# Vapor-Liquid Equilibrium Data for the System *n*-Heptane–*n*-Butyl Alcohol at Medium Pressures

S. V. VIJAYARAGHAVAN, P. K. DESHPANDE, and N. R. KULOOR
Department of Chemical Engineering, Indian Institute of Science, Bangalore, India

**Vapor-liquid equilibrium data for the system *n*-heptane–*n*-butyl alcohol at pressures of 1445, 2205, 2965, and 3725 mm. of Hg have been reported. The data are correlated with Chao's modified Redlich-Kister equation.**

VAPOR-LIQUID equilibrium data for the systems *n*-heptane–*n*-butyl alcohol are available at 685 mm. of Hg pressure (*7*) and at isothermal conditions (*5*). In the present work the system has been studied at 1445, 2205, 2965, and 3725 mm. of Hg pressure to find the effect of pressure on the azeotrope.

## EXPERIMENTAL

The equilibrium still and the experimental procedure have been described earlier (*6*). The properties of reagents used are given in Table I. The samples were analyzed by density determination at 25 ± 0.1° C., reproducible within ±0.0001. The pressure in the still was measured by a bourdon gage with an accuracy of 0.5 lb. per sq. inch, the temperature by a thermometer of 0.1° C. accuracy.

## THERMODYNAMIC CONSISTENCY

The experimental vapor-liquid equilibrium data for this system are presented in Table II and Figure 1.

Liquid phase activity coefficients are calculated from the equation,

$$\gamma_i = \frac{y_i \pi}{x_i P_i} \theta_i \qquad (1)$$

The vapor pressure data are taken from the literature (*2*). Since the vapor phase imperfection correction factor, $\theta$, varied from 0.961 to 0.987 for *n*-butyl alcohol and from 0.955 to 1.013 for *n*-heptane, it was taken into account in calculating the values of activity coefficients. The $\theta$ values were taken from Scheibel's nomograph (*4*).

The system forms an azeotrope at all pressures studied. The data are correlated with Chao's modified Redlich-Kister equation (*1*). The constants of the equation,

$$\log \gamma_1/\gamma_2 = a + b(x_2 - x_1) + c(6x_1x_2 - 1) + d(x_2 - x_1)(1 - 8x_1x_2)$$

at all pressures studied are given below.

| Pressure, Mm. of Hg | Constants | | | |
|---|---|---|---|---|
| | *a* | *b* | *c* | *d* |
| 1445 | 0.018 | 0.644 | 0.130 | −0.030 |
| 2205 | −0.035 | 0.644 | 0.067 | 0.003 |
| 2965 | −0.073 | 0.644 | 0.069 | 0.010 |
| 3725 | −0.065 | 0.644 | 0.025 | 0.017 |

Table I. Properties of Pure Components

| Compound | Density, at 20° C. | | Refractive Index, at 20° C. | |
|---|---|---|---|---|
| | Exptl. | Lit. (*2*) | Exptl. | Lit. (*2*) |
| *n*-Heptane | 0.6838 | 0.68376 | 1.3880 | 1.3876 |
| 1-Butanol | 0.8099 | 0.80978 | 1.3988 | 1.3991 |

The values of constants *a*, *b*, *c*, *d* are correlated with pressure and the following relationships are obtained:

$$a = -0.00005789 \times \pi + 0.104$$

$$b = 0.644$$

Table II. System: *n*-Heptane(1)–*n*-Butyl Alcohol(2).

