Vapor-Liquid Equilibrium for the Hexamethyldisiloxane–*n*-Propyl Alcohol System

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Vapor-liquid equilibrium data have been determined at 750 mm. of Hg pressure for the *n*-propyl alcohol–hexamethyldisiloxane system using a modified Othmer still. A thermodynamic evaluation proved the data to be consistent. A minimum boiling azeotrope is formed at 0.495 mole fraction silicone and a temperature of 85.15° C. Density-composition data also have been determined for this binary system.

HEXAMETHYLDISILOXANE is the simplest of the methyl silicones, which are being used as coatings, impregnants, and water repellants. Since they may be applied from solvent solutions, knowing the properties of these solutions is necessary. The data, presented herein, are part of a continuing study to determine these properties.

A review of the literature indicates that neither the density-composition data nor the vapor-liquid equilibrium data for this system have been reported. The data, determined at 750 mm. of Hg pressure, deviate considerably from liquid phase ideality. A minimum boiling azeotrope is formed by this system at 0.495 mole fraction hexamethyldisiloxane and at a temperature of 85.15° C. A thermodynamic evaluation proved the data to be consistent.

MATERIALS

The materials used were of reagent grade, redistilled in a laboratory column to ensure uniform properties. Table I compares the experimentally determined densities with those reported in the literature.

ANALYSIS

Vapor and liquid equilibrium samples were analyzed by density measurements at 25° C. For this purpose, a density-composition curve was plotted from measurements with samples of known composition (Figure 3). During density determinations, room temperature was controlled at 25° C. to facilitate more accurate weighings of the calibrated pycnometers. The temperature of the sample (25° C.) was indicated by a thermometer, which was an integral part of the pycnometer.

APPARATUS AND PROCEDURE

The experimental equilibrium runs were carried out in a modified Othmer still (*4*, *5*). This still made use of the U-tube arrangement with an external Nichrome heater as suggested by Othmer (*4*). The boiling flask was of the short necked variety (*5*) and insulated to minimize fractionation. The temperature of the boiling mixture was measured by a Leeds and Northrup platinum resistance thermometer (Type 8163) located slightly above the surface of the liquid. Resistances were measured on a Mueller Bridge (Type G-2) manufactured by Leeds and Northrup Co. The Callendar equation (*2*) was used to relate resistances to temperatures which are reported to the nearest 0.05° C. The pressure was maintained constant to within 1 mm. of Hg by a No. 6A Cartesian manostat.

The still was charged initially with approximately 300 cc. of a binary mixture and operated for at least 3 hours. The criterion for equilibrium was a constant boiling temperature that had been maintained for at least 15 minutes.

Table I. Physical Properties of Materials

Material	Density (Grams/Cc. at 25° C.) Literature (*1, 6*)	Density (Grams/Cc. at 25° C.) Experimental
Hexamethyldisiloxane	0.7584	0.7579
n-Propyl alcohol	0.7997	0.7993

RESULTS

The uncertainties in the measurements are shown in Table II, and the experimental results are given in Table III. Temperature-composition and *x-y* curves are shown in Figure 1. A diagram of the ratio of the activity coefficients *vs.* composition is shown in Figure 2, and the experimentally determined density-composition data used in the analytical procedure are presented in Figure 3. The activity coefficients were calculated by the following relationships:

$$\gamma_1 = \frac{y_1 \pi}{x_1 P_1} \tag{1}$$

$$\gamma_2 = \frac{y_2 \pi}{x_2 P_2} \tag{2}$$

The vapor pressures for *n*-propyl alcohol were obtained from Perry's Handbook (*6*) and those for hexamethyldisiloxane from the Dow Corning Silicone Notebook (*1*).

The thermodynamic consistency of the data first was evaluated by the Gibbs-Duhem Equation for binary mixtures as presented by Orr (*3*). Equation 3 presents the Gibbs-Duhem equation in a form

$$x_1 \left(\frac{d \log \gamma_1}{dx_1}\right)_{T,\pi} = x_2 \left(\frac{d \log \gamma_2}{dx_2}\right)_{T,\pi} \tag{3}$$

Table II. Estimated Uncertainty in the Over-all Data Determined from the Uncertainty in Each Variable

Variable	Estimated Experimental Accuracy	Estimated Uncertainty in the Data, Mole %
Temperature	±0.025° C.	±0.03
Pressure	±1.0 mm. of Hg	±0.04
Density	±0.0005 grams	±0.04
	Over-all data	±0.11

Table III. Equilibrium Concentrations, Equilibrium Temperatures, and Activity Coefficients for the System *n*-Propyl Alcohol–Hexamethyldisiloxane at 750 mm. of Hg

