Table III. Solubility of Kojic Acid in Acetone and DMF

| | $x \times 10^2$ | | | $x \times 10^2$ | |
$t/°C$	acetone	DMF	$t/°C$	acetone	DMF
1.5	0.0048	0.183	36		0.353
12		0.234	40	0.0175	
15	0.0072		50	0.0227	0.445
23	0.0106		57	0.0260	
25		0.309	60		0.524
30.5	0.0136				

Table IV. Constants of Equation 1 Describing Solubility in Water

compd	temp range/°C	A	B	C
itaconic acid	0.5–65	−13.516	−969.28	6.018
kojic acid	1.5–69	−118.29	3493.72	42.146

Table V. Metastable Zone Width of Aqueous Solutions

compd	rate/(K·h^{-1})	$t_{sat.}$^{a}/°C	Δt_{max}/°C
itaconic acid	5	34.4	9.2
		50.1	6.1
		58.6	4.6
		63.7	4.5
	20	34.4	11.2
		50.1	9.0
		58.6	6.1
		63.7	5.7
kojic acid	10	36.0	13.5
		50.5	12.0
		65.0	8.5

$^a t_{sat.}$ = temperature at which the solution is saturated.

temperature at which the first crystals appeared was taken as the metastable zone width. Then the temperature was raised above the saturation temperature, and when all crystals dissolved, the solution cooling was started again. This procedure was repeated three times for each combination of the saturation temperature and the cooling rate. The difference among individual values was less than 0.5 K for each combination employed. Reported values represent an arithmetic average of respective values.

The itaconic (fy Ulajne, Latvia) and kojic (our own product) acids used for experiments contained a minimum 99.5% of pure substance. Purity was determined by isotachophoresis and spectrophotometry in the case of itaconic and kojic acid, respectively. Distilled water, acetone containing 0.3% water, and AnalaR grade N,N-dimethylformamide were used as solvents.

Results

The measured solubilities are given in Tables I–III. The solubility of itaconic and kojic acids in water were correlated according to the equation (7)

$$\log x = A + B/T + C \log T \tag{1}$$

where A, B, and C are adjustable constants, T is absolute temperature, and x represents the mole fraction of dissolved compound. Constants of this equation determined by the least-squares method are listed in Table IV. The standard deviation of $\log x$ in this correlation was 0.0155 and 0.0179 for itaconic and kojic acid, respectively.

The metastable zone width of aqueous solution for both acids expressed as the temperature difference Δt_{max} together with the saturation temperature $t_{sat.}$ is reported in Table V.

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Equilibrium Diagram of the Ternary System Water–Malic Acid–Tributyl Phosphate and the Influence of Temperature

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In this work the possibility of recovery of malic acid from wastewater by solvent extraction was studied. Tributyl phosphate mixed with dodecane was chosen as solvent. Equilibrium diagrams at 25, 35, and 45 °C were established in order to know the property of tributyl phosphate as solvent and the influence of temperature. It was found that tributyl phosphate was a very selective solvent for extracting malic acid from wastewater since it gave high selectivities which were between 1.3 and 17.4.

Introduction

Malic acid, $C_4H_6O_5$, is increasingly used in food and nonfood applications because of its pleasant tartness, flavor-retention characteristics, high water solubility, and chelating and buffering properties. Malic acid also is a reactive intermediate in chemical synthesis (1).

The processing of grape must using ion-exchange resins produces large quantities of pollutant effluent involving organic materials which are constituted principally of malic acid and tartaric acid.

In order to reduce the industrial pollution and waste effluent, malic acid can be recovered from effluent by the technique of liquid–liquid extraction.

Previous studies on liquid–liquid extraction of malic acid from

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Table I. Ternary System of Water (w_A) + Malic Acid (w_B) + (Tributyl Phosphate (75 vol %) + Dodecane (25 vol %)) (w_S) at 25 °C

