SEPARATION OF MIXED TRIGLYCERIDES

Triglycerides tend to be attracted by polar solvents according to the degree of unsaturation. It was assumed that the selectivity of the furfural-rich phase, as compared with the *n*-heptane-rich phase, for triolein, trilinolein, and the related mixed triglycerides, is geometrically proportional to the number of unsaturated carbon linkages in the molecule. The distribution coefficient for dioleolinolein between the *n*-heptane-rich phase and the furfural-rich phase would be 9.5 at 70° C. in dilute solutions. The corresponding figure for dilinoleo-olein would be 7.5. The selectivity of the furfural-rich phase for the latter would be 1.26 in dilute solutions.

The separation of an equiweight mixture of dioleolinolein and dilinoleo-olein into one mixture containing 90 wt. % of the former and 10 wt. % of the latter and another mixture containing 10 wt. % of the former and 90 wt. % of the latter is calculated to require 37 theoretical stages or about three times as many as for the similar separation of triolein and trilinolein. The amounts of solvents would be 340 lb. of furfural saturated with *n*-heptane and 40 lb. of *n*-heptane saturated with furfural for one lb. of feed. These quantities are about three times those for the separation of triolein and trilinolein.

Separation of Triolein and Trilinolein in the Presence of Mixed Triglycerides. A mixture of triglycerides in which the acid groups are oleic acid and linoleic acid in equal amounts and in which these groups are randomly distributed between the molecules (*2*) would consist of 17% triolein, 33% dioleolinolein, 33% dilinoleo-olein, and 17% trilinolein. Since the molecular weights of oleic acid and linoleic acid are nearly the same, this relation is true for both a weight basis and a molar basis. On assumptions previously made, the same separation of triolein and trilinoelin is calculated to require 12 theoretical stages, or the same number as before. The one product stream would contain 31 wt. % triolein, 46 wt. % dioleolinolein, 20 wt. % dilinoleo-olein, and 3 wt. % trilinolein, and the other product stream would contain 3 wt. % triolein, 20 wt. % dioleolinolein, 46 wt. % dilinoleo-olein and 31 wt. % trilinolein. Both compositions are on a solvent-free basis. The amounts of solvents required would be 420 lb. of furfural saturated with *n*-heptane and 50 lb. of *n*-heptane saturated with furfural per lb. of triolein and trilinolein in the feed.

LITERATURE CITED

(1) Briggs, S.W., Comings, E.W., *Ind. Eng. Chem.* **35**, 411 (1943).
(2) Eckey, E.W., "Vegetable Fats and Oils," ACS Monograph Series, Reinhold, New York, 1954.
(3) Scatchard, G., Hamer, W.J., *J. Am. Chem. Soc.* **57**, 1805 (1935).
(4) Timmermans, J., "Physico-Chemical Constants of Pure Organic Compounds," Elsevier, New York, 1950.
(5) Treybal, R.E., "Liquid Extraction," 2nd ed., McGraw-Hill, 1963.
(6) Wheeler, D.H., Riemeschneider, R.W., Sando, C.S., *J. Biol. Chem.* 132, 687 (1940).
(7) Wohl, K., *Trans. Am. Inst. Chem. Engrs.* **42**, 215 (1946).

RECEIVED for review March 8, 1963. Accepted October 25, 1963.

Vapor-Liquid Equilibria for the Methanol–Toluene System

D. E. BURKE, G. C. WILLIAMS, and C. A. PLANK
University of Louisville, Louisville, Ky.

Vapor-liquid equilibrium data have been determined at one atmosphere pressure for the methanol–toluene system using a modified Altsheler still. A thermodynamic evaluation proved the data to be consistent. A minimum boiling azeotrope is formed at 0.885 mole fraction methanol and a temperature of 63.6° C. Refractive index–concentration data have also been determined for this binary system.

MIXTURES OF METHYL ALCOHOL and toluene are used in chemical processing. Because these solvents are frequently recovered or repurified by distillation, columns designed for this operation require a knowledge of the binary vapor-liquid equilibria.

A review of the literature indicates only one set of vapor-liquid equilibrium data for this binary system (*2*). In an attempt to duplicate and extend the data of Benedict and coworkers, a somewhat different set of values were obtained and are reported in this investigation.

The data were obtained at one atmosphere pressure and were found to deviate considerably from liquid phase ideality. A minimum boiling azeotrope is formed by this binary system at 0.885 mole fraction methanol and at a temperature of 63.6° C. A thermodynamic evaluation proved the data to be consistent. The experimental results are given in Table I and the temperature—composition and *x*-*y* curves are shown in Figures 1 and 2, respectively. The activity coefficient—composition curves are shown in Figure 3. The refractive index—concentration data experimentally determined and used in the analytical procedure are listed in Table II.