| Temp., ° C. | $x_1$ | $y_1$ | $\gamma_1$ | $\gamma_2$ | $y_{1\text{calcd.}}$ |
|---|---|---|---|---|---|
| | | 1445 mm. | | | |
| 128.5 | 9.4 | 21.9 | 2.972 | 1.001 | 31.9 |
| 124.4 | 15.6 | 43.9 | 2.726 | 1.004 | 44.5 |
| 118.3 | 32.3 | 60.7 | 2.122 | 1.075 | 61.3 |
| 116.6 | 40.2 | 64.1 | 1.861 | 1.172 | 64.6 |
| 115.4 | 49.7 | 66.6 | 1.627 | 1.355 | 65.6 |
| 115.0 | 58.6 | 68.5 | 1.436 | 1.571 | 66.6 |
| 114.8 | 65.1 | 69.4 | 1.317 | 1.831 | 67.3 |
| 114.8 | 76.4 | 72.0 | 1.161 | 2.463 | 69.7 |
| 115.3 | 81.2 | 74.0 | 1.116 | 2.839 | 71.4 |
| 117.2 | 90.6 | 80.9 | 1.041 | 3.941 | 79.2 |
| | | 2205 mm. | | | |
| 146.3 | 6.8 | 22.5 | 2.884 | 1.023 | 23.8 |
| 142.0 | 12.7 | 35.0 | 2.649 | 1.040 | 35.8 |
| 136.1 | 24.3 | 48.2 | 2.191 | 1.117 | 47.9 |
| 131.6 | 38.7 | 56.5 | 1.803 | 1.314 | 53.5 |
| 130.4 | 48.1 | 59.5 | 1.576 | 1.496 | 56.1 |
| 129.9 | 55.2 | 61.2 | 1.431 | 1.690 | 57.9 |
| 130.4 | 72.1 | 65.4 | 1.156 | 2.378 | 64.2 |
| 130.9 | 76.3 | 67.0 | 1.106 | 2.638 | 66.4 |
| 132.5 | 84.8 | 70.9 | 1.009 | 3.438 | 72.1 |
| 132.4 | 90.4 | 78.2 | 1.004 | 3.912 | 79.2 |
| | | 2965 mm. | | | |
| 155.0 | 11.4 | 30.0 | 2.558 | 1.003 | 30.0 |
| 150.6 | 19.8 | 41.4 | 2.254 | 1.062 | 45.2 |
| 148.0 | 26.5 | 46.5 | 1.982 | 1.145 | 46.9 |
| 145.8 | 32.8 | 51.0 | 1.842 | 1.224 | 48.6 |
| 144.1 | 40.1 | 53.6 | 1.648 | 1.363 | 51.3 |
| 142.5 | 51.2 | 57.4 | 1.436 | 1.608 | 54.7 |
| 142.0 | 59.8 | 59.5 | 1.286 | 1.879 | 57.5 |
| 142.4 | 70.2 | 62.3 | 1.134 | 2.344 | 65.4 |
| 143.0 | 78.3 | 65.0 | 1.047 | 2.925 | 66.4 |
| 145.0 | 87.9 | 72.0 | ... | 3.966 | 74.2 |
| | | 3725 mm. | | | |
| 161.2 | 10.8 | 28.6 | 2.849 | 1.068 | 27.8 |
| 157.3 | 18.7 | 38.5 | 2.401 | 1.129 | 36.9 |
| 153.9 | 30.2 | 47.5 | 1.973 | 1.240 | 44.1 |
| 131.8 | 41.3 | 51.7 | 1.636 | 1.438 | 48.1 |
| 150.8 | 50.8 | 54.3 | 1.427 | 1.685 | 51.4 |
| 150.4 | 60.4 | 57.6 | 1.287 | 1.965 | 54.5 |
| 150.9 | 68.7 | 59.7 | 1.159 | 2.331 | 58.7 |
| 151.3 | 72.4 | 61.3 | 1.122 | 2.505 | 60.2 |
| 152.8 | 79.7 | 64.5 | 1.036 | 2.979 | 65.7 |
| 156.6 | 89.8 | 72.5 | ... | 4.099 | 67.1 |

$$c = -0.00004605 \times \pi + 0.197$$

$$d = 0.00002632 \times \pi - 0.068$$

where $\pi$ is pressure in mm. of Hg.

The area test of Redlich-Kister (*3*) for thermodynamic consistency is satisfied by the data for all the pressures studied.

## SHIFT OF AZEOTROPE WITH PRESSURE

The shift of azeotropic composition with temperature is expressed by the following equation:

$$t_{az} = -260.0x_{az} + 301.0 \qquad (2)$$

where $t_{az}$ = azeotropic temperature, ° C.; $x_{az}$ = composition of the azeotrope (mole fraction of *n*-heptane).

The following relationship is obtained for the variation of the azeotropic temperature and the total pressure:

$$\log T = 0.0963 \log \pi + 2.285 \qquad (3)$$

where $T$ is the azeotropic temperature in °K. and $\pi$ is total pressure in mm. of Hg.

## MODIFIED METHOD OF PRESENTING THE $x$-$y$ DATA

Log $x_1/x_2$ is plotted against log $y_1/y_2$ in Figure 2, yielding straight lines for different pressures which are expressed by the following relationship:

$$\log y_1/y_2 = m \log x_1/x_2 + c \qquad (4)$$

Since at azeotrope

$$\log x_1/x_2 = c/(1 - m) \qquad (5)$$

the azeotropic compositions are evaluated from the above equations. The relationship between the constants $m$ and $c$ in the above equations and total pressure is given by:

$$m = -(140.0/\pi) + 0.303 \qquad (6)$$

$$c = -0.521 \log \pi + 1.935 \qquad (7)$$

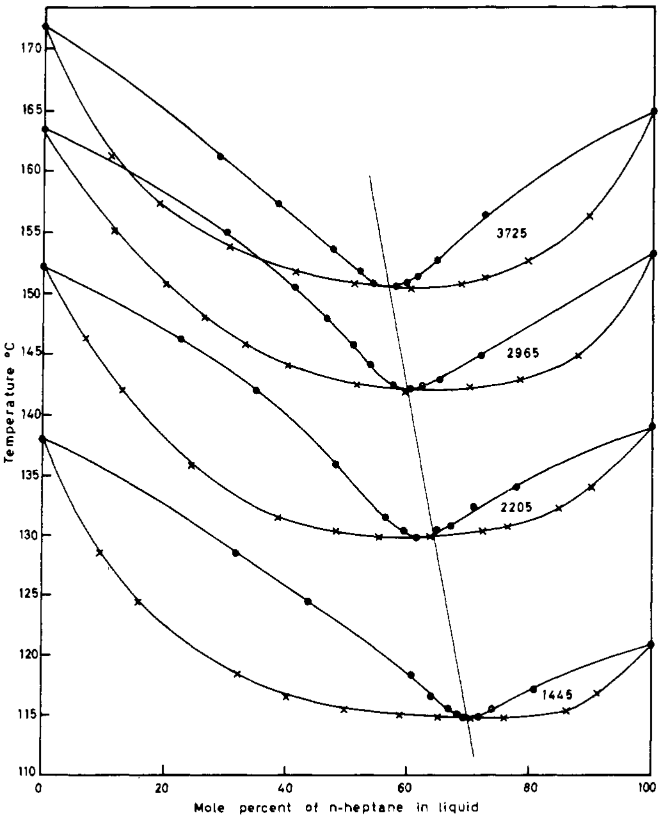

Figure 1. $t - x - y$

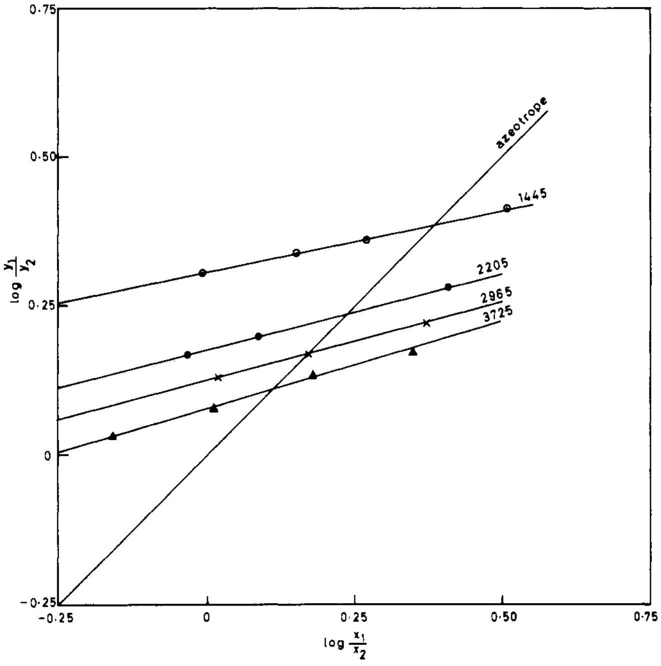

Figure 2. log $x_1/x_2$ *vs.* log $y_1/y_2$

## CORRELATION AND PREDICTION OF AZEOTROPIC DATA

By combining Equations 5, 6, and 7, an equation for the change of azeotropic composition with total pressure can be obtained:

$$x_{az} = 1/(1 + 10^K)$$

where

$$K = \frac{(0.747 \log \pi - 2.776)\pi}{200.86 + \pi}$$

The calculated and experimental values of azeotropic composition and azeotropic temperature at the pressures studied are given below:

| Total Pressure, Mm. of Hg | $t_{az}$ |  | $x_{az}$ |  |
|---|---|---|---|---|
|  | Exptl. | Calcd. | Exptl. | Calcd. |
| 1445 | 114.8 | 115.3 | 0.707 | 0.699 |
| 2205 | 129.8 | 131.2 | 0.635 | 0.643 |
| 2965 | 142.4 | 143.1 | 0.602 | 0.597 |
| 3725 | 150.5 | 152.2 | 0.570 | 0.560 |

## NOMENCLATURE

$a,b,c,d$ = constants in Chao's equation
$m,c,K$ = constants
$P$ = vapor pressure of pure component
$x$ = mole fraction in liquid phase
$y$ = mole fraction in vapor phase
$\gamma$ = activity coefficient
$\pi$ = total pressure, mm. of Hg
$t$ = temperature, ° C.