(a) Binodal Curve Results

$100w_A$	$100w_B$	$100w_S$	$100w_A$	$100w_B$	$100w_S$	$100w_A$	$100w_B$	$100w_S$
				Organic Rich Side (E)				
3.5	13.2	83.3	3.5	8.4	88.1	4.2	3.4	92.4
3.5	11.4	85.1	3.6	7.2	89.2	4.3	2.2	93.5
3.5	10.6	85.9	3.9	6.2	89.9	4.4	1.0	94.6
3.5	9.7	86.8	4.0	5.7	90.3	4.5	0.2	95.3
3.5	9.0	87.5	4.1	5.2	90.7	4.6	0.0	95.4
				Aqueous Rich Side (R)				
42.0	55.8	2.2	80.6	18.4	1.0	94.6	4.7	0.7
47.2	50.7	2.1	85.3	13.9	0.8	97.3	2.2	0.5
54.8	43.3	1.9	89.2	10.1	0.7	98.3	1.3	0.4
60.3	38.0	1.7	91.6	7.7	0.7	99.6	0.0	0.4
73.8	25.0	1.2						

(b) Mutual Solubility Data

$100w_A$	$100w_B$	$100w_S$	$100w_A$	$100w_B$	$100w_S$	$100w_A$	$100w_B$	$100w_S$
42.0	58.0	0.0	2.2	12.6	85.2	0.0	11.9	88.1
3.6	13.2	83.2	1.2	12.2	86.6			

(c) Tie-Line Data

aqueous phase (R)			organic phase (E)				
$100w_A$	$100w_B$	$100w_S$	$100w_A$	$100w_B$	$100w_S$	m	β
98.7	0.9	0.4	4.4	0.6	95.0	0.66	12.8
96.8	2.7	0.5	4.3	1.6	94.1	0.59	9.9
93.5	5.9	0.6	4.3	3.2	92.5	0.54	7.2
87.0	12.1	0.9	4.1	4.4	91.5	0.36	4.2
81.4	17.7	0.9	3.9	5.7	90.4	0.32	3.3
76.6	22.4	1.0	3.6	6.6	89.8	0.29	2.9
70.9	27.7	1.4	3.6	7.3	89.1	0.26	2.4
66.6	31.8	1.6	3.5	8.1	88.4	0.25	2.2
62.8	35.5	1.7	3.5	8.6	87.9	0.24	2.0
57.8	40.4	1.8	3.4	9.4	87.2	0.23	1.8
52.5	45.5	2.0	3.5	10.5	86.0	0.23	1.6
48.8	49.1	2.1	3.5	11.3	85.2	0.23	1.5
42.0	55.9	2.1	3.6	13.3	83.1	0.24	1.4

aqueous solution were made using solvents such as methyl isobutyl ketone, methylisobutylcarbinol, 2-methyl-1-propanol, 1-pentanol, and 3-methyl-1-butanol, which belong to the category of carbon-bonded oxygen-donor compounds. This type of solvent has an extracting ability with regard to the carboxylic acid resulting from the solvation character of the oxygen group attached to a carbon atom, which acts as a Lewis base. The partition coefficients for these compounds are fairly small, ranging between 0.018 and 0.75, so their selectivities are only between 1.09 and 2.22 (2-5). In addition the solubilities of these solvents in water are relatively high (at 25 °C, 8.23 mass % for 2-methyl-1-propanol, 2.04 mass % for 1-pentanol, and 2.61 mass % for 3-methyl-1-butanol) (5), which would make a solvent recovery cycle costly and yield poor process economy.

The solvent selected for our studies was tributyl phosphate. It contains a phosphoryl group which is a stronger Lewis base than the carbon-bonded oxygen compounds. Further, this solvent coextracts less water and at the same time is less soluble in water (<0.6 mass %) than those solvents mentioned above (6), so that it can offer higher selectivities. Since tributyl phosphate has a high viscosity of 3.56 × 10⁻³ Pa s and a specific gravity close to unity (0.98), it is necessary to mix it with a diluent of low viscosity and density in order to facilitate good phase separation. Dodecane was chosen because of its low viscosity (1.15 × 10⁻³ Pa s), its low specific gravity of 0.75, and furthermore its insolubility in water. According to Figure 1, the percentage of tributyl phosphate in the mixture should be as high as possible to obtain high partition coefficients. Taking both partition coefficient and phase separation into consideration, we have chosen the mixture of 75 vol % tributyl phosphate with 25 vol % dodecane as the solvent (organic phase).
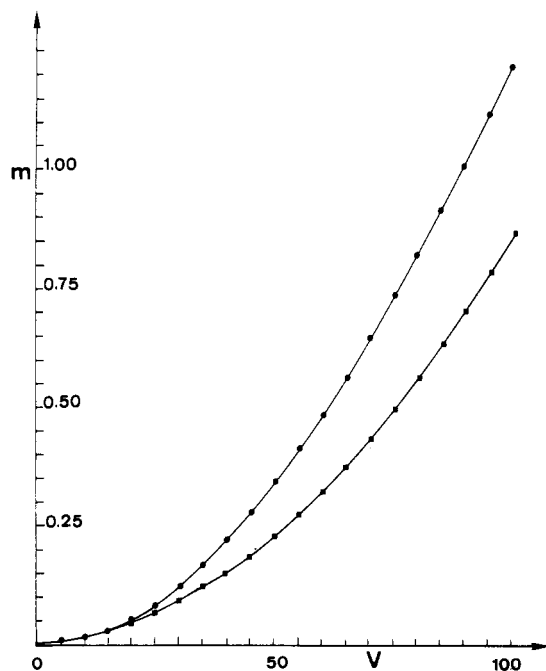

