Table II. Constants for Equations 1 and 3

	Equation 1				
R in $B(OR)_3$	a	$-b$	$-c$	d	S
CH_3	0.92726	1.3731×10^{-3}	7.0987×10^{-7}	3.5502×10^{-9}	5.80×10^{-5}
C_2H_5	0.85767	1.1675×10^{-3}	2.2279×10^{-7}	2.7603×10^{-9}	8.68×10^{-5}
C_3H_7	0.85454	9.5121×10^{-4}	5.0998×10^{-7}	-4.3784×10^{-11}	2.59×10^{-4}
iso-C_3H_7	0.81251	1.0374×10^{-3}	2.7087×10^{-7}	-3.3009×10^{-9}	1.83×10^{-4}
C_4H_9	0.85366	8.5287×10^{-4}	4.0483×10^{-7}	5.0421×10^{-10}	3.18×10^{-4}
iso-C_4H_9	0.83992	8.5608×10^{-4}	8.3089×10^{-7}	2.3275×10^{-9}	1.89×10^{-4}

	Equation 3			
	$-A$	B	C	S
CH_3	3.71465	7.21879×10^2	2.78780×10^4	2.07×10^{-5}
C_2H_5	4.32480	1.15434×10^3	-1.82476×10^4	7.23×10^{-4}
C_3H_7	4.58674	1.42978×10^3	-1.72043×10^4	4.07×10^{-3}
iso-C_3H_7	4.86188	1.46513×10^3	-2.39146×10^4	1.49×10^{-3}
C_4H_9	4.17103	1.23605×10^3	4.65993×10^4	2.39×10^{-3}
iso-C_4H_9	3.66779	7.28965×10^2	1.61627×10^5	4.75×10^{-3}

mole), should have the following temperature-dependence

$$E^* = R(B + 2C/T) \tag{4}$$

where R is the gas constant. Equation 4 predicts that E^* should decrease with increasing T, but the Table II data indicate that this is true only for methyl, butyl, and isobutyl borates. The opposite effect displayed by the remaining borates would suggest that the mechanism for activation is complex in these instances. For the unbranched homologs, E^* at the boiling point is related to n, the number of carbon atoms in a single alkyl group, by the expression

$$E^* = 377\ n + 1403 \tag{5}$$

Equation 5 gives an average error of $\pm 3.1\%$. The molar volume at the boiling point, V_b (ml. per mole), can also be correlated to n, by the relationship

$$V_b = 75.77\ n + 43.55 \tag{6}$$

which obtains an average error of $\pm 0.23\%$.

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

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Isothermal equilibrium vapor and liquid composition measurements have been made for the heptane–ethyl butyrate system at 74.7° and 100° C., using equilibrium samples produced with the aid of a vapor recirculation equilibrium still. Vaporization equilibrium constants (*K*-values) were calculated from the equilibrium compositions, and the thermodynamic consistency was checked by the method of Redlich and Kister. Composition and liquid specific volume data were obtained for this binary system at 20° C.

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 system heptane–ethyl butyrate in the vicinity of 75° and 100° C. Because of this, the determinations of 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*), and by the authors in an earlier paper (*6*).

Briefly, a modification of the vapor recirculation 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 and ±0.5 mm. 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 and 690.3 mm. of Hg (48.44° 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 pycnometers of the type described by Lipkin *et al.* (*3*). The pycnometers were calibrated by the authors prior to beginning the sample analyses. The over-all precision of the composition analyses is somewhat better than ±0.1 mole %. Specific volume and composition data at 20° ±0.05° C. are contained in Table I.

The heptane and ethyl butyrate 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. As a result of these analyses, the materials are believed to have a purity greater than 99.5%.

Table I. Composition, Specific Volume Data for the System Heptane–Ethyl Butyrate at 20° C.