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# Vapor-Liquid Equilibrium Data for the Systems Diisopropyl Ether–n-Heptane and Diisopropyl Ether–Carbon Tetrachloride at Medium Pressures

S. V. VIJAYARAGHAVAN, P. K. DESHPANDE, and N. R. KULOOR
Department of Chemical Engineering, Indian Institute of Science, Bangalore, India

**Vapor-liquid equilibrium data for the systems diisopropyl ether–*n*-heptane and diisopropyl ether–carbon tetrachloride have been reported at pressures of 760, 1520, and 2280 mm. of Hg. The systems form ideal mixtures under the pressure range studied.**

VAPOR-LIQUID equilibrium data for the systems diisopropyl ether–*n*-heptane (*3*) and diisopropyl ether–carbon tetrachloride (*4*) are reported in the literature only at 685 mm. of Hg pressure. In the present work the systems have been studied at 760, 1520, and 2280 mm. of Hg.

## EXPERIMENTAL

The equilibrium still and experimental procedure have been described earlier (*2*). The properties of reagents used are given in Table I. The samples were analyzed by the refractive index using Abbe's refractometer at 25 ± 0.1° C. The refractive index values are reproducible within ±0.0001. The pressure in the still was measured by a bourdon gage with an accuracy of 0.5 lb./sq. in., the temperature by a thermometer of 0.1° C. accuracy.

## THERMODYNAMIC CONSISTENCY

The experimental vapor-liquid equilibrium data are given in Tables II and III and Figures 1 and 2.

Table I. Properties of Pure Components

| Compound | Density | | Refractive Index | |
|---|---|---|---|---|
| | Exptl. | Lit. (*1*) | Exptl. | Lit. (*1*) |
| Diisopropyl ether | 0.7250[a] | 0.7258[a] | 1.3672[b] | 1.3678[b] |
| *n*-Heptane | 0.6838[a] | 0.68376[a] | 1.3880[a] | 1.3876[a] |
| Carbon tetrachloride | 1.5840[a] | 1.5845[a] | 1.4606[a] | 1.4607[a] |

[a] At 20° C.
[b] At 23° C.

Liquid phase activity coefficients are calculated from the equation,

$$\gamma_i = \frac{y_i \pi}{x_i P_i}$$

Table II. System. Diisopropyl Ether (1)–*n*-Heptane (2)

| Temp., ° C. | $x_1$ | $y_1$ | $\gamma_1$ | $\gamma_2$ | $y_{1\text{calcd.}}$ |
|---|---|---|---|---|---|
| | | 760 mm. | | | |
| 90.3 | 18.7 | 36.0 | 0.984 | 1.006 | 36.6 |
| 85.8 | 30.3 | 51.0 | 0.975 | 1.035 | 52.3 |
| 84.3 | 35.4 | 56.7 | 0.968 | 1.035 | 58.6 |
| 82.2 | 41.6 | 63.2 | 0.975 | 1.042 | 64.8 |
| 79.7 | 49.8 | 71.0 | 0.984 | 1.036 | 72.1 |
| 78.4 | 54.5 | 74.9 | 0.986 | 1.050 | 75.9 |
| 76.2 | 63.4 | 81.2 | 0.980 | 1.037 | 82.8 |
| 74.2 | 71.3 | 85.9 | 0.979 | 1.062 | 87.7 |
| 71.0 | 85.4 | 93.2 | 0.978 | 1.125 | 95.3 |
| 69.2 | 93.2 | 97.2 | 0.988 | 1.050 | 98.4 |
| | | 1520 mm. | | | |
| 115.7 | 20.5 | 38.0 | 0.985 | 0.965 | 38.6 |
| 111.0 | 32.0 | 52.5 | 0.975 | 0.981 | 53.9 |
| 108.2 | 39.8 | 60.7 | 0.974 | 0.988 | 62.3 |
| 106.8 | 43.2 | 64.1 | 0.982 | 1.001 | 65.3 |
| 105.1 | 48.9 | 69.5 | 0.973 | 0.986 | 71.2 |
| 103.2 | 54.4 | 74.2 | 0.989 | 0.986 | 75.0 |
| 101.4 | 60.1 | 78.7 | 0.995 | 0.979 | 79.1 |
| 98.0 | 75.2 | 88.0 | 0.972 | 1.009 | 90.6 |
| | | 2280 mm. | | | |
| 134.0 | 19.3 | 34.7 | 0.941 | 0.968 | 36.9 |
| 130.7 | 25.4 | 42.5 | 0.942 | 0.978 | 45.0 |
| 125.8 | 38.3 | 57.3 | 0.941 | 0.991 | 60.9 |
| 122.7 | 46.5 | 65.2 | 0.947 | 1.006 | 68.9 |
| 120.3 | 53.7 | 72.1 | 0.959 | 0.991 | 75.2 |
| 116.8 | 64.2 | 80.1 | 0.969 | 1.000 | 82.7 |
| 113.8 | 72.8 | 85.2 | 0.977 | 1.061 | 87.2 |
| 111.9 | 80.1 | 90.1 | 0.973 | 1.021 | 92.6 |