Isothermal Vapor-Liquid Equilibrium Data for the Heptane–Butyl Acetate System at 74.7° and 100° C.

WILLIAM A. SCHELLER, ALBERTO R. TORRES-SOTO, and KAUSHIK J. DAPHTARY
The University of Nebraska, Lincoln, Neb. 68508

Isothermal equilibrium vapor and liquid composition measurements have been made for the heptane–butyl acetate system at 74.7° and 100° C. using equilibrium samples produced with the aid of a vapor recirculation–type equilibrium still. Vaporization equilibrium constants (K-values) were calculated from the equilibrium compositions and the thermodynamic consistency checked by the method of Redlich and Kister. Composition–liquid specific volume data were obtained for the binary system at 20° C. Vapor pressure–temperature measurements were made for pure butyl acetate between 20.5° C. (13.3 mm. of Hg) and 124.6° C. (730.5 mm. of Hg) and fitted to an Antoine equation:

$$\log P^\circ = 7.5332 - 1.7478\left(\frac{10^3}{t + 250}\right)$$

with an average absolute deviation of 3.5 mm. of Hg and a maximum deviation of 9.1 mm. of Hg.

ISOTHERMAL vapor-liquid equilibrium data at low pressures are useful for studying the thermodynamics of nonideal solutions and desirable for establishing the vaporization equilibrium constants (K-values) used for the design of equilibrium stage processes.

A survey of the literature indicates that no such isothermal data have been published for the heptane–butyl acetate system in the vicinity of 75° and 100° C. The same literature survey uncovered only one set of subatmospheric vapor pressure measurements (*7*) for butyl acetate. Therefore, the determinations of vapor pressure and equilibrium composition reported here were made.

EXPERIMENTAL

A detailed description of the experimental equipment, calibrations, procedures, and methods has been given by Lodl and Scheller (*4*).

Briefly, a modification of the vapor recirculation–type equilibrium still described by Hipkin and Myers (*2*) was used in this work. Pressure in the still was controlled by a Cartesian manostat of the type described by Gilmont (*1*) and was measured with a mercury manometer to ±0.1 mm. for the 74.7° C. measurements, the vapor pressure measurements, and ±0.5 mm. of Hg for the 100° C. measurements.

Temperature was measured with an iron-constantan thermocouple and a Leeds and Northrup Type K-2 potentiometer to ±0.1° C.

The thermocouple was calibrated at the solid state transition point of sodium sulfate decahydrate (32.384° C.) and also against the boiling point of water. Distilled water was placed in the equilibrium still, the pressure was adjusted to the desired value with the aid of the Cartesian manostat, and the system was allowed to operate until a constant millivolt reading was obtained on the potentiometer. The temperature was determined from the measured pressure and the steam tables. Twenty-three experimental points between 85.6 mm. of Hg and 690.3 mm. of Hg (48.44° C. and 97.33° C.) were used in the calibration. A linear equation of temperature as a function of voltage was fitted to these 23 points by the method of least squares. The absolute average deviation between the experimental and calculated temperatures is 0.13° C.

Compositions of equilibrium samples were obtained from specific volume measurements made with the aid of calibrated pycnometers of the type described by Lipkin *et al.* (*3*). Weighings were made with a precision of ±0.0001 gram, and the volume of liquid in the pycnometer was known to ±0.0002 cc. These give a precision of ±0.0003 cc. per gram in the specific volume determination which in turn gives an over-all precision for the composition analyses of somewhat better than ±0.1 mole %. Specific volume–composition data at 20° C. are contained in Table I.

The vapor pressure of butyl acetate was measured by placing a pure sample in the equilibrium still and contactor, adjusting the manostat to the desired pressure, and observing the equilibrium temperature.

The heptane and butyl acetate were obtained from Phillips Petroleum Co. and Distillation Products Industries, respectively. Densities, refractive indexes, and normal boiling points were measured and compared with literature values (Table II). The reagent purities were checked further by gas-liquid chromatography, and very small secondary peaks were found. These analyses indicate that the materials have a purity greater than 99.5%.

