Isothermal Vapor–Liquid Equilibrium Data for the System *n*-Heptane–*n*-Valeraldehyde at 75 and 90 °C

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Isothermal vapor–liquid equilibrium data for the *n*-heptane–*n*-valeraldehyde system have been measured at 75 and 90 °C. The system exhibits a minimum-boiling azeotrope at each temperature. The azeotropic composition is 59 mol % at 75 °C and 54 mol % at 90 °C. The data have been analyzed by the total pressure method and the liquid-phase activity coefficients expressed by the Margules three-suffix equation.

Introduction

Isothermal vapor–liquid equilibrium data at low pressures are useful for studying the thermodynamics of nonideal solutions and are desirable for establishing the equilibrium ratios (K values) used for design of equilibrium stage processes. A survey of the literature indicates that such data on systems containing the aldehyde group are particularly scarce. In this paper we report vapor–liquid equilibrium data for the *n*-heptane–*n*-valeraldehyde system at 75 and 90 °C.

Equipment and Materials

The vapor recirculating still and the pressure control device used in this study were identical with those described by Lodl and Scheller (5).

Temperature was measured with a calibrated iron–constantan thermocouple, the cold junction being immersed in distilled water and ice at 0 °C. The voltage between the junctions was measured by a digital multimeter, and the temperature measurements are believed to be accurate to within ±0.05 °C.

The pressure was measured by a mercury manometer capable of measuring within ±0.1 mmHg.

The samples were analyzed in a gas chromatograph. The detector output was fed to a strip chart recorder which was directly connected to a printing integrator. The composition was read from a calibration curve plotted to read with an accuracy of ±0.001 mol fraction. The calibration curve was made by plotting on expanded coordinates the area fraction of the heptane peak for 14 samples of known composition.

The *n*-heptane and the valeraldehyde were obtained from Phillips Petroleum Co. and Eastman Kodak Co., respectively. These samples, as obtained, exhibited secondary peaks upon chromatographic analysis. They were therefore further purified by distilling at high reflux.

Aldehydes are easily oxidized and polymerized. Hence the valeraldehyde was distilled just prior to each run. For the same reason, the equilibrium samples were analyzed immediately after withdrawal from the still. Polymerization, if any, during the experimental time interval, was not significant enough to show

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Table I. Reagent Properties

	n-heptane		*n*-valeraldehyde	
	measd	lit.[a]	measd	lit.[a]
density, g/mL (20 °C)	0.6837	0.68376	0.8089	0.8095
normal bp, °C	98.45	98.42	102.4	103[b]

[a] Literature values are from ref 2. [b] The literature value of 103 °C, with no decimal places, indicates considerable uncertainty in the normal boiling point of valeraldehyde.

Table II. Experimental and Smoothed Vapor-Liquid Equilibrium Data for the System *n*-Heptane-*n*-Valeraldehyde[a]

experimental			smoothed values, at exptl x's			
P, mmHg	x_1	y_1	P, mmHg	y_1	γ_1	γ_2
75 °C						
316.3	0.0	0.0	316.3	0.0	2.183	1.000
364.8	0.120	0.237	365.2	0.222	1.878	1.010
391.5	0.223	0.340	391.5	0.342	1.663	1.036
402.2	0.278	0.411	401.7	0.391	1.563	1.057
421.2	0.438	0.528	419.6	0.503	1.329	1.158
422.5	0.544	0.573	424.1	0.564	1.214	1.264
423.0	0.658	0.644	423.6	0.631	1.119	1.429
420.8	0.714	0.672	421.0	0.667	1.083	1.534
398.0	0.893	0.827	396.8	0.825	1.012	2.032
381.8	0.964	0.920	376.1	0.929	1.001	2.326
361.4	1.0	1.0	361.4	1.0	1.000	2.506
90 °C						
531.6	0.0	0.0	531.6	0.0	2.467	1.000
617.1	0.124	0.227	622.6	0.228	1.956	1.015
646.6	0.171	0.297	643.5	0.282	1.810	1.029
673.5	0.215	0.386	674.3	0.374	1.555	1.075
684.2	0.318	0.416	682.8	0.404	1.471	1.100
687.4	0.345	0.442	687.1	0.422	1.424	1.118
696.6	0.438	0.486	697.0	0.479	1.288	1.193
694.2	0.681	0.651	692.5	0.629	1.079	1.491
671.1	0.791	0.742	673.4	0.718	1.032	1.687
644.3	0.877	0.823	647.8	0.809	1.011	1.873
632.9	0.922	0.855	630.1	0.869	1.004	1.983
615.1	0.962	0.922	611.0	0.931	1.001	2.089
589.3	1.0	1.0	589.3	1.0	1.000	2.197

[a] Subscript 1 is heptane.

up on the chromatographic analysis.

Measured and literature values of the density and normal boiling point of the reagents are listed in Table I.