EXPERIMENTAL

Materials. Both materials were of analytical reagent grade. The toluene had a quoted boiling point range of 110.4-110.7° C., but the equilibrium boiling point was experimentally determined in the apparatus of this investigation to be 110.6° C. Prior to use the methanol was distilled over calcium oxide and its boiling point was found to be 64.6° C., the accepted literature value. The refractive indices (n_{D}^{25}) of the methanol and toluene were found to be 1.32691 and 1.49428 at 25° C., respectively. These values

Table I. Experimental Data for Methanol-Toluene at 760 mm. of Hg

	Mole Fraction Methanol		Activity Coefficients	
Temp., ° C.	x_1	y_1	γ_1	γ_2
110.60	0.000	0.000	...	1.000
89.90	0.046	0.519	4.566	0.945
84.80	0.058	0.627	5.194	0.878
80.40	0.070	0.704	5.630	0.819
74.75	0.094	0.777	5.666	0.773
71.30	0.114	0.793	5.417	0.831
69.70	0.132	0.801	5.018	0.865
66.75	0.234	0.813	3.215	1.028
65.75	0.330	0.822	2.396	1.162
65.10	0.439	0.828	1.861	1.375
64.15	0.675	0.842	1.277	2.261
63.70	0.830	0.866	1.087	3.730
63.60	0.870	0.878	1.056	4.459
63.70	0.930	0.912	1.022	5.950
64.10	0.974	0.957	1.008	7.707
64.60	1.000	1.000	1.000	...

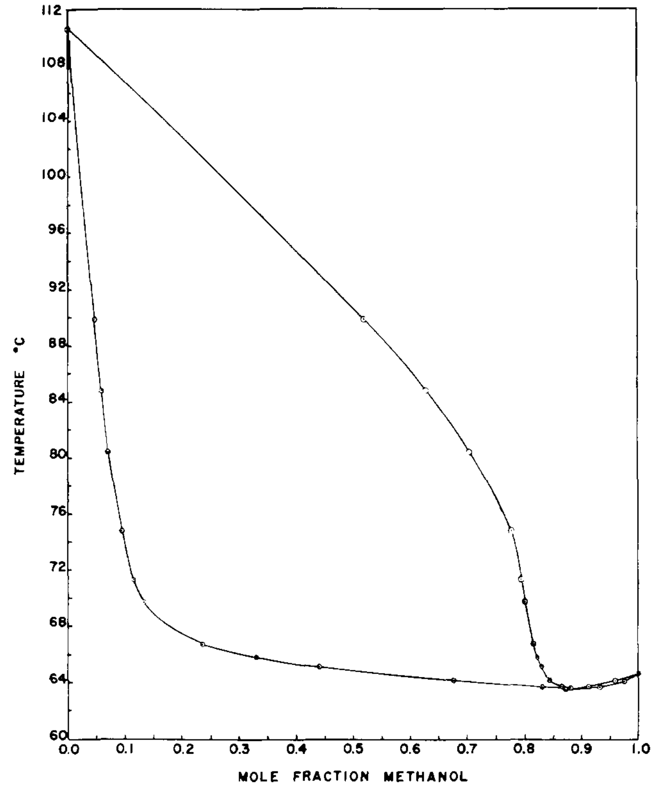

Figure 1. Temperature-composition curves for the methanol-toluene system

fall within the range of values reported in the literature for these substances at 25° C.

Analysis. The vapor and liquid equilibrium samples were analyzed by measuring their refractive index at 25° C. For this purpose a curve of refractive index *vs.* concentration was plotted from measurements with samples of known composition (Table II). A Bausch and Lomb precision refractometer was employed in which the fifth decimal place of the refractive index was estimated, *i.e.*, ±0.00003 units. The temperature of the prism was maintained at ±0.05° C. by a precision constant temperature bath. This equipment yielded analyses with an estimated maximum error of ±0.03 mole % absolute. The data are reported to the nearest 0.1 mole %.

Apparatus and Procedure. The experimental equilibrium runs were carried out in an Altsheler still (*1*). The temperature of the boiling mixture was measured by a No. 28 B&S guage copper-constantan thermocouple located approximately one inch above the surface of the liquid and directly above the Cottrell pump (*3*). The e.m.f. of the thermocouple was measured with a Minneapolis-Honeywell potentiometer which could be read with an accuracy of ±3 microvolts. This is equivalent to an error in temperature of ±0.03° C. The equilibrium temperatures are reported to the nearest 0.05° C. The pressure was maintained constant in the system to within ±1 mm. Hg by a No. 6 Cartesian manostat.