Table I. Composition–Specific Volume Data for the Heptane–Butyl Acetate System at 20° C.

Mole Fraction Heptane	Molar Volume, Ml./G.-Mole	Specific Volume, Ml./G.
0.0000	131.8	1.135
0.0214	132.6	1.145
0.0899	133.7	1.165
0.1702	134.8	1.188
0.1862	135.0	1.192
0.4190	139.1	1.271
0.5000	140.0	1.294
0.6285	142.0	1.338
0.6747	142.8	1.355
0.8038	144.2	1.395
0.8064	144.3	1.397
0.9090	145.8	1.434
0.9742	146.3	1.454
1.0000	146.5	1.462

Table II. Reagent Properties

Property	Heptane			Butyl Acetate		
	Measured	Lit.	Ref.	Measured	Lit.	Ref.
Density, 20° C.	0.6840	0.6838	*6*	0.8814	0.8815	*7*
Refractive Index, 20° C.	1.3878	1.3876	*6*	1.3960	1.3961	*6*
Normal Boiling Point, ° C.	98.1	98.4	*6*	125.7[a]	126.1	*6*
Chromatographic Analysis, % >	99.5	. . .		99.5	. . .	

[a] Calculated from Equation 3.

Table III. Isothermal Vapor-Liquid Equilibrium Data for the Heptane–Butyl Acetate System at 74.7° and 100° C.

P, Mm. Hg	x_H	y_H	K_H	K_B	$\ln(\gamma_H/\gamma_B)$
TEMPERATURE, 74.7° C.					
141.9	0.000	0.000	. . .	1.000	. . .
144.4	0.010	0.035	3.500	0.975	0.343
148.9	0.020	0.082	4.100	0.937	0.547
163.7	0.050	0.180	3.600	0.863	0.492
174.2	0.072	0.245	3.403	0.814	0.488
190.1	0.100	0.325	3.250	0.750	0.531
225.6	0.190	0.490	2.579	0.630	0.474
238.6	0.228	0.535	2.346	0.602	0.427
256.2	0.285	0.590	2.070	0.573	0.348
270.0	0.340	0.650	1.911	0.530	0.347
285.8	0.405	0.675	1.667	0.546	0.180
298.3	0.495	0.728	1.471	0.539	0.066
311.7	0.565	0.760	1.345	0.552	−0.044
324.1	0.675	0.805	1.193	0.600	−0.249
337.5	0.768	0.860	1.120	0.603	−0.315
347.6	0.855	0.905	1.058	0.655	−0.456
354.6	0.920	0.930	1.011	0.875	−0.791
361.7	1.000	1.000	1.000	. . .	. . .
TEMPERATURE, 100.0° C.					
358	0.000	0.000	. . .	1.000	. . .
391	0.045	0.165	3.667	0.874	0.636
452	0.120	0.358	2.983	0.730	0.610
500	0.175	0.420	2.400	0.703	0.432
506	0.168	0.425	2.530	0.691	0.500
541	0.233	0.500	2.146	0.652	0.394
568	0.285	0.545	1.912	0.636	0.302
594	0.315	0.575	1.825	0.620	0.281
613	0.345	0.610	1.768	0.595	0.290
650	0.440	0.668	1.518	0.593	0.143
679	0.525	0.725	1.381	0.579	0.071
689	0.580	0.760	1.310	0.571	0.032
699	0.615	0.770	1.252	0.597	−0.058
720	0.685	0.800	1.168	0.635	−0.189
760	0.810	0.860	1.062	0.737	−0.433
770	0.863	0.898	1.041	0.745	−0.463
790	0.975	0.979	1.004	0.840	−0.620
796	1.000	1.000	1.000	. . .	. . .

