Glossary

A_{ij}	parameters used in the Margules, Van Laar, Wilson, NRTL, and UNIQUAC equations
AAD	average absolute deviation
a_{mn}	interaction parameters in the UNIFAC equations
F	objective function to be minimized in determining UNIFAC parameters
m	number of data points
P	pressure
s	objective function to be minimized in fitting $P-T-x-y$ data
T	temperature
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 in the liquid phase
σ	standard deviation
σ^2	variance

Registry No. PhCl, 108-90-7; $PhNO_2$, 98-95-3; Cl_2, 7782-50-5.

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Vapor Pressure of Pivalaldehyde

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The vapor pressure of pivalaldehyde was measured over the temperature range of 34.6–62.6 °C by use of a Stage–Muller equilibrium still. The experimental data obtained were correlated by the Antoine equation: log $P = A - B/(T + C)$, with $A = 7.08801$, $B = 1206.631$, and $C = 214.887$ and where the vapor pressure (P) is in mmHg and the temperature (T) is in °C.

Introduction

There is a relative scarcity of experimental data on the physical properties of pure aldehydes and mixtures containing aldehydes. Undoubtedly, this scarcity derives from the considerable difficulties associated with working with aldehydes in the laboratory, resulting from their instability due to oxidation and polymerization. Thus, for example, in the most recent compilation by Gmehling et al. (*1*) of binary group interaction parameters in the UNIFAC group contribution method for estimating vapor-liquid equilibria (VLE), many of these parameters for the interaction of the aliphatic aldehyde group (CHO) with the other 39 groups currently in this method are not available, including, for example, olefins, aromatic hydrocarbons, aliphatic acids, and multiply chlorinated hydrocarbons.

Pivalaldehyde (or trimethylacetaldehyde) is the simplest aliphatic aldehyde not containing any α-hydrogen atoms. It is also available in relatively pure form at moderate cost. Thus, the objective of this work was the measurement of the vapor pressure of pivalaldehyde at various temperatures. The resulting data should be useful in themselves as pure component information, as well as in support of VLE studies involving this particular aldehyde and aldehydes in general.

Equipment and Experiments

Pivalaldehyde was purchased from Fluka Chemicals in a stated purity of at least 99%. This purity was checked by gas chromatographic analysis prior to the actual vapor pressure measurements.

Table I. Physical Properties of Pivalaldehyde (Trimethylacetaldehyde), $C_5H_{10}O$

property	this study[a]	ref *6*	% Δ[b]
NBP, °C	71.9	74	-2.838
η_D, 20 °C	1.3769	1.3791	-0.159

[a] With trace of hydroquinone (<0.2 wt %) added. [b] % Δ = ((measd prop. − lit. prop.)/lit. prop.) × 100.

The equilibrium vessel used in this work was an all-glass, Stage–Muller dynamic still equipped with a Cottrell pump and was manufactured by Fischer Labor- und Verfahrenstechnik of West Germany. The essential features of the still and the basic procedures for these measurements were as described by Eng and Sandler (*2*) and by Willman (*3*).

All experiments were carried out under an inert nitrogen atmosphere. The temperature was measured with an accuracy of 0.2 °C by use of a total immersion thermometer, and the pressure was measured by use of a mercury manometer whose flexible seals allowed compensation for local gravity and temperature effects. A Fisher VKH100 vacuum/pressure controller maintained the pressure constant to within 0.05 mmHg by usng a solenoid valve. Further details on the experimental apparatus, calibration of the thermometer, and calibration of the equilibrium still are given by Varughese (*4*).

To avoid any oxidation of the pivalaldehyde, a trace of hydroquinone (<0.2 wt. % of the pivalaldehyde used) was introduced into the equilibrium still as described by Wojtasinski (*5*). Analysis for impurities was carried out by chromatographic and refractometric methods. In Table I the characteristics of the pivalaldehyde utilized have been compared with those of the pure material as given in the literature. It is evident from this table that the addition of hydroquinone did not affect the physical properties of pivalaldehyde significantly. No deterioration of the pivalaldehyde was observed in this work; thus, with the precautions noted above, the usage of pivalaldehyde in VLE

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Table II. Vapor Pressure of Pivalaldehyde