Temp. ° C.	Mole % Silicone		Activity Coefficients	
	Liquid	Vapor	γ_1	γ_2
99.85	100.0	100.0	1.000	. . .
98.00	95.8	91.8	0.984	1.902
97.10	95.5	90.4	1.013	2.120
96.15	94.8	86.4	1.005	2.700
94.50	93.8	83.5	1.026	2.980
92.40	90.8	77.3	1.047	2.960
91.60	88.0	75.2	1.076	2.585
89.10	85.7	67.2	1.070	3.180
88.55	83.1	64.2	1.072	3.000
87.60	80.1	61.7	1.120	2.830
86.20	78.9	56.8	1.090	3.180
85.75	71.4	54.4	1.164	2.520
85.55	64.7	53.3	1.280	2.115
85.15	51.6	49.6	1.500	1.680
85.25	43.0	47.9	1.738	1.460
85.45	31.4	44.6	2.181	1.290
86.10	20.2	40.1	3.040	1.160
86.75	16.0	34.9	3.270	1.175
88.50	10.4	28.5	3.840	1.117
89.95	7.6	23.1	4.070	1.114
91.20	5.9	17.5	3.770	1.095
92.45	4.4	14.3	4.000	1.075
93.20	3.7	10.5	3.405	1.080
94.25	2.8	8.7	3.610	1.042
95.00	2.0	6.5	3.690	1.038
95.55	1.7	5.2	3.420	1.032
95.75	1.25	4.0	3.570	1.038
96.65	0.0	0.0	. . .	1.000

convenient for checking the thermodynamic consistency of vapor-liquid equilibrium data by comparing the slopes of the activity coefficient curves when plotted against the more volatile component in the liquid. T and π refer to conditions of constant system pressure, which must be met in order for the equation to be valid. An analysis of the data by this method showed the data to be consistent in all concentrations except the dilute regions.

A thermodynamic evaluation of the data by the method of Redlich and Kister (7) is presented in Figure 2. This method requires

$$\int_0^1 (\gamma_1/\gamma_2)dx = 0 \qquad (4)$$

the net area of the diagram to be equal to zero (Equation 4). This requirement is met in Figure 2; however, there is a degree of uncertainty in the location of the curve in the dilute regions. The scattering of the data in the dilute regions has been experienced by many investigators and only points up the need for further research in these areas.

Van Laar constants for this system are $A = 0.829$ and $B = 0.767$ as determined from the azeotropic conditions.

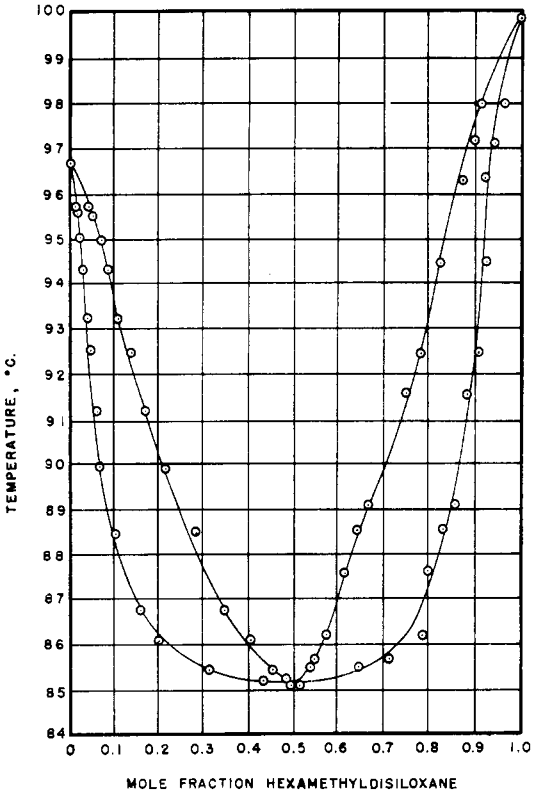

Figure 1. Temperature-composition diagrams for the system hexamethyldisiloxane–*n*-propyl alcohol at 750 mm. of Hg

