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

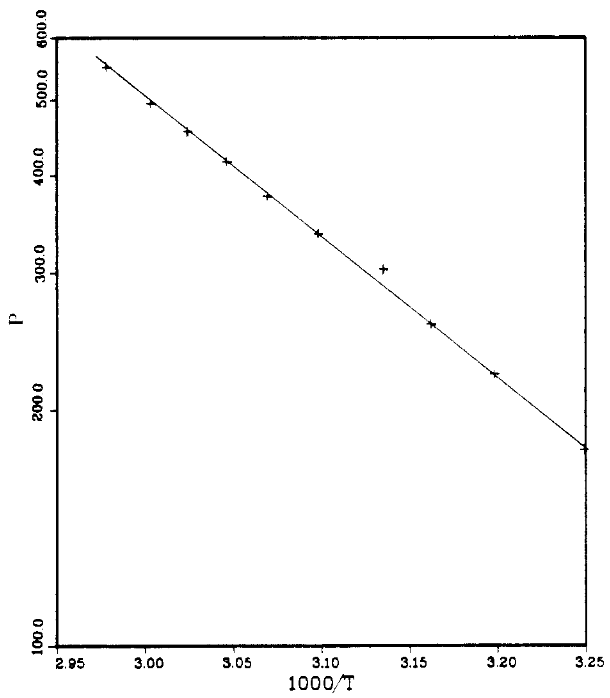

Figure 1. Vapor pressure (P/mmHg) of pivalaldehyde as a function of temperature (T/K).

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:

$$\log P = A - \frac{B}{T + C} \tag{1}$$

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.

Literature Cited

(1) Gmehling, J.; Rasmussen, P.; Fredenslund, A. *Ind. Eng. Chem. Process Des. Dev.* **1982**, *21*, 118-127.
(2) Eng, R.; Sandler, S. I. *J. Chem. Eng. Data* **1984**, *29*, 156-161.
(3) Willman, B. M.S. Thesis, Georgia Institute of Technology, Atlanta, GA, 1983.
(4) Varughese, B. M.S. Thesis, Georgia Institute of Technology, Atlanta, GA, 1986.
(5) Wojtasinski, J. G. *J. Chem. Eng. Data* **1963**, *8*, 381-385.
(6) Campbell, K. N. *J. Am. Chem. Soc.* **1937**, *59*, 1980-1983.

Received for review October 21, 1986. Accepted September 21, 1988.

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

B. Sambi Reddy* and B. V. Subba Rao

Department of Chemical Engineering, Andhra University, Visakhapatnam 530003, India

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

0021-9568/89/1734-0026$01.50/0

Table I. Physical Properties and Antoine Constants for Vapor Pressure

	normal bp, °C		refract. index at 25 °C		Antoine constants^a (5)		
compound	exptl	lit. (*1*)	exptl	lit. (*1*)	*A*	*B*	*C*
tert-butyl alcohol	82.4	82.4	1.3820	1.3823	16.8548	2658.29	−95.50
chlorobenzene	131.7	132.1	1.5220	1.5220	16.0676	3295.12	−55.60

^{a} $\ln P(\text{mmHg}) = A - B/T(\text{K}) + C$.

Table II. Vapor–Liquid Equilibrium Data for the System *tert*-Butyl Alcohol (1)–Chlorobenzene (2) at 101.3 kPa

			$y_{1,\text{calcd}}$		
t, °C	x_1	$y_{1,\text{exptl}}$	Wilson	UNIQUAC	UNIFAC
131.7	0.0000	0.0000	0.0000	0.0000	0.0000
128.3	0.0080	0.1040	0.0966	0.0945	0.0956
120.9	0.0380	0.2820	0.3299	0.3286	0.3320
110.5	0.0750	0.4700	0.4826	0.4840	0.4873
100.6	0.1480	0.6100	0.6303	0.6326	0.6332
97.5	0.1880	0.6820	0.6759	0.6774	0.6766
95.4	0.2240	0.7040	0.7066	0.7071	0.7053
94.4	0.2860	0.7440	0.7456	0.7444	0.7413
91.7	0.3400	0.7780	0.7710	0.7683	0.7645
90.2	0.4440	0.8080	0.8076	0.8027	0.7987
88.3	0.5280	0.8140	0.8311	0.8257	0.8219
86.9	0.5580	0.8360	0.8389	0.8331	0.8300
86.6	0.6360	0.8500	0.8589	0.8534	0.8512
84.9	0.7520	0.8940	0.8901	0.8869	0.8864
84.6	0.7840	0.9040	0.8998	0.8975	0.8974
83.8	0.8410	0.9290	0.9192	0.9186	0.9191
82.7	0.9380	0.9650	0.9618	0.9632	0.9640
82.4	1.0000	1.0000	1.0000	1.0000	1.0000

been described elsewhere (*3*). When the equilibrium temperature is attained in the still, this temperature is maintained for 1 h to ensure equilibrium conditions. The equilibrium temperature is measured by using a standard mercury-in-glass thermometer having an accuracy of ±0.1 °C.