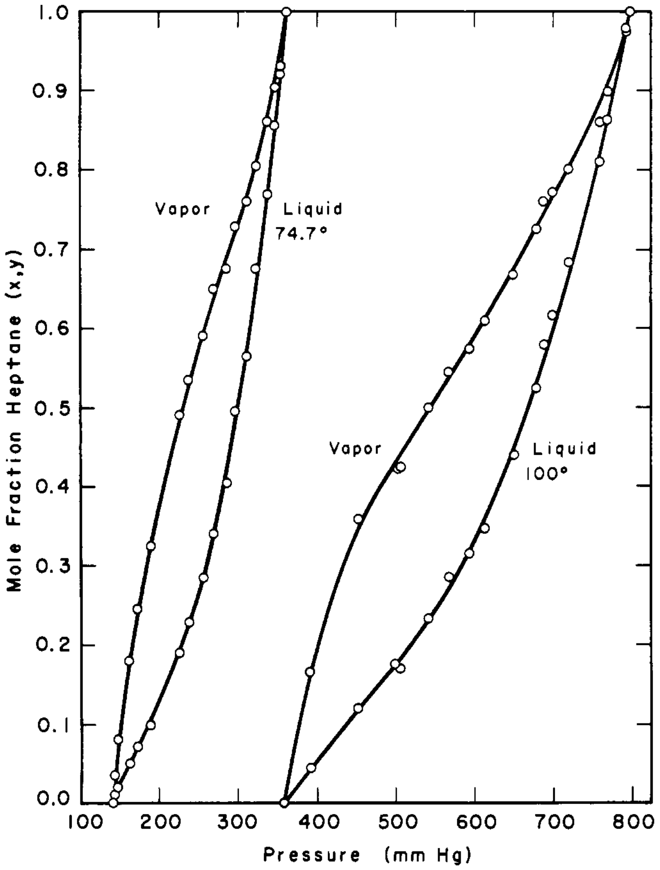

Figure 1. Pressure-composition diagram for the heptane–butyl acetate system at 74.7° and 100° C.

DISCUSSION OF RESULTS

Table III contains the experimental *x*, *y*, *P* equilibrium data obtained at 74.7° and 100° C. Figure 1 is a plot of these data. The vaporization equilibrium constants (K = *y*/*x*) were calculated at the two temperatures, tabulated in Table III, and are shown graphically as a function of pressure in Figure 2. The experimental vapor pressure–temperature data for pure butyl acetate are tabulated in Table IV.

The over-all thermodynamic consistency of the experimental equilibrium data was checked by the method of Redlich and Kister (*5*). For an isothermal binary system with the vapor phase displaying ideal gas behavior and the liquid phase having a zero volume change on mixing, the data are consistent if:

$$\int_{x_1=0}^{x_1=1} \ln \frac{\gamma_1}{\gamma_2}\, dx_1 = 0 \qquad (1)$$

Expressing Equation 1 as two integrals in terms of the K-values and letting x_1^0 represent the value of x_1 for which $\ln\left[(K_1 P_2^\circ)/(K_2 P_1^\circ)\right] = 0$ gives:

$$\int_{x_1=0}^{x_1=x_1^\circ} \ln\left(\frac{K_1 P_2^\circ}{K_2 P_1^\circ}\right) dx_1 = \int_{x_1=1}^{x_1=x_1^\circ} \ln\left(\frac{K_1 P_2^\circ}{K_2 P_1^\circ}\right) dx_1 \qquad (2)$$

For the system studied, the compressibility factors of the saturated vapors of heptane and butyl acetate at 100° C. are 0.952 and 0.98 based on data obtained from Timmermans (*6*). The volume change on mixing at 20° C. appears to be less than 2 cc. per gram-mole. In view of these values, Equation 2 appears to be suitable for checking the consistency of the equilibrium data.

For the heptane–butyl acetate system at 74.7° C., the left side of Equation 2 is 0.178 and the right side 0.171. At 100° C. the left and right side values are 0.189 and 0.182, respectively.