Figure 1. Partition coefficient, m, plotted as a function of the volume percent of tributyl phosphate in a mixture of tributyl phosphate + dodecane, V, at 25 °C. The initial aqueous solution contains (■) 0.10 mass fraction of malic acid or (●) 0.01 mass fraction of malic acid.

Experimental Section

Chemicals. Tributyl phosphate and dodecane with a minimum purity of 98% were used for the experiment. Malic acid

Table II. Ternary System of Water (w_A) + Malic Acid (w_B) + (Tributyl Phosphate (75 vol %) + Dodecane (25 vol %)) (w_S) at 35 °C
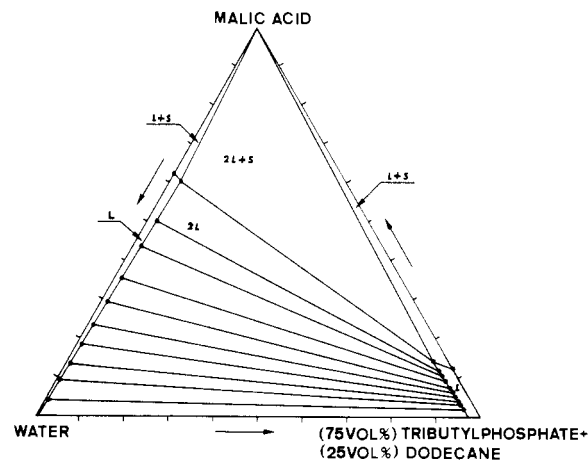
(a) Binodal Curve Results

$100w_A$	$100w_B$	$100w_S$	$100w_A$	$100w_B$	$100w_S$	$100w_A$	$100w_B$	$100w_S$
				Organic Rich Side (E)				
3.1	14.2	82.7	3.1	7.2	89.7	3.3	1.0	95.7
3.1	12.1	84.8	3.1	6.1	90.8	3.5	0.3	96.2
3.1	10.3	86.6	3.1	3.5	93.4	3.5	0.0	96.5
3.1	8.9	88.0	3.2	2.2	94.6			
				Aqueous Rich Side (R)				
37.5	60.3	2.2	69.7	29.2	1.1	96.2	3.3	0.5
41.8	56.2	2.0	79.5	19.6	0.9	98.4	1.1	0.5
49.5	48.5	2.0	87.9	11.4	0.7	99.1	0.5	0.4
56.0	42.2	1.8	91.2	8.1	0.7	99.7	0.0	0.3
62.4	36.0	1.6	93.8	5.6	0.6			

(b) Mutual Solubility Data

$100w_A$	$100w_B$	$100w_S$	$100w_A$	$100w_B$	$100w_S$	$100w_A$	$100w_B$	$100w_S$
37.6	62.4	0.0	2.1	12.9	85.0	0.0	12.4	87.6
3.8	13.7	82.5	1.1	12.5	86.4			

