	52.4
9.5	40.6	49.9	7.0	33.7	59.3	11.6	40.0	48.4
10.7	43.9	45.4	8.5	36.5	55.0	12.7	44.4	42.9
10.9	44.6	44.5	10.5	40.5	49.0	13.1	49.7	37.2
11.0	44.5	44.5	10.2	41.0	48.8	12.2	52.9	34.9
12.0	48.1	39.9	10.4	41.9	47.7	11.3	58.5	30.3
11.4	51.2	37.4	11.1	44.2	44.7	11.1	59.0	29.9
10.8	59.0	30.2	11.8	47.8	40.4	9.4	64.8	25.8
8.8	66.7	24.5	11.6	50.2	38.2	8.6	67.9	23.5
5.5	76.4	18.1	11.8	52.6	35.6	7.5	70.9	21.6
4.4	79.2	16.4	11.3	55.4	33.3	7.1	71.8	21.1
			10.3	60.4	29.3			
			9.9	63.6	26.5			
			7.2	71.3	21.5			
			5.8	75.2	19.0			
			4.4	78.8	16.8			
			Solvent-Rich Zone					
T = 18 °C			T = 19 °C			T = 20 °C		
4.4	79.3	16.3	3.9	80.6	15.5	5.2	77.8	17.0
6.1	75.0	18.9	7.1	73.0	19.9	7.3	73.0	19.7
6.9	73.0	20.1	8.8	68.6	22.6	9.3	68.2	22.5
9.6	65.8	24.6	9.8	65.4	24.8	10.7	63.8	25.5
11.7	57.8	30.5	10.2	64.3	25.5	11.8	60.2	28.0
11.8	57.3	30.9	12.7	55.7	31.5	12.9	57.3	29.9
11.9	57.8	30.3	14.0	51.6	34.4	13.3	56.4	30.3
12.9	52.6	34.5	14.6	50.1	35.3	15.3	50.2	34.5
13.1	52.0	34.9	14.9	47.9	37.2	16.9	46.1	37.0
13.2	49.8	37.0	15.1	46.5	38.4	17.9	44.6	37.5
14.0	44.5	41.5	15.4	47.8	36.8	18.2	43.8	38.0
14.6	42.3	43.1	15.8	45.0	39.2	20.2	41.8	38.0
15.7	40.1	44.2	16.9	42.9	40.2	22.1	39.9	38.0
16.3	38.9	44.7	18.1	41.5	40.4	23.9	38.8	37.3
18.0	38.6	43.4	19.0	40.5	40.5	25.0	38.1	36.9
20.2	37.5	42.3	19.6	40.0	40.4	29.5	35.3	35.2