Mole Fraction Heptane	Molar Vol., Ml./Gram-Mole	Sp. Vol., Ml./Gram
0.0000	132.2	1.138
0.0210	132.6	1.145
0.1686	135.1	1.191
0.2029	135.6	1.201
0.2643	137.7	1.230
0.3678	138.3	1.254
0.5145	140.8	1.304
0.5213	140.7	1.305
0.5218	140.6	1.304
0.5925	141.4	1.325
0.6530	142.7	1.350
0.7009	142.7	1.361
0.7204	143.2	1.368
0.7652	143.7	1.382
0.7781	143.8	1.386
0.7828	144.4	1.393
0.9604	146.3	1.451
0.9842	146.4	1.458
1.0000	146.5	1.462

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 over-all thermodynamic consistency of the experimental equilibrium data was checked by the method of Redlich and Kister (*5*). For an isothermal binary system having a zero volume change on mixing over the entire composition range, the data are consistent if

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

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

P, Mm. of Hg	x_1	y_1	K_1	K_2	$\ln(\gamma_1/\gamma_2)$
		74.7° C.			
169.0	0.000	0.000	. . .	1.000	. . .
171.7	0.010	0.025	2.500	0.985	0.171
179.3	0.026	0.090	3.462	0.934	0.549
182.0	0.040	0.146	3.650	0.890	0.651
192.4	0.055	0.180	3.273	0.868	0.567
202.4	0.085	0.230	2.706	0.842	0.407
221.5	0.125	0.347	2.776	0.746	0.553
234.7	0.155	0.365	2.355	0.751	0.381
237.3	0.180	0.416	2.311	0.712	0.416
254.1	0.232	0.430	1.853	0.742	0.154
267.9	0.304	0.525	1.727	0.682	0.163
310.6	0.520	0.725	1.394	0.573	0.128
316.4	0.555	0.705	1.270	0.663	−0.111
318.9	0.575	0.737	1.283	0.619	−0.030
326.6	0.625	0.742	1.187	0.688	−0.213
337.3	0.745	0.827	1.110	0.678	−0.269
347.4	0.820	0.875	1.067	0.694	−0.331
351.1	0.845	0.895	1.059	0.677	−0.314
354.2	0.900	0.930	1.033	0.700	−0.371
358.8	0.950	0.980	1.032	0.400	+0.186
361.0	0.975	0.985	1.010	0.600	−0.240
361.7	1.000	1.000	1.000	. . .	. . .
		100° C.			
399	0.000	0.000	. . .	1.000	. . .
411	0.015	0.050	3.333	0.964	0.550
463	0.070	0.215	3.071	0.844	0.541
478	0.085	0.228	2.682	0.844	0.467
544	0.155	0.350	2.258	0.769	0.389
568	0.195	0.410	2.103	0.733	0.366
588	0.233	0.470	2.017	0.691	0.382
628	0.333	0.545	1.637	0.682	0.187
664	0.440	0.638	1.450	0.646	0.120
694	0.520	0.680	1.308	0.667	−0.014
709	0.600	0.715	1.192	0.713	−0.166
722	0.647	0.750	1.159	0.708	−0.196
738	0.700	0.790	1.129	0.700	−0.210
742	0.767	0.833	1.086	0.717	−0.274
749	0.805	0.860	1.068	0.718	−0.357
755	0.858	0.885	1.031	0.810	−0.444
760	0.885	0.900	1.017	0.870	−0.484
770	0.895	0.915	1.022	0.810	−0.456
795	1.000	1.000	1.000	. . .	. . .

Table II. Reagent Properties

	Heptane		Ethyl Butyrate		
Property	Measured	Lit. (*7*)	Measured	Lit.	Ref.
Density, 20° C.	0.6835	0.6838	0.8840	0.8794	(*8*)
Refractive index, 20° C., n_D	1.3878	1.3876	1.3995	1.3928	(*7*)
Normal boiling point, ° C.	98.1	98.4	120.8	121.5	(*7*)
Chromatographic analysis, %>	99.5	. . . .	99.5	. . .	. . .