T/°C	P/mmHg	P/mmHg, estd	T/°C	P/mmHg	P/mmHg, estd
34.6	178.0	178.5	52.7	376.3	379.1
39.5	222.3	221.2	55.1	416.6	415.7
43.1	257.5	257.6	57.5	455.5	455.2
45.8	303.1		59.8	494.7	495.7
49.6	336.4	335.6	62.6	550.4	549.0

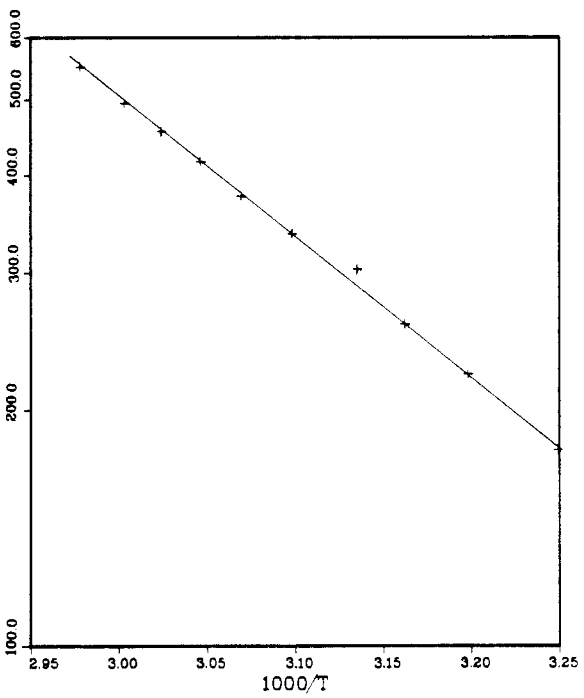

Figure 1. Vapor pressure (P/mmHg) of pivalaldehyde as a function of temperature (T/K).

and other experimental studies can be recommended.

Results and Discussion

Even though the Stage–Muller still used in this study is capable of handling temperatures up to 250 °C and pressures up to 1200 mmHg, it is not recommended to operate this still at such high temperatures and pressures. This is due to complications in estimating an accurate total system pressure, resulting from the effect of the nitrogen partial pressure on the system (*4*). The lowest temperature reading we were able to measure was 34.6 °C, using the total immersion thermometer. Thus, the vapor pressure of pivalaldehyde was measured at temperatures between 34.6 and 62.6 °C. The experimental results are summarized in Table II and plotted in Figure 1.

Using non-weighted least-squares regression analysis, these data were fitted to the Antoine equation:

$$\log P = A - \frac{B}{T + C} \qquad (1)$$

with the vapor pressure (P) in mmHg and the temperature (T) in °C. For pivalaldehyde, the Antoine constants obtained are

$$A = 7.08801 \qquad B = 1206.631 \qquad C = 214.887$$

The sum of the squared errors (SSQ) from this regression analysis was equal to 2.08×10^{-5}. The fourth data point in Table II (at T = 45.8 °C) was eliminated from this regression analysis determination of the Antoine constants.

Registry No. $C_5H_{10}O$, 630-19-3.

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Vapor–Liquid Equilibrium Data of *tert*-Butyl Alcohol–Chlorobenzene at 101.3 kPa

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Isobaric vapor–liquid equilibria of *tert*-butyl alcohol and chlorobenzene mixtures at 101.3 kPa are measured and reported. The experimental data are correlated with Wilson and UNIQUAC equations. The VLE for these mixtures are predicted by use of the UNIFAC method.

As part of a continuing study of vapor–liquid equilibria of alcohol–chlorohydrocarbon systems, the isobaric VLE data at 101.3 kPa of *tert*-butyl alcohol–chlorobenzene mixtures have been determined in a vapor recirculatory still. The vapor–liquid equilibrium data of this system have not been reported previously.

Experimental Section

Analytical grade *tert*-butyl alcohol from British Drug House Co. (India) and chlorobenzene from Sarabhai Merck (India) are purified by distilling in a laboratory packed column. For each chemical the fraction whose boiling point at atmospheric pressure coincided with that reported in literature is collected and used. Table I compares the physical properties of the chemicals with the literature values (*1*).

Equilibrium Still. A vapor recirculatory still of Jones as modified by Ward (*2*) is used to determine the vapor–liquid equilibrium compositions. A still with a total capacity of about 60 mL is used. The still and the experimental technique have

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