Isobaric Vapor-Liquid Equilibria of the 1-Propanol–n-Heptane System

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Phase equilibrium data at atmospheric pressure for the system 1-propanol–n-heptane were determined in a vapor recirculatory equilibrium still. The data, corrected for pressure, were tested by Herington's area condition and correlated by Wilson's equations.

VAPOR-LIQUID equilibrium data of alcohol-n-paraffin systems are of theoretical and industrial importance. Experimental studies of vapor-liquid equilibria of the system 1-propanol–n-heptane were made as part of a continuing study of the phase equilibria of the ternary system 1-propanol–water–n-heptane.

EXPERIMENTAL

Purity of Liquids. The liquids supplied for this work were of analytical reagent grade. The 1-propanol (Veb Labor Chemie Apolda, Germany) was purified by refluxing over quicklime for 4 hours and distilling over metallic sodium in a glass column packed with McMahon packings. The n-heptane (E. Merck, Germany) was distilled in the same column. In distillation, the predistillate and residue liquids, each approximately one sixth of the charge, were discarded,

and the heartcut was used for experimental work. Proper precautions were taken to minimize absorption of atmospheric moisture by 1-propanol and n-heptane. The properties of the purified liquids are listed in Table I together with reliable literature values.

Analytical Method. Density was used as a means of analysis of the unknown binary mixtures. Densities were determined using a 10-ml. specific gravity bottle at $25° \pm 0.2°$ C. Measurements were reproducible to within ± 0.0002. Table II shows the analytical data for the binary system.

Apparatus. Experimental data were obtained by the use of a vapor-recirculatory equilibrium still designed by Raju, Ranganathan, and Rao (7). Mercury (fractional) thermometers were used to measure the equilibrium temperatures to within $\pm 0.1°$ C. The barometric pressure varied between 757 and 760 mm. of mercury during the experimentation. The observed boiling points were not corrected to 760 mm. of mercury.

Table I. Physical Properties of Pure Liquids Used

Liquid	Boiling Point, °C. Exptl.	Lit. (8)	Density, 30° C. Exptl.	Lit. (8)	Refractive Index, 29° C. Exptl.	Lit. (8)
1-Propanol	97.1	97.15	0.7953	0.7956	1.3820	1.3820
n-Heptane	98.4	98.40	0.6753	0.6759(25°)	1.3832	1.3852

Table II. Data for Analysis of the System 1-Propanol–n-Heptane

Mole Fraction, 1-Propanol	Density, 30° C.
0.000	0.6753
0.100	0.6783
0.200	0.6825
0.300	0.6900
0.400	0.6995
0.500	0.7105
0.600	0.7230
0.700	0.7355
0.800	0.7520
0.900	0.7715
1.000	0.7953

VAPOR-LIQUID EQUILIBRIA

Table III shows the smoothed experimental t-x-y data and activity coefficient data calculated from them by the following equation (2):

$$\ln \frac{y_1}{x_1} = \ln \frac{\gamma_1 P_1^0}{\pi} - \frac{(V_1 - \beta_1)(P_1^0 - \pi)}{RT} \quad (1)$$

Virial coefficients were calculated by the Wohl generalized relation (2). Vapor pressures were estimated from Equations 19, 20, and 32 of reference (4). The equations put forth by Barile and Thodos (1) were used for computing molal liquid volumes.

Table III. Experimental Vapor-Liquid Equilibrium Data for 1-Propanol–n-Heptane System

Temp., °C.	x_1	y_1	P_1^0, Mm. of Hg	P_2^0, Mm. of Hg	$\ln \gamma_1$	$\ln \gamma_2$	$\ln \gamma_1$ (Calcd.)	$\ln \gamma_2$ (Calcd.)
88.8	0.100	0.315	543.4	566.9	1.5221	0.0053	1.5132	0.0333
86.1	0.200	0.400	485.6	519.8	1.3080	0.0732	1.1618	0.0486
85.2	0.300	0.425	468.0	505.3	0.8180	0.1905	0.7783	0.2085
84.7	0.400	0.450	459.2	497.2	0.6094	0.3155	0.4319	0.2373
84.6	0.500	0.475	456.2	495.2	0.4496	0.4556	0.3777	0.4736
84.8	0.600	0.510	459.8	498.8	0.3273	0.6036	0.2824	0.6371
85.7	0.700	0.555	472.9	513.5	0.2310	0.7805	0.2620	0.8291
87.1	0.800	0.610	507.0	539.4	0.1234	0.9914	0.0618	1.0541
89.5	0.900	0.720	559.4	579.5	0.0755	1.2867	0.0121	1.3229