Results and Discussion

The experimental data obtained from this study are listed in Table II. For each point the temperature, the pressure, the liquid composition, and the vapor composition were measured. The data were smoothed by the total pressure method, using the Margules three-suffix equation to represent liquid-phase activity coefficients. Details of the total pressure method can be found elsewhere, for example in Prausnitz (6). Essentially, the method employs the Gibbs–Duhem equation to obtain vapor composition from measured values of the total pressure and the liquid composition. Comparison of the experimental y's
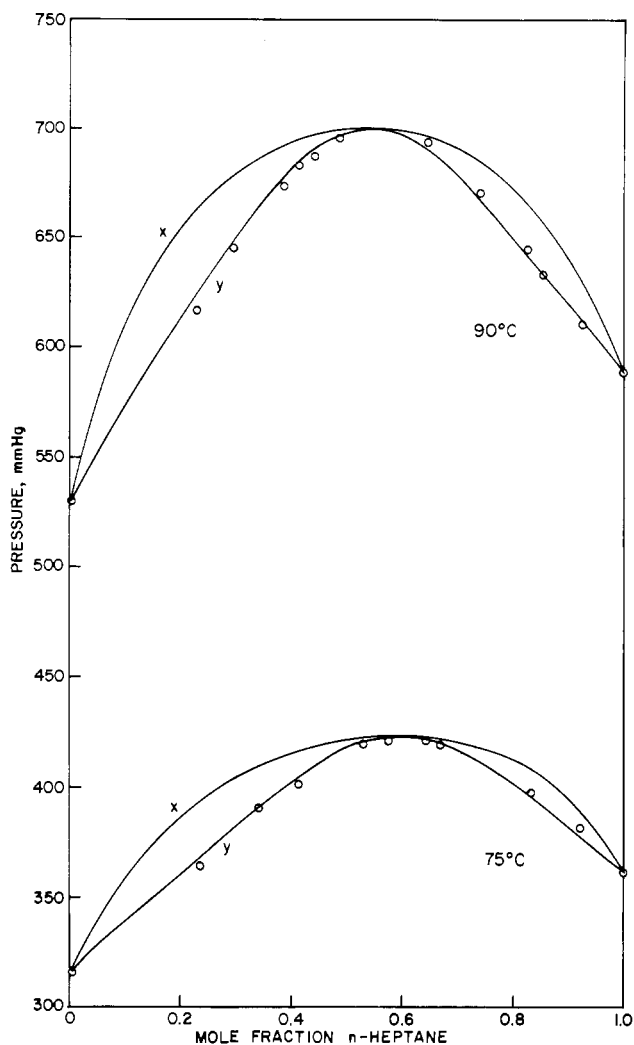
Figure 1. Pressure–composition diagram for the heptane–valeraldehyde system at 75 and 90 °C (—, smoothed values; O, experimental y's).

against those obtained from the total pressure method provides an indirect test of the consistency of the data.

The equation for vapor–liquid equilibrium was written as

$$\gamma_i x_i p_i{}^\circ \phi_i{}^\circ = P \phi_i y_i \tag{1}$$

The vapor-phase fugacity coefficient ϕ_i and the saturation fugacity coefficient $\phi_i{}^\circ$ were calculated by the virial equation. The necessary second virial coefficients were estimated by the method of Hayden and O'Connell (3) and are listed in Table III. The second virial coefficients for n-heptane are in excellent agreement with Dymond and Smith (1). No literature values could be located for the second virial coefficients of n-valeraldehyde and for the interaction second virial coefficient.

Table IV lists constants for the three-suffix Margules equation. Figure 1 is a plot of the p-x-y data, the y's being smoothed

Table III. Second Virial Coefficients, Estimated by the Method of Hayden and O'Connell[a]

T, °C	B_{11}	B_{22}	B_{12}
75.0	-1826	-1749	-1491
90.0	-1617	-1547	-1328

[a] B's are in mL/mol. Subscript 1 is n-heptane. Subscript 2 is n-valeraldehyde.

Table IV. Constants for the Margules Three-Suffix Equation[a]

T, °C	A_{12}	A_{21}
75.0	0.3390	0.3989
90.0	0.3922	0.3418

[a] Note: $\log \gamma_1 = [A_{12} + 2(A_{21} - A_{12})x_1]x_2{}^2$. $\log \gamma_2 = [A_{21} + 2(A_{12} - A_{21})x_2]x_1{}^2$.

values obtained by the total pressure method. Experimental y's are also shown for comparison. It can be seen that the n-heptane–n-valeraldehyde system exhibits a minimum-boiling azeotrope at both temperatures investigated here. From the smoothed data the azeotropic composition was calculated as 59 mol % at 75 °C and 54 mol % at 90 °C. The corresponding azeotropic pressures are 424 and 700 mmHg, respectively. It may be noted that Horsley (4) does not report an azeotrope for the n-heptane–n-valeraldehyde system.

A comparison between y values calculated by the total pressure method and the experimentally measured y's is also shown in Table II. The mean absolute deviation between calculated and experimental y's is 0.011 at 75 °C and 0.014 at 90 °C.

Glossary

B	second virial coefficient, mL/mol
$f_i{}^\circ$	fugacity of pure liquid i
p	pressure, mmHg
x_i	mole fraction of i in the liquid phase
y_i	mole fraction of i in the vapor phase
γ_i	liquid phase activity coefficient of component i
ϕ_i	vapor phase fugacity coefficient of component i in mixture
$\phi_i{}^\circ$	saturation fugacity coefficient of component i

Literature Cited

(1) Dymond, J. H., Smith, E. B., "The Virial Coefficient of Gases", Clarendon Press, Oxford, England, 1969, p 145.
(2) "Handbook of Chemistry and Physics", Section C, Chemical Rubber Co., Cleveland, Ohio, 1972.
(3) Hayden, J. G., O'Connell, J. P., *Ind. Eng. Chem., Process Des. Develop.*, **14**, 209 (1975).
(4) Horsley, L. H., "Azeotropic Data—III", American Chemical Society, Washington, D.C., 1973.
(5) Lodl, S. J., Scheller, W. A., *J. Chem. Eng. Data*, **12**, 485 (1967).
(6) Prausnitz, J. M., "Molecular Thermodynamics of Fluid-Phase Equilibria", Prentice-Hall, Englewood-Cliffs, N.J., 1969, p 203.