X_1	X_2	X_3	X_1	X_2	X_3	X_1	X_2	X_3
24.9	36.3	38.8	22.4	38.5	39.1	30.8	34.9	34.3
28.7	34.6	36.7	25.3	37.1	37.6	32.4	34.3	33.4
32.3	32.9	34.8	28.9	35.3	35.8	35.1	32.3	32.6
34.0	32.0	34.0	32.2	33.5	34.3	40.5	28.8	30.7
40.2	28.3	31.5	32.7	33.2	34.1	41.6	27.8	30.6
40.7	28.1	31.2	36.0	31.2	32.8	42.7	27.4	29.9
41.3	27.7	31.0	40.6	28.6	30.8	45.2	25.8	29.0
43.3	26.5	30.3	42.3	27.4	30.3	47.9	23.9	28.2
45.4	24.7	29.9	43.9	26.2	29.9	50.5	21.8	27.7
50.3	21.6	28.1	50.2	21.5	28.3	55.8	18.3	25.9
55.9	18.0	26.1	50.2	22.4	27.5	59.2	15.9	24.9
59.6	15.4	25.0	59.5	15.4	25.1	64.5	12.1	23.4
66.8	10.6	22.6	64.0	11.9	24.1	69.8	8.2	22.0
71.1	6.9	22.0	69.8	8.8	21.3	74.7	4.6	20.7
74.4	4.6	21.0	71.2	6.8	22.1			
			74.6	4.3	21.2			
			Water-Rich Zone					
T = 18 °C			T = 19 °C			T = 20 °C		
1.5	27.9	70.6	2.0	28.2	69.8	1.8	27.7	70.5
2.2	27.9	69.9	3.8	27.6	68.6	3.9	27.0	69.1
3.0	28.3	68.7	6.2	27.4	66.4	5.1	26.9	68.0
4.4	28.5	67.1	7.3	27.2	65.5	6.0	26.3	67.7
7.3	29.0	63.7	8.4	25.8	65.8	7.6	24.9	67.5
9.1	28.8	62.1	8.9	24.4	66.7	8.2	23.6	68.2
10.4	26.2	63.4	9.0	22.1	68.9	8.0	23.6	68.4
9.9	24.4	65.7	8.7	16.3	75.0	8.4	21.9	69.8
9.2	20.9	69.9	8.3	13.6	78.1	8.9	21.1	70.0
9.3	19.5	71.2	7.9	12.2	79.9	8.4	16.5	75.1
8.4	13.8	77.8	7.7	9.2	83.1	8.2	13.4	78.4
8.1	12.5	79.4	7.5	5.2	87.4	8.2	10.8	81.0
7.5	6.5	86.0	7.8	2.5	89.7	7.5	7.5	85.0
7.7	3.4	88.9				7.4	5.3	87.3
						7.3	4.0	88.7
			Solvents-Rich Zone					
T = 25 °C			T = 30 °C					
0.0	87.5	12.5	0.0	87.0	13.0			
3.6	79.5	16.9	9.1	72.2	18.7			
7.0	73.3	19.7	11.9	66.0	22.1			
9.2	69.7	21.1	12.7	64.9	22.4			
14.4	60.1	25.5	14.9	59.9	25.2			
20.0	49.9	30.1	15.4	59.4	25.2			
22.7	43.9	33.4	17.9	53.8	28.3			
26.4	39.3	34.3	20.9	48.8	30.3			
33.4	33.2	33.4	24.6	45.2	30.3			
41.1	27.1	31.8	27.4	41.4	31.2			
49.1	21.0	29.9	31.0	37.8	31.2			
59.5	14.6	25.9	34.8	34.9	30.3			
67.7	9.1	23.2	38.8	31.2	30.0			
70.0	7.2	22.8	42.5	28.2	29.3			
79.0	0.0	21.0	59.3	15.5	25.2			
			65.4	11.5	23.1			
			71.1	7.2	21.7			
			78.9	0.0	21.1			
			Water-Rich Zone					
T = 25 °C			T = 30 °C					
0.0	25.3	74.7	0.0	25.2	74.8			
2.5	22.5	75.0	6.4	15.0	78.6			
3.5	21.0	75.5	6.9	13.0	80.1			
4.5	18.2	77.3	6.8	10.8	82.4			
6.7	15.6	77.7	6.8	6.6	86.6			
7.0	11.8	81.2	7.0	5.3	87.7			
7.0	8.9	84.1	6.8	3.3	89.9			
7.0	7.0	86.0	7.2	0.0	92.8			
6.6	6.5	86.9						
6.9	4.6	88.5						
7.2	3.1	89.7						
7.2	1.8	91.0						
7.4	0.0	92.6						

chromatographic analysis. Both of them contained negligible amounts of volatile impurities (less than 0.1%).

***Procedure*.** Data for the saturation curves were determined by using the cloud-point method. In all cases mixtures located in the heterogeneous region were titrated until turbidity disappeared, and the weights of titrated and titrating mixtures were measured. We used the experimental device given by Ruiz and Prats (*4*). This experimental procedure permits control of the

Table II. Tie-Line Data (Weight Percent) for 1-Butanol (1)-Butanone (2)-Water (3)