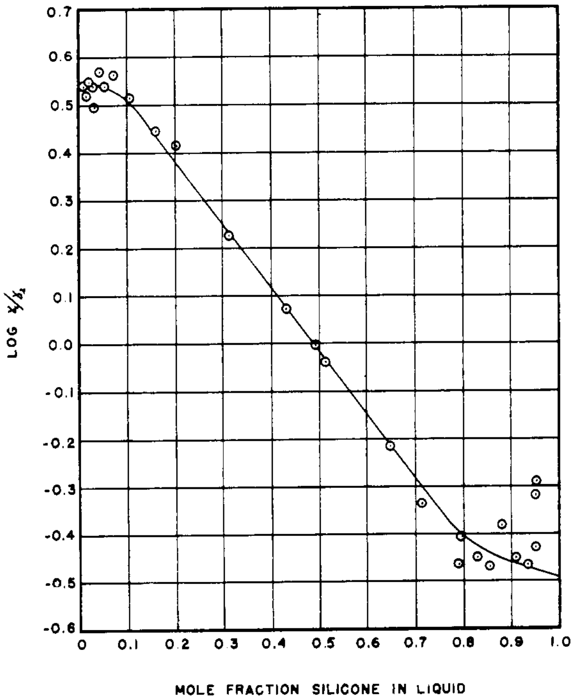

Figure 2. Ratio of activity coefficients, composition curve for the system hexamethyldisiloxane–*n*-propyl alcohol at 750 mm. of Hg

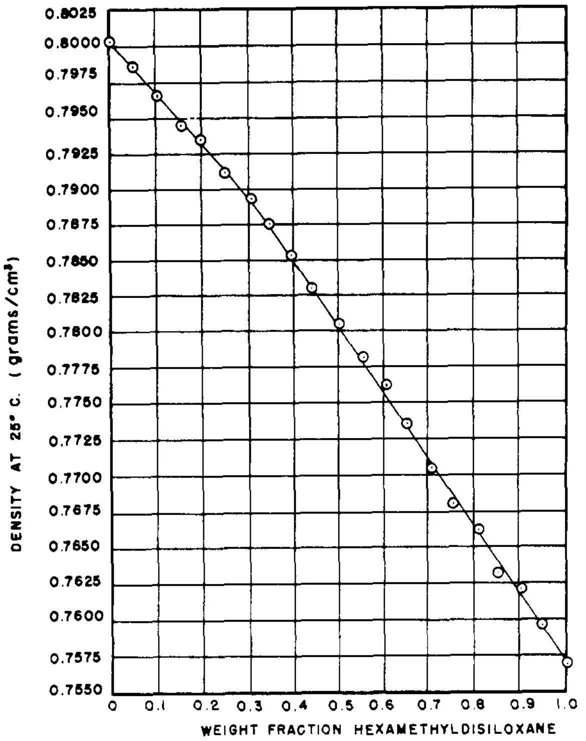

Figure 3. Density at 25° C. vs. weight fraction hexamethyldisiloxane for the system hexamethyldisiloxane–*n*-propyl alcohol

NOMENCLATURE

P_i = vapor pressure of pure component i at equilibrium temperature, mm. of Hg
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
π = total pressure, mm. of Hg

Subscripts

1 = hexamethyldisiloxane
2 = *n*-propyl alcohol

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Solubility of Helium in Liquid Argon, Oxygen, and Carbon Monoxide

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Data were obtained for the solubility of helium at pressures up to 2000 p.s.i.a. in liquid argon at temperatures of −125°, −140°, −160°, and −180° C.; in liquid oxygen at −130°, −145°, −160°, −180°, and −195.8° C.; and in liquid carbon monoxide at −145°, −160°, −180°, and −195.8° C. A static sampling technique was used and samples were analyzed by gas chromatography. The data are presented in temperature-composition and pressure-composition diagrams. A comparison is made between the data of this study and previously published data for the helium-argon and helium-oxygen systems.

THE SOLUBILITY of helium in certain liquefied gases is of interest because of the limited availability of helium and the method of producing it. Helium is obtained by extraction from either liquefied natural gases or liquefied air. The efficiency of the recovery process depends upon the solubility of helium in the liquid.

A number of investigators (*3-7, 9, 12*) have directed their attention to the solubility of helium in liquid nitrogen. Several studies of the solubility of helium in liquid methane also have been made (*8, 10, 14, 15*) and data have recently been reported for the helium-argon system (*11*) and the helium-oxygen system (*1, 2*). The object of this investigation was to determine the solubility of helium in the liquefied gases argon, oxygen, and carbon monoxide.

EXPERIMENTAL

Materials. The helium used was a special analyzed stock furnished by the United States Bureau of Mines and had a maximum impurity of 12.0 p.p.m. The argon and oxygen were commercial grades, purchased from the Linde Co. with specified purities of 99.996 and 99.7%, respectively. Carbon monoxide was obtained from Olin-Matheson with a purity of 99.5%. All gases were used without further purification.

APPARATUS AND PROCEDURE

The experimental apparatus and operating procedures have been described in detail (*13,14*). A static sampling cell of approximately 100-cc. volume was placed in a controlled low temperature bath. The contents of the cell

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