(c) Tie-Line Data

aqueous phase (R)			organic phase (E)				
$100w_A$	$100w_B$	$100w_S$	$100w_A$	$100w_B$	$100w_S$	m	β
99.0	0.6	0.4	3.5	0.4	96.2	0.67	17.4
96.7	2.7	0.6	3.4	1.5	95.2	0.55	11.2
95.2	4.2	0.6	3.3	2.1	94.6	0.50	9.3
92.3	7.0	0.6	3.2	3.3	93.5	0.47	7.1
89.9	9.4	0.7	3.1	3.7	93.2	0.39	5.7
85.8	13.4	0.8	3.1	4.6	92.3	0.34	4.4
80.1	19.0	0.9	3.1	5.7	91.2	0.30	3.2
75.4	23.6	0.9	3.1	6.6	90.3	0.28	2.8
69.4	29.5	1.2	3.1	7.5	89.4	0.25	2.4
63.0	35.6	1.4	3.1	9.0	87.9	0.25	2.1
54.5	43.7	1.8	3.1	10.5	86.4	0.24	1.7
47.8	50.1	2.1	3.1	11.5	85.4	0.23	1.5
37.5	60.3	2.3	3.1	14.2	82.7	0.24	1.3
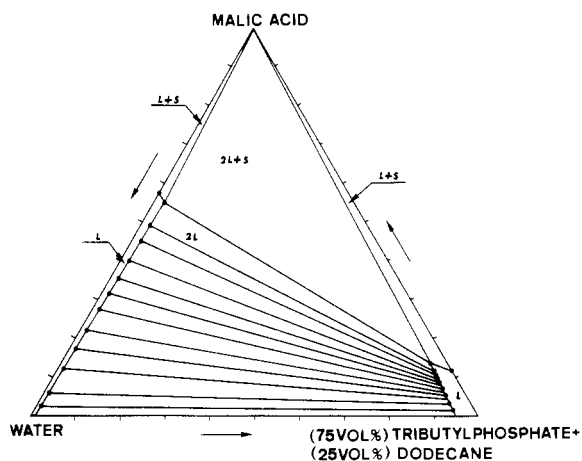
Figure 2. Equilibrium diagram of the water + malic acid + tributyl phosphate system at 25 °C.

Figure 3. Equilibrium diagram of the water + malic acid + tributyl phosphate system at 35 °C.

used had a purity of 99%. The analysis by high-performance liquid chromatography (HPLC) bore out these purities.

Experimental Procedures. Solubility isotherms and tie-line data for the ternary system water + malic acid + (tributyl phosphate + dodecane) were determined at 25, 35, and 45 °C. The experimental devices were maintained at a desired temperature with an accuracy of ±1 °C.

At each temperature, 13 samples of malic acid + water were used to determine the tie lines. The samples were mixed with varying amounts of tributyl phosphate + dodecane by shaking in glass-stoppered separatory funnels and thermostated for $1^1/_2$ h. After decantation over a period of 1 h, the aqueous phase and organic phase in each of the funnels were separated from each other. Malic acid, being present in each phase in

equilibrium, was neutralized with standard sodium hydroxide (0.1 or 1.0 mol dm^{-3}), and phenolphthalein was used as indicator. The error induced from titrating and weighing was less than 1%. Water contained in each phase was determined by the Karl-Fischer method.

The cloud-point method was used to determine liquid–liquid solubility isotherms. Binary mixtures of malic acid + water of known composition were prepared. For the water + malic acid rich system, tributyl phosphate + dodecane was added until the solution became turbid. For the solvent rich side, water was added to a mixture of known concentration of malic acid + tributyl phosphate + dodecane until the mixture became turbid.

Solid–liquid saturation results were obtained with a relative accuracy of 1% from saturated solutions. Malic acid was

Table III. Ternary System of Water (w_A) + Malic Acid (w_B) + (Tributyl Phosphate (75 vol %) + Dodecane (25 vol %)) (w_S) at 45 °C

(a) Binodal Curve Results

$100w_A$	$100w_B$	$100w_S$	$100w_A$	$100w_B$	$100w_S$	$100w_A$	$100w_B$	$100w_S$
			Organic Rich Side (E)					
3.1	15.0	81.9	2.6	8.6	88.8	3.2	1.5	95.3
2.9	14.0	83.1	2.6	7.4	90.0	3.4	0.9	95.7
2.7	12.3	85.0	2.9	5.9	91.2	3.6	0.0	96.4
2.7	9.9	87.4	3.1	3.1	93.8			
			Aqueous Rich Side (R)					
32.4	65.2	2.4	72.4	26.5	1.1	93.2	6.2	0.6
41.3	56.7	2.0	77.6	21.5	0.9	95.2	4.3	0.5
49.9	48.2	1.9	83.5	15.7	0.8	97.6	1.9	0.5
57.7	40.7	1.6	88.9	10.4	0.7	99.2	0.4	0.4
65.9	32.9	1.2				99.6	0.0	0.4