aqueous phase			organic phase		
X_1	X_2	X_3	X_1	X_2	X_3
1-Butanol-Rich Zone; $T = 15$ °C					
8.3	0.0	91.7	80.1	0.0	19.9
8.0	2.3	89.7	70.4	7.4	22.2
8.0	4.7	87.3	60.7	14.4	24.9
8.1	7.3	84.5	51.2	20.8	28.0
8.4	10.1	81.5	42.3	26.5	31.3
9.2	13.8	77.0	33.5	31.0	35.5
11.1	19.7	69.2	24.0	33.5	42.5
16.0^a	29.0^a	55.0^a			
Butanone-Rich Zone; $T = 15$ °C					
0.0	29.1	70.9	0.0	88.0	12.0
1.2	29.7	69.1	3.9	79.4	16.7
3.2	30.5	66.3	8.3	67.0	24.7
7.8	36.6	55.6	10.5	46.8	42.7
9.8^a	40.8^a	49.4^a			
1-Butanol-Rich Zone; $T = 16$ °C					
8.2	0.0	91.8	80.3	0.0	19.7
8.0	2.4	89.6	70.4	7.3	22.2
8.0	4.7	87.3	60.7	14.4	24.9
8.1	7.2	84.7	51.3	20.8	27.9
8.3	9.9	81.8	42.4	26.6	31.0
9.0	13.5	77.6	33.9	31.3	34.8
10.2	18.6	71.2	25.4	34.3	40.3
15.1^a	29.9^a	55.0^a			
Butanone-Rich Zone; $T = 16$ °C					
0.0	28.9	71.1	0.0	88.2	11.8
0.9	29.2	69.9	3.1	81.5	15.4
3.1	29.8	67.1	8.5	67.4	24.1
6.5	32.3	61.2	11.6	50.7	37.6
9.8^a	39.0^a	51.2^a			
1-Butanol-Rich Zone; $T = 17$ °C					
8.1	0.0	91.9	80.3	0.0	19.7
7.9	2.2	90.0	70.2	7.5	22.3
7.9	4.7	87.4	60.9	14.3	24.8
7.8	7.0	85.3	51.5	21.0	27.5
8.1	9.6	82.3	42.6	26.9	30.5
8.5	13.1	78.4	34.1	31.9	33.9
9.6	18.3	72.0	25.8	35.2	38.9
11.1	24.4	64.5	18.9	35.7	45.4
14.0^a	31.5^a	54.5^a			
Butanone-Rich Zone; $T = 17$ °C					
0.0	28.5	71.5	0.0	88.2	11.8
0.9	28.0	71.1	3.0	81.8	15.2
2.9	28.2	68.9	8.6	68.4	23.0
5.7	29.2	65.1	12.3	53.7	34.0
11.0^a	36.5^a	52.5^a			
$T = 18$ °C					
8.0	0.0	92.0	80.2	0.0	19.8
7.9	2.5	89.6	70.1	7.5	22.4
7.7	4.7	87.6	60.5	14.5	25.0
7.8	6.9	85.3	51.4	21.2	27.5
8.0	9.5	82.5	42.7	26.9	30.4
8.5	13.1	79.4	34.4	31.9	33.7
8.9	17.2	73.9	26.5	36.1	37.4
9.8	22.8	67.4	20.4	37.9	41.7
9.7	28.3	62.0	15.6	40.4	44.0
5.6	28.8	65.6	12.7	54.4	32.9
2.9	28.4	68.6	8.7	68.3	23.0
0.9	28.1	71.0	3.1	81.8	15.1
0.0	28.0	72.0	0.0	88.2	11.8
$T = 19$ °C					
7.8	0.0	92.2	80.1	0.0	19.9
7.7	2.4	89.9	69.9	7.6	22.5
7.7	4.7	87.6	60.6	14.5	24.9
7.7	7.1	85.2	51.4	21.2	27.4
7.9	9.6	82.5	42.7	27.1	30.2
8.3	13.0	78.7	34.5	32.2	33.4
8.6	17.0	74.3	26.8	36.4	36.8
9.0	21.5	69.5	21.3	39.1	39.6
8.5	25.7	65.8	17.0	43.2	39.8
5.2	27.8	67.0	13.0	55.5	31.5
2.8	27.8	69.4	8.7	68.6	22.7
0.9	27.8	71.3	3.1	81.8	15.1
0.0	27.6	72.4	0.0	88.2	11.8
$T = 20$ °C					
7.7	0.0	92.3	80.0	0.0	20.0
7.6	2.4	90.0	69.9	7.6	22.5
7.5	4.5	88.0	60.7	14.4	24.9
7.6	6.9	85.5	51.5	21.0	27.5
7.8	9.5	82.6	42.9	27.1	30.0
8.0	12.6	79.4	34.9	32.1	33.0
8.4	16.8	74.7	27.4	36.9	35.6
8.5	20.8	70.7	21.8	40.1	38.1
7.5	23.9	68.6	17.9	45.0	37.1
4.9	26.4	68.7	13.3	56.7	30.0
2.7	27.1	70.2	8.8	69.0	22.2
0.8	27.1	72.1	3.1	82.0	15.0
0.0	27.4	72.6	0.0	88.2	11.8