The butyl acetate vapor pressure data were fitted to an Antoine equation giving:

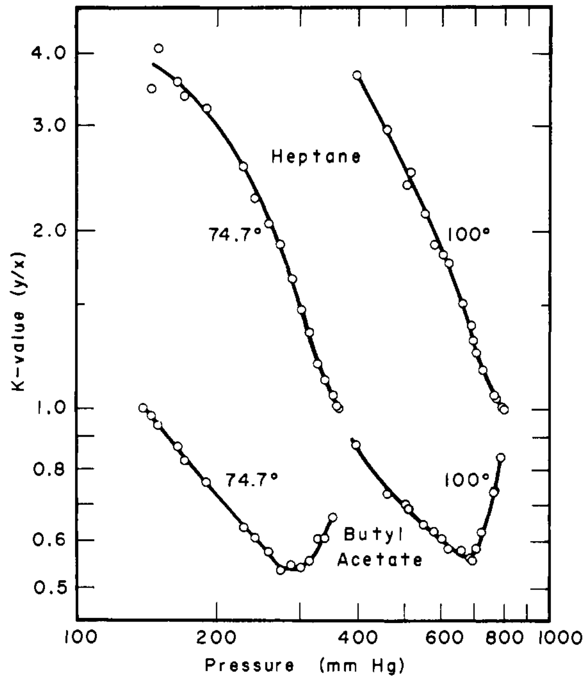

Figure 2. K-values for the heptane–butyl acetate system

Table IV. Vapor Pressure and Temperature Data for Butyl Acetate

T., ° C.	*P.*, Mm. Hg
20.5	13.3
30.8	20.4
46.3	38.8
62.2	79.8
73.8	136.3
84.1	201.2
93.2	276.7
101.2	363.3
105.4	421.6
109.5	476.6
115.1	563.5
118.9	627.0
120.7	658.0
124.6	730.5

$$\log P^{\circ} = 7.5332 - 1.7478\left(\frac{10^3}{t + 250}\right) \qquad (3)$$

The value of the temperature constant, 250° C., was determined by trial and error, and the other two constants were determined by the method of least squares. Comparison of the calculated vapor pressures with the experimental values indicates an average absolute deviation of 3.5 mm. of Hg and a maximum deviation of 9.1 mm. of Hg.

Calculated vapor pressures using Equation 3 were compared with the data of Kliment, Fried, and Pick contained in Timmermans (*7*). The average absolute deviation is 10.8 mm. of Hg with a maximum deviation of 12.6 mm. of Hg. In this case, all calculated vapor pressures are greater than the experimental values.

The calculated normal boiling point of butyl acetate using Equation 3 is 125.7° C. compared with the literature (*6*) value of 126.1° C.

NOMENCLATURE

K = vaporization equilibrium constant = y/x
P° = vapor pressure of a pure component, mm. of Hg
t = temperature, ° C.
x = equilibrium mole fraction of a component in the liquid phase
y = equilibrium mole fraction of a component in the vapor phase
γ = liquid phase activity coefficient

Subscripts

1 = more volatile component, heptane
2 = less volatile component, butyl acetate
H = heptane
B = butyl acetate

LITERATURE CITED

(1) Gilmont, R., *Ind. Eng. Chem., Anal. Ed.* **18**, 663 (1946).
(2) Hipkin, H., Myers, H.S., *Ind. Eng. Chem.* **46**, 2524 (1954).
(3) Lipkin, M.R., Davidson, J.A., Harvey, W.T., Kurtz, S.S., Jr., *Ibid.*, **16**, 55 (1944).
(4) Lodl, S.J., Scheller, W.A., J. CHEM. ENG. DATA **12**, 485 (1967).
(5) Redlich, O., Kister, A.T., *Ind. Eng. Chem.* **40**, 345 (1948).
(6) Timmermans, J., "Physico-Chemical Constants for Pure Organic Compounds," Vol. I., pp. 60–5, 413, 415, 418, 419, Elsevier Publishing Co., Inc., New York, N. Y., 1950.
(7) *Ibid.*, Vol. **II**, pp. 288–9, Elsevier Publishing Co., Inc., New York, N. Y., 1965.

RECEIVED for review April 1, 1968. Accepted September 30, 1968.