THERMODYNAMIC TESTING AND CORRELATIONS

The experimental activity coefficient data were found to satisfy Herington's area condition (3). The data are correlated by Wilson's equations (5, 9):

$$\ln \gamma_1 = - \ln (x_1 + \Lambda_{12}x_2) + x_2 \left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{12}}{\Lambda_{21}x_1 + x_2} \right] \quad (2)$$

$$\ln \gamma_2 = - \ln (x_2 + \Lambda_{21}x_1) - x_1 \left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2} \right] \quad (3)$$

The values of the parameters Λ_{12} and Λ_{21} obtained from a least-squares fit are 0.19644 and 0.42955, respectively. The average deviations of the calculated activity coefficients from the experimental values are expressed by the following equation (6):

$$\omega_1 = \frac{\Sigma k_1^2 - (\Sigma k_1)^2 \, n_1^{1/2}}{n_1 - 1} \quad (4)$$

The small deviations ($\omega_1 = -0.0602$ and $\omega_2 = -0.0055$) indicate that Wilson's equations correlate the data very well.

ACKNOWLEDGMENT

NOMENCLATURE

K = deviation of calculated $\ln \gamma$ from experimental $\ln \gamma$
P^0 = pure component vapor pressure

R = gas law constant
T = absolute temperature
V = molal liquid volume
x = mole fraction in liquid phase
y = mole fraction in vapor phase

Greek Letters

β = second virial coefficient
γ = liquid activity coefficient
Λ = Wilson's parameter
Σ = summation
π = total pressure
ω = defined deviation of k from mean value of k

Subscripts

1, 2 = components 1 and 2
12, 21 = binary system

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Vapor Pressure Relations of 36 Sulfur Compounds Present in Petroleum

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Compilations of vapor pressures measured by static and ebulliometric methods, covering more than five orders of magnitude in pressure, are given for "key" members of classes of alkane thiols, alkane sulfides, alkane disulfides, and cyclic sulfides which were selected for a comprehensive study of their thermodynamic properties. Constants of the Antoine and Cox vapor pressure equations are provided as an aid to interpolating or extrapolating the experimental results.

SINCE 1948 thermochemical studies of organic sulfur compounds either in or related to petroleum have been in progress at the Bureau of Mines under the sponsorship of the American Petroleum Institute Project 48A. The purpose of this paper is to assemble and summarize the vapor pressure–temperature relationships of 36 of the sulfur compounds selected from the program. Previously, White, Barnard-Smith, and Fidler (33) presented vapor pressure–temperature relationships and Antoine equation constants for 15 alkane sulfides, 8 alkane disulfides, 9 cyclic sulfides, and 3 thiophenes

During the early years of the program, when the pressure and temperature ranges were usually smaller than for the modern equipment now in use, the Antoine equation (1), log $p = A - B/(t + C)$, was capable of representing

the results within experimental error and was adopted generally for correlating purposes. With improvements in apparatus that led to results of greater precision, accuracy, and range, the need for a more accurate equation became apparent. Also, the moderately polar character of sulfur compounds gives a type of behavior in vapor pressure that cannot be correlated accurately with the Antoine equation. Consequently, the Cox equation (4), log $(p/760) = A(1 - \text{B.P.}/T)$ where log $A = a + bT + cT^2$, was adopted because it was more versatile in fitting data. However, for the sake of continuity with previous work on sulfur compounds, the evaluation of Antoine constants was continued, and compounds previously correlated in terms of the Antoine equation were recorrelated in terms of the Cox equation. Therefore, constants for both equations were