^{a} Calculated, plait point.

temperature and the end point to be observed clearly. Data for the ternary tie lines and solubility of the binary systems were determined by an intensive stirring of known amounts of the constituents for at least 2 h at each temperature, the phases being allowed to settle and separate. Samples were analyzed by chromatography, using a Shimadzu chromatograph GCR1A, equipped with an electronic integrator RPR-G1. A good separation of the components was obtained on a 2 m × $^1/_8$ in. column, packed with polystyrene-divinylbenzene polymers. The column temperature was 190 °C and the detection was carried out by thermal conductivity. The detector current was 100 mA at a helium flow rate of 40 mL/min. For the quantitative results we have applied the internal standard method, 1-propanol being the standard compound used for this purpose.

Temperature Error. In all cases, ambient temperature was higher than those under study. Thus, the water thermostat used in the determination of solubility points and tie lines was equipped with a refrigerator. A mercury thermometer was used to measure temperatures. Temperature fluctuations were about ±0.05 °C.

Solubility-Point Error. The weights of titrating and titrated mixtures were determined in a Mettler PC440 balance. The error introduced during the determination of titration end point in combination with the error in weighing permits one to obtain solubility points with a relative accuracy of about 1 wt %.

Tie-Line Error. A study of reproducibility was carried out by analyzing the conjugated phases from 10 different initial mixtures of the same composition. A reproducibility of 0.5 wt. % for each component was found. Besides, the analysis of the three components for both conjugated phases and the initial composition mixture allows us to test tie lines by material balance. Tie lines with deviation higher than 1 wt % for any component were rejected.

Results and Discussion

Binodal Curves. Table I shows the mutual solubility data for 15, 16, 17, 18, 19, 20, 25, and 30 °C. The values at 25 and 30 °C were reported by Galán (*3*). The representation of the binodal curves is shown in Figure 1, where the solubility-curve evolution with temperature between 15 and 20 °C can be seen. The central region shows complete solubility at 15, 16, and 17 °C and heterogeneity from 18 °C. A small increase of temperature causes a significant decrease of solubility.

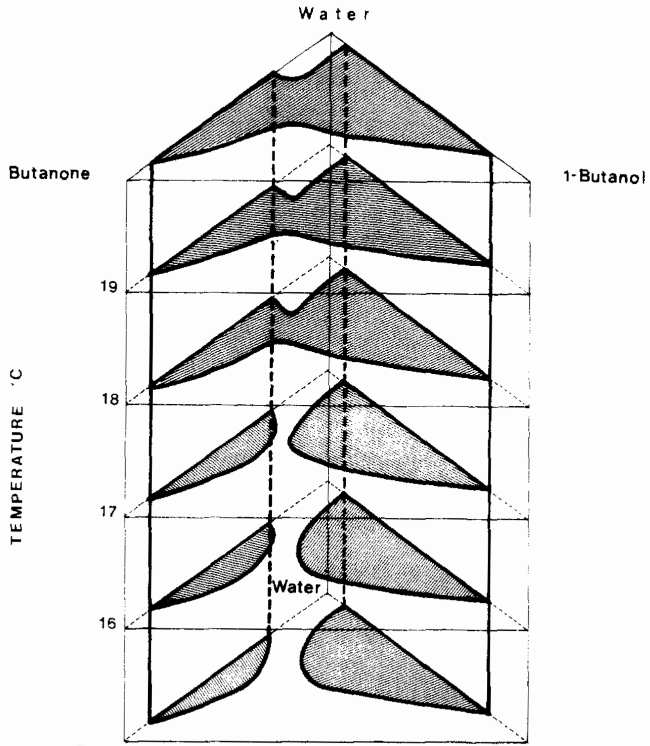

Figure 1. Mutual solubility for the system 1-butanol–butanone–water.