The still was initially charged with 300 cc. of a binary mixture and operated for at least four hours to insure the attainment of equilibrium. The criterion for equilibrium was a constant boiling temperature for the particular mixture. Analyses of the vapor-liquid equilibrium samples were made immediately upon completion of a run.

RESULTS

Vapor and liquid concentrations, equilibrium temperatures, and acitvity coefficients for the binary system are listed in Table I. The activity coefficients were calculated by the following relationships which ignore vapor phase nonideality.

$$\gamma_1 = (y_1 \pi)/(x_1 P_1) \qquad (1)$$

$$\gamma_2 = (y_2 \pi)/(x_2 P_2) \qquad (2)$$

where 1 = methanol
2 = toluene

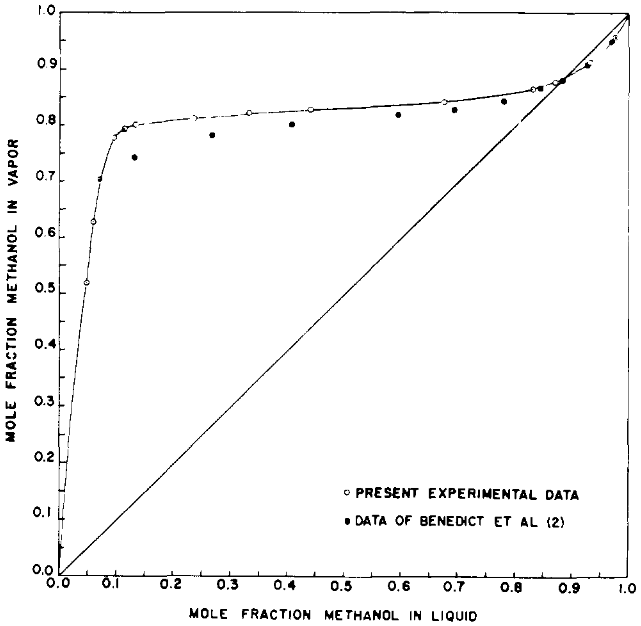

Figure 2. Vapor-liquid equilibrium curve for the methanol-toluene system

Table II. Refractive Indices of Mixtures of Methanol-Toluene at 25° C.

Mole Fraction Methanol	Refractive Index	Mole Fraction Methanol	Refractive Index
0.0000	1.49428	0.7289	1.40986
0.0967	1.48772	0.7663	1.40112
0.2246	1.47775	0.8426	1.38158
0.3527	1.46562	0.8861	1.36870
0.4829	1.45033	0.9296	1.35390
0.5312	1.44370	0.9685	1.33997
0.6037	1.43268	1.0000	1.32691
0.7025	1.41497		

The vapor pressures for methanol and toluene used in the calculations were obtained from the Handbook of Chemistry (*6*) and Dreisbach (*4*).

The calculated activity coefficients based on experimental data are plotted *vs.* methanol concentration in Figure 3.

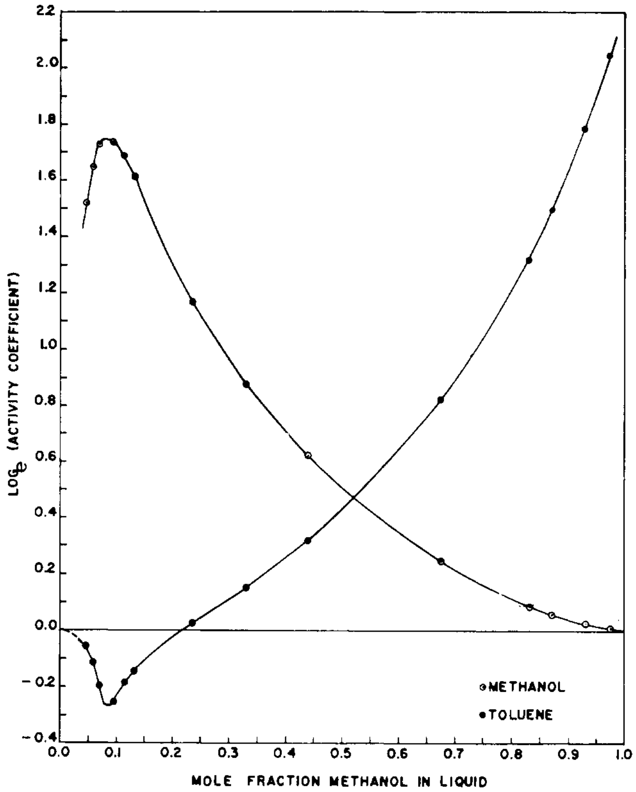

Figure 3. Activity coefficient-composition curves for the methanol-toluene system

