Equilibria Data for Two Viscous Ternary Liquid Systems

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For research being initiated at the University of Virginia on liquid-liquid extraction it was desired to determine the effect of viscosity on the efficiency of extraction. The problem arose of finding viscous systems for which data have been determined. Of all the ternary liquid systems of pure components known to be reported in the literature, the only one composed of viscous components is furfural-docosane-diphenylhexane (*5*) and only furfural is commercially available. Most of the data reported on liquid-liquid extraction using viscous liquids are based upon petroleum or vegetable hydrocarbon mixtures which cannot be exactly duplicated, and it is difficult to compare operating systems and conditions.

To conduct research with viscous systems, about 30 liquids of high viscosities were tested for mutual solubility. Possible ternary systems were noted and tested to determine whether the region of immiscibility was great enough for liquid-liquid extraction. With this preliminary information, two systems—propylene glycol–tributyrin–di(methoxyethyl) phthalate at 25° C. and diethylene glycol–di(2-ethylhexyl) phthalate-tetrabromoethane at 30° C.—were selected and their equilibria data obtained.

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METHODS OF INVESTIGATION

To define liquid-liquid isothermal systems of pure components, it is necessary to determine the curve or curves of saturation compositions of mixtures of the three components and the equilibrium compositions, represented by the extremities of the conjugation or tie lines, at the specified temperature. All data reported here were at atmospheric pressure, and pressure variations were neglected.

Saturation Curve. In the systems studied, the saturation compositions were determined as follows:

Mixtures of varying amounts of the solvent and solute were made, and titrated to the cloud point with the carrier. Similarly, mixtures of varying amounts of the carrier and solute were titrated to the cloud point (at which the system clouds from the last drop added and fails to clear in 20 minutes) with the solvent.

Cylinders, containing the liquids, were weighed as the components were added and the weight per cent was calculated at the cloud point. The saturation curve was obtained at T° C. by placing the cylinders in a constant temperature bath.

The refractive index was measured at the cloud point by raising the temperature several degrees centigrade to clear up the system. The data (Table I) serve as the basis for a simple analysis of any phase known to be saturated.

Table I. Properties of Pure Materials

Substance	Source	Boiling Point (Lit.), °C.	Density (Lit.), G./Ml.	Refractive Index 35° C. (Abbe Refractomer)	Lit. Cited	Viscosity[a] Temp., °C.	Viscosity[a] Cps.
Propylene glycol	Fisher Scientific	185-6	1.040 at 20° C.	1.4277	(*4*)	0	310
						10	140
						20	65
						30	32
						40	19
Diethylene glycol	Union Carbide	245	$1.1184\frac{20}{20}$	1.4423	(*6*)	0	107
						10	60
						20	35.7
						30	23
						40	17
Tributyrin	Tennessee Eastman	315	1.0350 at 20° C.	1.4301	(*4*)	0	24.2
						10	14.5
						20	10.1
						30	7.2
						40	5.3
Di(methoxyethyl) phthalate	Tennessee Eastman and Union Carbide	340	1.170 at 20° C.	1.4972	(*3*)	10	104
						20	53
						30	30
						40	17.7
Di(2-ethylhexyl) phthalate	Tennessee Eastman Union Carbide	230 at 5 mm.	$0.986\frac{20}{20}$	1.4762	(*1*)	0	381
						20	81.4
						40	22.3
Tetrabromoethane	Matheson, Coleman & Bell	151 at 54 mm.	$2.964\frac{20}{20}$	1.6312	(*6*)	25	9.27
						37.8	6.58
						71.1	3.27

[a]Source of data

Dow Chemical Co.	Union Carbide Chemicals Co.	Eastman Chemical Products
Propylene glycol	Diethylene glycol	Diethylene glycol
Tetrabromoethane	Di(2-ethylhexyl)phthalate	Tributyrin
		Di(methoxyethyl) phthalate

Table II. Saturation and Equilibrium Data on Viscous Systems

Propylene Glycol–Tributyrin–Di(methoxyethyl) Phthalate

Saturation Data (25° C.)