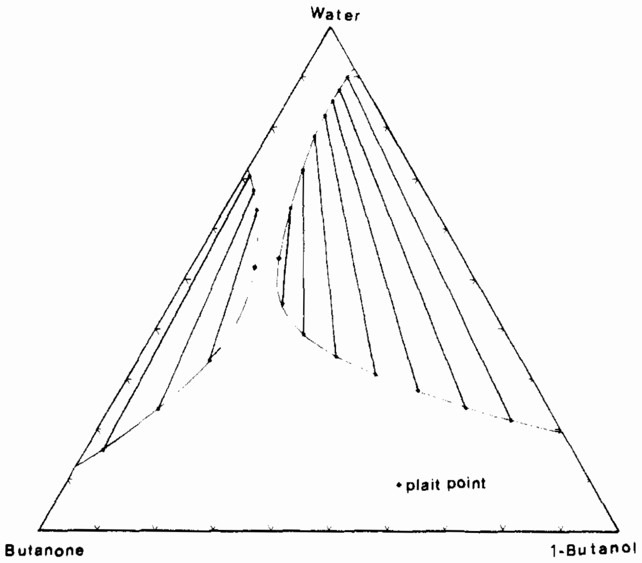

Figure 2. Phase equilibria for 1-butanol–butanone–water at 17 °C.

There are two cases in the reviewed literature which show behavior similar to that indicated above: the propane–oleic acid–refined cottonseed oil ternary system that was studied by Hixon and Bokelmann (*5*) at 85 and 98.5 °C and the triethylamine–ether–water ternary system that was studied at 0, 12.4, and 30.5 °C by Meerburg (*6*). Both of them show solubility decrease when temperature increases.

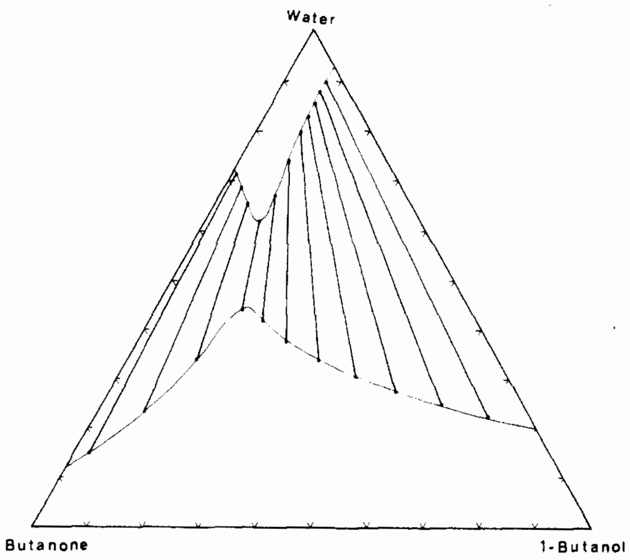

Figure 3. Phase equilibria for 1-butanol–butanone–water at 18 °C.

Tie Lines. Tie-line data for each temperature are reported in Table II, in weight percent. The mutual solubilities of the binary systems are also included in this table. The coordinates of the plait points given in the tables were calculated by the graphic method described by Coolidge (*7*).

Ternary-system equilibria at 17 and 18 °C are shown in Figures 2 and 3, respectively, as examples.

The results of the tie lines are in complete agreement with binodal-curve data.

Registry No. 1-Butanol, 71-36-3; butanone, 78-93-3.

Literature Cited

(1) Treybal, R. E. "Liquid Extraction", 2nd ed.; McGraw-Hill: New York, 1963.

(2) Francis, A. W. "Liquid-Liquid Equilibriums"; Interscience: New York, 1963.

(3) Galán, M. I. Ph.D. Thesis, Universidad de Barcelona, Barcelona, Spain, 1979.

(4) Ruiz, F.; Prats, D. *Fluid Phase Equilib.* **1983**, *10*, 77–93.

(5) Hixon, A. W.; Bockelmann, J. B. *Trans. Am. Inst. Chem. Eng.* **1942**, *38*, 891–930.

(6) Meerburg, "International Critical Tables"; McGraw-Hill: New York, 1928; Vol. III, p 415.

(7) Coolidge, A. S. "International Critical Tables"; McGraw-Hill: New York, 1928; Vol. III, pp 398–400.

Received for review December 27, 1982. Revised manuscript received June 20, 1983. Accepted July 18, 1983.