The ln γ_1 curve exhibits a maximum at approximately 0.085 mole fraction methanol while the ln γ_2 curve exhibits a minimum at the same concentration. In addition, at a concentration of 0.5 mole fraction the value of ln γ_1 is greater than that of ln γ_2. This relationship is necessary for thermodynamic consistency since the value of ln γ_2 at $x_1 = 1.0$ is greater than that for ln γ_1 at $x_1 = 0$. The values obtained in this investigation for ln γ_1 and ln γ_2 at $x_1 = 0.5$ were 0.503 and 0.438, respectively. The data of Benedict and coworkers yielded corresponding values of 0.477 and 0.531, respectively. An additional thermodynamic check was made of the experimental data using a modification of the method of Redlich and Kister (*6*). The Redlich-Kister equation which is given below applies only to isothermal data.

$$\int_0^1 \ln \frac{\gamma_1}{\gamma_2}\, dx_1 = 0 \tag{3}$$

Herington (*5*) extended the method to include isobaric data. In this case the integral of Equation 3 does not equal zero and the condition necessary for thermodynamic consistency is:

$$D < J \tag{4}$$

where D is the percentage deviation from zero of the quantity calculated in Equation 3. D is calculated as follows:

$$D = \frac{100\left|\int_0^1 \ln \frac{\gamma_1}{\gamma_2}\, dx_1\right|}{\left|\sum \text{Area}\right|} \tag{5}$$

where $|\sum|$ is the sum of the absolute values of the areas calculated by Equation 3.

The quantity J is a function of the over-all boiling point range of the system and is defined by the following equation:

$$J = \frac{150\,|\theta|}{T_{\min}} \tag{6}$$

where θ is the over-all range of boiling points of the system and $T_{\min}$ is the lowest measured boiling point of the system in degrees Kelvin.

For the methanol-toluene system, $D = 4.99$ and $J = 20.95$. Hence, the data are thermodynamically consistent.

Corrections for vapor phase nonideality by the method suggested by Benedict (*2*) were found to be of the same order of magnitude (1% or less) as the data available for such calculations. Hence the corrections were not made. These corrections would result in a slight increase in the activity coefficients for toluene and a slight decrease for those of methanol.

Comparison of the x-y data (Figure 2) obtained in this investigation shows it to be consistently higher than that reported by Benedict and coworkers. The largest deviations occur in the dilute methanol region with a gradual convergence of both sets of data in the high methanol range. Such behavior could result if the batch technique employed by Benedict failed to yield equilibrium values for the increasingly methanol dilute experimental runs or if any material losses had accumulated.

NOMENCLATURE

D = percentage deviation from zero in the Redlich-Kister test
J = function of boiling point range and boiling temperature, $(150|\theta|/T_{\min})$
P_i = vapor pressure of pure component i at equilibrium temperature, mm. of mercury
$T_{\min}$ = lowest measured boiling point of the system, ° K.
x_i = mole fraction of component i in the liquid phase
y_i = mole fraction of component i in the vapor phase
γ_i = activity coefficient of component i
θ = over-all range of boiling points of the system, ° C.
π = total pressure on the system, mm. of mercury
$|\sum|$ = sum of the absolute values of the areas calculated in the Redlich-Kister test

Subscripts

1 = methanol
2 = toluene

LITERATURE CITED

(1) Altsheler, W.B., Unger, E.D., Kolachov, P., *Ind. Eng. Chem.* **43**, 2559 (1951).
(2) Benedict, M., Johnson, C.A., Solomon, Ernest, Rubin, L.C., *Trans. Am. Inst. Chem. Engrs.* **41**, 371 (1945).
(3) Cottrell, F.G., *J. Am. Chem. Soc.* **41**, 721 (1919).
(4) Dreisbach, R.R., *Advan. Chem. Ser.* **15**, 12 (1955).
(5) Herington, E.F.G., *J. Inst. Petrol.* **37**, 457 (1951).
(6) Lange, N.A., Handbook of Chemistry, 10th Ed., 1432, McGraw-Hill, New York, 1961.
(7) Redlich, O., Kister, A.T., *Ind. Eng. Chem.* **40**, 345 (1948).

RECEIVED for review July 29, 1963. Accepted November 4, 1963.