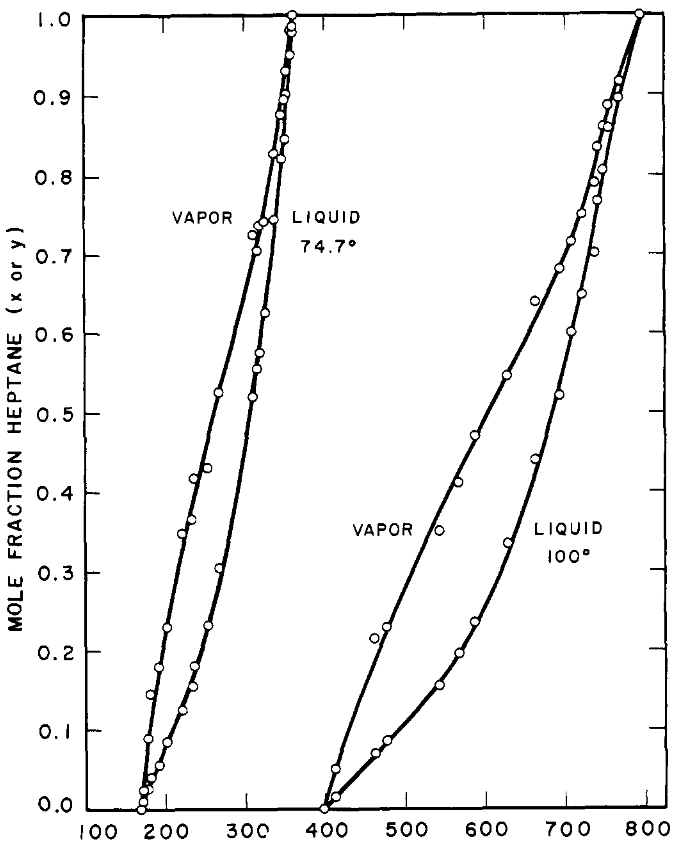

Figure 1. Pressure-composition diagram for the system heptane–ethyl butyrate at 74.7° and 100° C.

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 $\ln[(K_1P_2^0)/(K_2P_1^0)] = 0$ gives

$$\int_{x_1=0}^{x_1=x_1^0} \ln\left(\frac{K_1P_2}{K_2P_1^0}\right) dx_1 = \int_{x_1=1}^{x_1=x_1^0} \ln\left(\frac{K_1P_2^0}{K_2P_1^0}\right) dx_1 \qquad (2)$$

For the system studied, the compressibility factors of the saturated vapors of heptane and ethyl butyrate at 100° C. are 0.952 and 0.99, based on data obtained from Timmermans (*7*). 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 suitable for checking the consistency of the present equilibrium data. For the heptane-ethyl butyrate system at 74.7° C., the left side of Equation 2 is 0.137 and the right side 0.129. At 100° C., the left and right side values are 0.152 and 0.145, respectively.

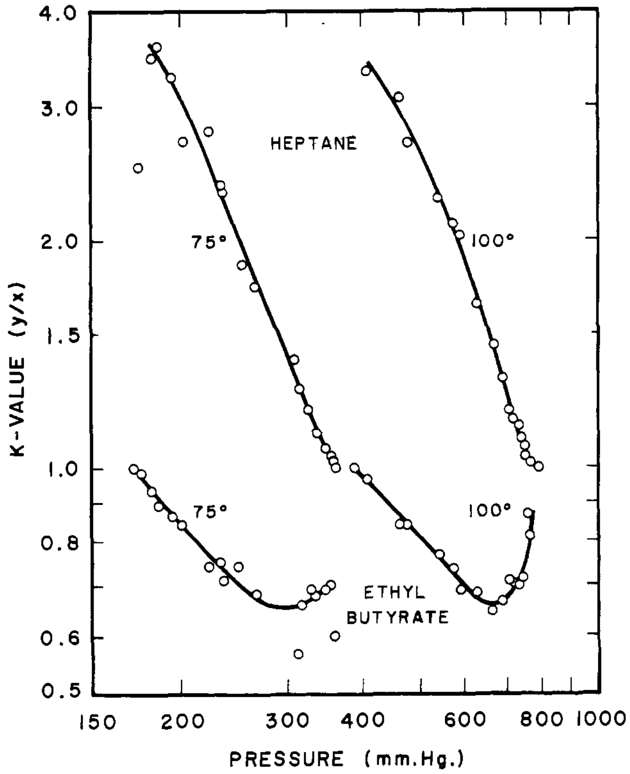

Figure 2. K-values for the system heptane–ethyl butyrate

NOMENCLATURE

K = vaporization equilibrium constant = y/x
P^0 = 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, ethyl butyrate

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