(b) Mutual Solubility Data

$100w_A$	$100w_B$	$100w_S$	$100w_A$	$100w_B$	$100w_S$	$100w_A$	$100w_B$	$100w_S$
33.3	66.7	0.0	2.2	14.1	83.7	0.0	12.9	87.1
3.8	14.8	81.4	1.6	13.6	84.8			

(c) Tie-Line Data

| aqueous phase (R)			organic phase (E)				
$100w_A$	$100w_B$	$100w_S$	$100w_A$	$100w_B$	$100w_S$	m	β
98.9	0.6	0.5	3.5	0.3	96.2	0.50	12.7
96.9	2.6	0.5	3.3	1.1	95.6	0.42	9.7
94.2	5.2	0.6	3.2	2.0	94.8	0.38	7.3
91.6	7.7	0.7	3.1	2.8	94.1	0.36	6.1
88.2	11.1	0.7	3.0	3.8	93.2	0.34	5.0
85.3	13.9	0.8	3.0	4.5	92.5	0.32	4.3
81.6	17.6	0.8	2.9	5.1	92.0	0.29	3.6
74.4	24.5	1.1	2.7	6.3	91.0	0.26	2.8
8.3	30.5	1.2	2.6	7.5	89.9	0.24	2.4
60.0	38.7	1.3	2.7	8.9	88.4	0.23	2.0
50.4	47.7	1.9	2.7	10.8	86.5	0.23	1.7
43.8	54.3	1.9	2.7	12.4	84.9	0.23	1.5
32.4	65.2	2.4	3.1	15.0	81.9	0.23	1.3
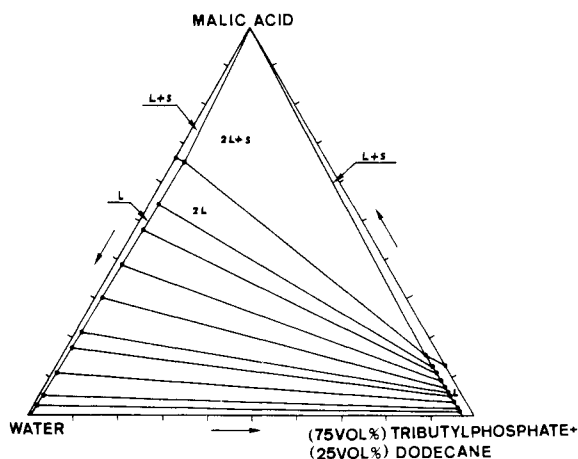
Figure 4. Equilibrium diagram of the water + malic acid + tributyl phosphate system at 45 °C.

titrated with standard sodium hydroxide (1.0 mol dm⁻³).

Results and Discussion

Tables I–III present the binodal curve data, solid–liquid saturation results, and tie-line results of the pseudo ternary system water + malic acid + tributyl phosphate at 25, 35, and 45 °C, respectively. Solubility isotherms and tie lines at each temperature are shown in Figures 2–4, respectively. There is a zone of solid phase for this ternary system which might belong to the type 4 classification proposed by Treybal (7).

The partition coefficients, defined as the ratio of acid concentration in mass percent in the organic phase to that in the aqueous phase, are also included in Tables I–III. The partition
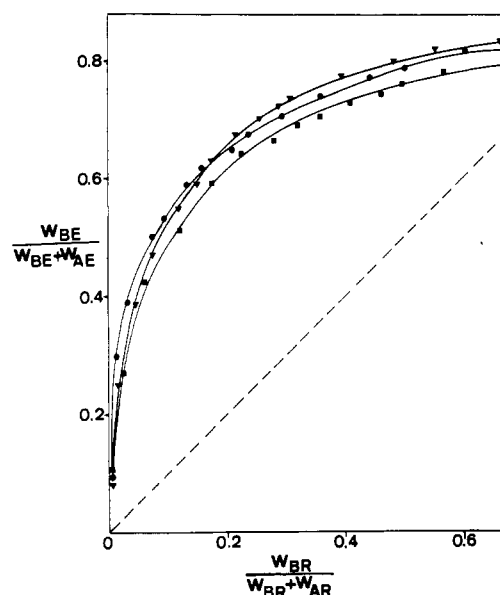

Figure 5. Selectivity curves at different temperatures. The ordinate represents the ratio of acid/(acid + water) in the solvent phase. The abscissa represents the ratio of acid/(acid + water) in the water phase: (■) 25, (●) 35, (▲) 45 °C.

coefficients do not vary significantly with temperature. Hence temperature has little influence on the extraction of malic acid by tributyl phosphate.