Propylene glycol, wt. %	Tributyrin, wt. %	Di(methoxyethyl) phthalate, wt. %	Refractive index (35° C.)
81.2	10.5	8.3	1.4320
70.8	11.9	17.3	1.4371
62.2	11.7	26.1	1.4434
52.1	13.8	34.1	1.4485
42.8	15.7	41.5	1.4534
32.7	18.2	49.0	1.4589
24.7	21.0	54.3	1.4627
16.0	34.2	49.8	1.4501
12.8	43.5	43.7	1.4560
11.8	53.1	35.2	1.4505
9.2	63.3	27.5	1.4460
8.7	73.8	17.5	1.4398
6.3	84.5	9.2	1.4347
5.9	94.1	0.0	1.4293

Diethylene Glycol–Tetrabromoethane–Di(2-ethylhexyl) Phthalate

Saturation Data (30° C.) (2)

Di(2-ethylhexyl) phthalate, wt. %	Tetrabromoethane, wt. %	Diethylene glycol, wt. %	Refractive index (34° C.)
0.6	0.0	99.4	1.4411
0.8	9.9	89.4	1.4480
0.9	19.8	79.4	1.4565
1.0	29.7	69.3	1.4650
1.2	39.5	59.3	1.4761
1.7	50.7	47.6	1.4909
2.5	58.5	39.0	1.5036
4.2	67.0	28.8	1.5190
7.8	76.1	15.0	...
19.4	77.6	3.0	1.5558
24.4	73.2	2.4	1.5465
29.4	68.5	2.1	1.5380
39.2	59.5	1.3	1.5248
48.4	50.6	1.0	1.5146
54.4	44.5	1.0	1.5086
59.5	39.6	1.0	1.5042
64.5	34.7	0.9	1.5002
69.1	29.6	1.3	1.4968
79.0	19.8	1.1	1.4905
88.5	10.6	1.1	1.4854
98.9	0.0	1.1	1.4807

Equilibrium Data (25° C.)

Heavy Layer				Light Layer			
Propylene glycol, wt. %	Tributyrin, wt. %	Di(methoxyethyl) phthalate, wt. %	Refractive index (35° C.)	Propylene glycol, wt. %	Tributyrin, wt. %	Di(methoyxethyl) phthalate, wt. %	Refractive index (35° C.)
14.9	36.8	48.2	1.4590	73.4	10.6	16.0	1.4364
14.0	39.5	46.4	1.4579	74.9	10.4	14.7	1.4356
13.3	41.9	44.8	1.4568	76.2	10.4	13.4	1.4347
12.1	46.1	41.7	1.4550	78.2	10.3	11.5	1.4335
11.3	49.9	38.8	1.4532	78.9	10.2	10.9	1.4331
10.3	54.7	35.0	1.4510	80.4	10.2	9.3	1.4320
9.3	60.7	30.0	1.4477	82.4	10.1	7.5	1.4308
7.8	70.9	21.3	1.4423	84.9	10.1	5.0	1.4292
7.0	75.3	17.7	1.4403	86.2	10.1	3.7	1.4283
6.5	79.7	13.8	1.4377	87.8	10.1	2.1	1.4272
6.1	84.6	9.3	1.4350	89.9	10.1	0.0	1.4259

Equilibrium Data (30° C.) (2)

Heavy Layer				Light Layer			
Di(2-ethylhexyl) phthalate, wt. %	Tetrabromoethane, wt. %	Diethylene glycol, wt. %	Refractive index (34° C.)	Di(2-ethylhexyl) phthalate, wt. %	Tetrabromoethane, wt. %	Diethylene glycol, wt. %	Refractive index (34° C.)
0.9	0.0	99.1	1.4412	99.0	0.0	1.0	1.4807
1.0	10.0	89.0	1.4488	89.0	10.0	1.0	1.4852
1.0	20.0	79.0	1.4564	79.0	20.0	1.0	1.4908
1.1	30.0	68.9	1.4657	69.0	30.0	1.0	1.4972
1.3	40.0	58.7	1.4768	59.0	40.0	1.1	1.5047
1.7	50.0	48.3	1.4900	48.9	50.0	1.1	1.5139
2.9	60.0	37.1	1.5066	38.6	60.0	1.4	1.5252
5.0	70.0	25.0	...	27.8	70.0	2.2	1.5406

Conjugate Lines. The conjugate or tie lines were obtained by placing various mixtures of the three components in pointed test tubes. The mixtures were agitated in the constant-temperature bath for 6 hours, and allowed to stand 2 hours, and then the refractive index of each phase was read. A drop was taken from the top layer, the tube broken at the pointed bottom, and a drop taken from the bottom layer. These two indices were used with the data of the saturation curve to locate the tie lines. (If the index of the conjugate phase is known, its position on the saturation curve can be determined by the indices of the saturation curve.)

All refractive indices were determined with an accuracy of 3 units in the fourth place by means of an Abbe refractometer with thermostatically controlled heating stage.

The data for the two systems determined are presented in Table II. Both systems have a single solubility curve.

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