Analysis. The composition of the equilibrium samples is examined by refractive index. Refractive index measurements are taken at 25 ± 0.1 °C for sodium light with an Abbe precision refractometer capable of reading up to 0.0005. Water from a constant-temperature bath maintained at 25 ± 0.1 °C is circulated through the prism of the refractometer. The compositions in mole percent are determined from a standard plot of refractive index vs composition prepared earlier by using mixtures of known composition. The maximum error in the composition measurement by refractive index is estimated to be ±0.0015 mole fraction.

Results and Discussion

The vapor–liquid equilibrium data at 101.3 kPa are presented in Table II.

The liquid-phase activity coefficients of the components are calculated according to the classical thermodynamic expression

$$\gamma_i = \frac{\phi_i P y_i}{f_i^\circ x_i} \qquad (1)$$

where

$$f_i^\circ = P_i^s \phi_i^s \exp\left[\int_{P_i^s}^{P} \frac{V_i}{RT}\, dP\right] \qquad (2)$$

Knowing the values y_i and x_i at 101.3 kPa, the vapor-pressure fugacity coefficient, ϕ_i, is calculated by the virial equation truncated up to the second virial coefficient. The second virial coefficients of the components are estimated by the method of Hayden and O'Connell (*4*). The standard-state fugacity is calculated from pure component vapor pressure, and the standard-state fugacity coefficient is computed by the modified Radlich–Kwong equation. Pure component vapor pressure data are obtained from Antoine constants (*5*) at equilibrium temperatures.

The experimental data are found to be thermodynamically consistent with the method of Fredenslund et al. (*6*).

The liquid-phase activity coefficients are correlated to the Wilson (*7*) and UNIQUAC (*8*) equations. The parameters in each of these equations are obtained by using the optimization procedure of Nelder and Mead (*9*) coupled with that of Davidon (*10*). The sum of the squares of relative deviations of the total pressure is minimized during optimization of the parameters. The objective function is given by

$$F = \frac{1}{N}\sum (P_{\text{exptl}} - P_{\text{calcd}})^2 \qquad (3)$$

For a binary mixture

$$P_{\text{calcd}} = x_1\gamma_1 f_1^\circ/\phi_1 + (1 - x_1)\gamma_2 f_2^\circ/\phi_2 \qquad (4)$$

where γ_1 and γ_2 are calculated with the model parameters. Vapor molar composition is calculated by

$$y_{1,\text{calcd}} = 1\Bigg/\left[1 + \frac{\phi_1\gamma_{2,\text{calcd}}(1 - x_1)f_2^\circ}{\phi_2\gamma_{1,\text{calcd}}x_1 f_1^\circ}\right] \qquad (5)$$

Bubble point temperature calculations are performed by use of the equilibrium relation (eq 1).

The Wilson parameters (original Wilson) for this system are found to be

$$A_{12} = 0.5854; \quad A_{21} = 0.4683$$

These parameters correlated the VLE data with an absolute average deviation of 0.009 between the experimental and calculated vapor compositions.

The temperature-independent UNIQUAC parameters (a_{ij}) are expressed as

$$a_{ij} = U_{ij} - U_{jj}/R \qquad (6)$$

Then the temperature-dependent parameter τ_{ij} are given as

$$\tau_{ij} = \exp(-a_{ij}/T) \qquad (7)$$

For this system the parameters are calculated to be

$$a_{12} = 58.01; \quad a_{21} = 57.82$$

These parameters correlated the experimental data with an average absolute deviation in experimental and calculated vapor compositions of 0.009.

The vapor–liquid equilibria for the binary mixtures of *tert*-butyl alcohol–chlorobenzene have also been predicted by the UNIFAC method (*11*). The mixtures of *tert*-butyl alcohol and chlorobenzene consist of 3 CH_3, 1 –C–, 1 OH, 5 ACH, and 1 ACCl groups. The group interaction parameters for these functional groups are reported by Skjold-Jørgensen et al. (*12*). The activity coefficients for each component in the mixture are estimated by using the group interaction parameters given in Table III, following the procedure given by Fredenslund et al. (*6*). The absolute average deviation between calculated and experimental vapor phase compositions is found to be 0.009.