The selectivity is the relation of the ratio of acid/(acid + water) in the solvent phase to that in the water phase. From the selectivities (c) given in Tables I–III, it is seen that tributyl phosphate is a very selective solvent in relation to malic acid,

because these selectivities are much greater than 1 (between 1.3 and 17.4). This conclusion is also reflected in Figure 5, where the selectivity curves are located well above the bisectrix, which represented the unity. Compared with solvents such as 1-pentanol, 1-propanol, and methyl-1-butanol, tributyl phosphate can be considered as a solvent more suitable for extraction of malic acid from wastewater.

Glossary

w_{AR}	mass fraction of water in the aqueous phase
w_{BR}	mass fraction of malic acid in the aqueous phase
w_{SR}	mass fraction of solvent in the aqueous phase
w_{AE}	mass fraction of water in the organic phase
w_{BE}	mass fraction of malic acid in the organic phase
w_{SE}	mass fraction of solvent in the organic phase
m	partition coefficient $= w_{BE}/w_{BR}$
β	selectivity $= (w_{BE}/(w_{BE} + w_{AE})/(w_{BR}/(w_{BR} + w_{AR}))$

S   solid phase
L   liquid phase

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Liquid–Liquid Equilibria for the Systems Perfluorodecalin + Heptane + 1-Hexene, Perfluorodecalin + 1-Hexene + Hexane, and Perfluorodecalin + Heptane + 1-Hexene + Hexane

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Liquid–liquid equilibria for the quaternary system perfluorodecalin + heptane + 1-hexene + hexane at 288.15 and 298.15 K and for the ternary systems perfluorodecalin + heptane + 1-hexene at 288.15, 298.15, and 303.15 K and perfluorodecalin + 1-hexene + hexane at 288.15 and 298.15 K are reported. The experimental results are compared with values predicted from the NRTL, the UNIQUAC and the UNIFAC models.

Introduction

Following our experimental determination of binary solubilities (*1*) and liquid–liquid equilibria for some multicomponent perfluorodecalin + hydrocarbon systems (*2*), this paper reports the results of measurements on liquid–liquid equilibria for quaternary and ternary systems containing perfluorodecalin, heptane, 1-hexene, and hexane.

Predictions of equilibrium data for these mixtures were made by using rhe NRTL and UNIQUAC perfluorodecalin + hydrocarbon parameters obtained from binary data. Hydrocarbon + hydrocarbon parameters were calculated by correlating the ternary data. The results are compared with experimental determinations.

The same calculations were made by using the UNIFAC model. The CH_2 + CF_2 and CH_2CH + CF_2 parameters were obtained from binary data (*1*, *3*).

Experimental Section

The experimental work was carried out by using a thermostated miniature cell similar to that described by Soares et al.

(*4*). Temperature was controlled within an accuracy of 0.01 K and was measured by a calibrated thermometer (German Government Calibration). The mixtures were stirred with a magnetic stirrer for at least 30 min and allowed to settle during a period of 4 h. The tie lines were obtained by analyzing the compositions of the two conjugate phases in equilibrium, by means of a gas chomatograph (flame ionization detector) connected to an integrator. An 8 ft × $^1/_4$ in. o.d. stainless steel column with 10% squalane in chromosorb PAW, 80/100 mesh was used. The flow rate of N_2 was 60 mL/min, and the oven temperature was 90 °C. Samples were alternatively withdrawn from the two phases with 1-μL chromatographic syringes (one for each phase) and injected into the chromatograph. Special care was taken with the tie-line determination above room temperature to avoid phase splitting due to cooling, by preheating the syringes.

Calibration curves were obtained by using at least 10 mixtures of known composition of which four to six chromatograms were obtained. Four to six samples of both phases were analyzed to minimize the experimental error. Mole fraction measurements were reproducible to within ±0.002.

Perfluorodecalin (Aldrich/Europe, cis + trans mixture, minimum purity 97%), hexane and heptane (Merck, minimum purity 99%), and 1-hexene (Fluka, minimum purity 99%) were used as supplied.

Quaternary tie-line data are presented in Table I. Tables II and III summarize the experimental results obtained for the ternary systems. Figures 1 and 2 represent the perfluorodecalin + heptane + 1-hexene system at 288.15 and 298.15 K, respectively. Both are type II systems. At 303.15 K this system is type I and is represented in Figure 3. Figures 4 and 5