Table III. Interaction Parameters and Group Volume and Area Parameters for UNIFAC

	group parameters					group vol param, R	group area param, Q
	CH_3	-C-	ACH	OH	ACCl		
CH_3	0.0	0.0	61.13	986.5	321.5	0.9011	0.8480
-C-	0.0	0.0	61.13	986.5	321.5	0.2195	0.0000
ACH	-11.12	-11.12	0.0	636.1	538.2	0.5313	0.4000
OH	1564.0	1564.0	89.6	0.0	2878.0	1.0000	1.2000
ACCl	1413.0	1413.0	2377.0	2489.0	0.0	1.1560	0.8440

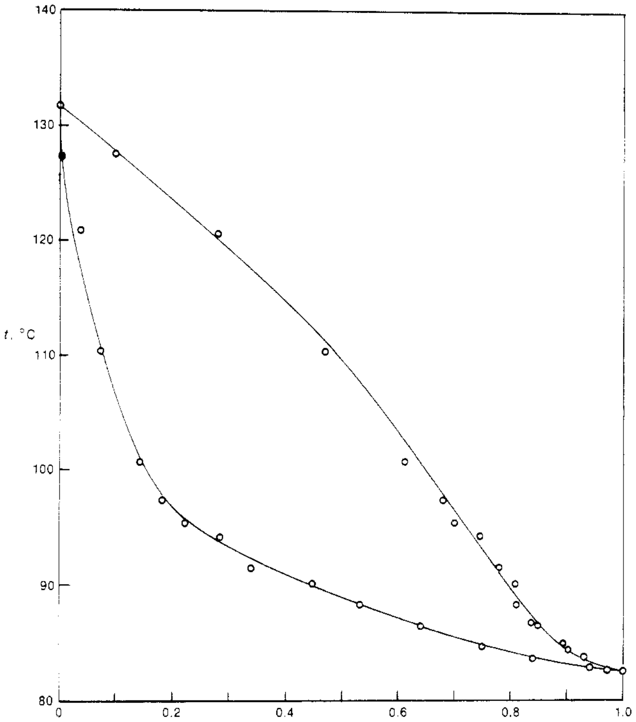

Figure 1. Equilibrium diagram of the system *tert*-butyl alcohol–chlorobenzene at 101.3 kPa: (O) experimental; (—) UNIFAC.

A comparison between the experimental and predicted values of the equilibrium temperature and composition is shown in Figure 1.

From the activity coefficient data calculated by use of eq 1, it is found that the system exhibits positive deviations from Raoult's law. Further, the infinite dilution activity coefficients have been calculated, using the UNIFAC method, to be $\gamma_1^\infty = 2.81$ and $\gamma_2^\infty = 3.307$ at 362.9 K and $\gamma_1^\infty = 2.548$ and $\gamma_2^\infty = 2.914$ at 397.5 K. Excellent agreement is found between the experimental data and that correlated and predicted by the activity coefficient models.

Glossary

a	energy parameter in UNIQUAC equation
A	parameter in Wilson equation
N	number of data points
f^0	pure component fugacity
P	total pressure
P^s	pure component vapor pressure
R	gas constant
T	equilibrium temperature
U	energy of interaction
V	molar volume
x	liquid-phase mole fraction
y	vapor-phase mole fraction

Greek Letters

γ	activity coefficient
ϕ	fugacity coefficient
τ	parameter in UNIQUAC equation

Subscripts

i, 1, 2	components

Registry No. 1, 75-65-0; 2, 108-90-7.

Literature Cited

(1) Wiessberger, A.; Proskauer, E. S.; Riddick, J. A.; Toops, E. E., Jr. *Organic Solvents*, 2nd ed.; Interscience: London, 1955.
(2) Ward, S. H. Ph.D. Thesis, The University of Texas, Austin, TX, 1952.
(3) Ravi Prasad, A.; Venkateswara Rao, K.; Chiranjivi, C. *Indian Chem. Eng.* **1977**, *19*, 29.
(4) Hayden, J. G.; O'Connell, J. P. *Ind. Eng. Chem. Process Des. Dev.* **1975**, *14*, 209.
(5) Reid, R. C.; Prausnitz, J. M.; Sherwood, T. K. *The Properties of Gases and Liquids*, 3rd ed.; McGraw-Hill: New York, 1977; pp 644, 647.
(6) Fredenslund, A.; Gmehling, J.; Rashmussen, P. *Vapour–Liquid Equilibria Using UNIFAC, A Group Contribution Method*; Elsevier: Amsterdam, 1977.
(7) Wilson, G. M. *J. Am. Chem. Soc.* **1964**, *86*, 127, 133.
(8) Abrams, D. S.; Prausnitz, J. M. *AIChE J.* **1975**, *21*, 116.
(9) Nelder, J.; Mead, R. *Comput. J.* **1967**, *7*, 308.
(10) Davidon, W. C. *Math. Progr.* **1975**, *9*, 1.
(11) Fredenslund, A.; Jones, R. L.; Prausnitz, J. M. *AIChE J.* **1975**, *21*, 1086.
(12) Skjold-Jørgensen, S.; Kolbe, B.; Gmehling, J.; Rasmussen, P. *Ind. Eng. Chem. Process Des. Dev.* **1979**, *18*, 714.

Received for review June 5, 1987. Accepted August 1, 1988.