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Vapor–Liquid Equilibria for the System Cyclohexane–*tert*-Butyl Alcohol

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Isothermal vapor pressure data over the whole range of composition were obtained for the binary system cyclohexane–*tert*-butyl alcohol. Data were taken at temperatures of 328.2 and 343.3 K by using a vapor-recirculating equilibrium still. Data were correlated by the Wilson, NRTL, and modified UNIQUAC equations. The Wilson equation gives the best fit for the two-parameter models. The three-parameter NRTL equation gives the best fit for all the models considered in this work.

Introduction

The vapor–liquid equilibria for the system cyclohexane–*tert*-butyl alcohol have been previously investigated (*1–6*). Most of these studies have been carried out under isobaric conditions (*2–5*). Prigogine and Desmyter (*1*) have measured this system at 300 K for a range of composition up to 60% of the alcohol mole fraction. Buchowski and Bartel (*6*) have reported data at 303.15 K over the whole range of composition.

The aim of this work was to provide equilibrium data for the binary system cyclohexane–*tert*-butyl alcohol at 328.2 and 343.3 K. This paper reports the results of these measurements and their correlation by the Wilson, Renon–Prausnitz (NRTL), and modified Abrams–Prausnitz (UNIQUAC) equations.

Experimental Section

Chemicals. Cyclohexane and *tert*-butyl alcohol were Merck analytical-grade reagents used without any further purification (minimum purities of 99.5%). Some physical properties of the chemicals are listed in Table I along with literature values.

Vapor Pressure Measurements. Vapor pressures were measured at constant temperature as a function of composition by using a vapor-recirculating equilibrium still. The equilibrium still was a simplified version of the one described by Hipkin and Myers (*7*). Instead of the vapor jacket used in the original design, the contactor is self-lagged with its own vapor assuring adiabatic conditions. A schematic view of the apparatus is shown in Figure 1. The equilibrium still was connected through a cold trap to the regulating and measurement pressure devices. Pressures were measured by a mercury manometer. Mercury heights were determined with a cathetometer whose accuracy was ±0.2 mm. All observed pressures were corrected to give the equivalent height of a mercury column at 273.2 K and standard gravity. Temperatures were measured with a certified thermometer (Will Scientific 710-5) with a stated accuracy of ±0.1 K.

Table I. Physical Properties of Chemicals

	refractive index at 298.2 K		vapor press./kPa			
			328.2 K		343.3 K	
	exptl	lit.	exptl	lit.	exptl	lit.
cyclohexane	1.4235	1.423 54[a]	43.72	43.68[c]	72.44	72.58[c]
tert-butyl alcohol	1.3860	1.385 2[b]	30.43	30.73[c]	60.98	60.82[c]

[a] Reference *16*. [b] Reference *17*. [c] Reference *18*.

Table II. Vapor–Liquid Equilibrium Data for the Binary System Cyclohexane (1)–*tert*-Butyl Alcohol (2) at 328.2 K

	P/kPa	x_1	y_1
1	30.43	0.000	0.000
2	35.32	0.034	0.166
3	38.15	0.069	0.253
4	41.56	0.128	0.334
5	44.00	0.156	0.393
6	48.00	0.231	0.474
7	50.37	0.315	0.531
8	51.96	0.391	0.567
9	53.26	0.471	0.609
10	54.04	0.536	0.628
11	54.26	0.601	0.657
12	54.44	0.679	0.683
13	54.42	0.736	0.705
14	54.13	0.802	0.729
15	53.82	0.835	0.738
16	51.08	0.948	0.821
17	43.72	1.000	1.000

Table III. Vapor–Liquid Equilibrium Data for the Binary System Cyclohexane (1)–*tert*-Butyl Alcohol (2) at 343.3 K

	P/kPa	x_1	y_1
1	60.98	0.000	0.000
2	65.33	0.018	0.073
3	69.61	0.073	0.187
4	74.40	0.111	0.264
5	79.26	0.144	0.329
6	83.64	0.202	0.391
7	90.89	0.342	0.496
8	93.57	0.444	0.523
9	93.94	0.489	0.575
10	94.40	0.504	0.587
11	95.10	0.599	0.628
12	94.81	0.618	0.623
13	94.96	0.643	0.643
14	94.93	0.655	0.630
15	93.41	0.783	0.695
16	87.76	0.941	0.790
17	77.85	0.994	0.924
18	72.44	1.000	1.000

Compositions of the liquid and condensed vapor were obtained from measurements of their refractive indices at 298.2

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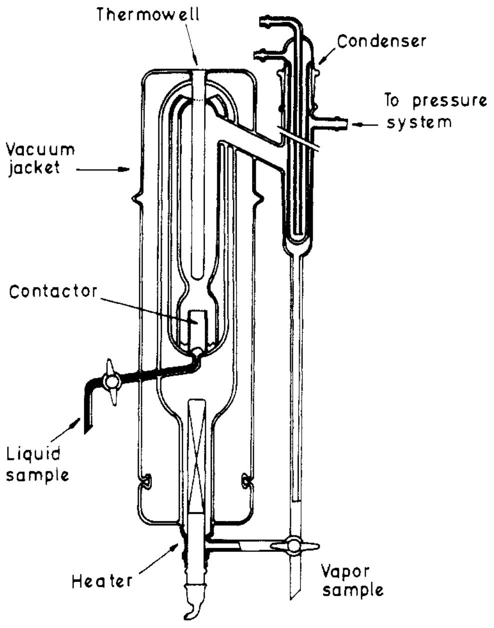

Figure 1. Schematic view of the equilibrium still.

K by using a Abbe-type refractometer with an accuracy of ±0.0002. Compositions were estimated to be within ±0.005 mole fraction accuracy for the liquid phase and ±0.010 for the vapor phase.

Considering the accuracy of the measured variables, the experimental vapor pressures are accurate to better than 0.1 kPa at both temperatures.

Results and Discussion

The vapor-liquid equilibrium data for the system cyclohexane-*tert*-butyl alcohol at 328.2 and 343.3 K are reported in Tables II and III, respectively.

The experimental data were correlated by the Wilson (*8*), Renon-Prausnitz (*9*), and modified Abrams-Prausnitz equations (*10*, *11*).

For binary system these models give the following forms for the excess Gibbs energy, g^E,

Wilson

$$g^E/RT = -x_1 \ln (x_1 + x_2\Lambda_{12}) - x_2 \ln (x_2 + x_1\Lambda_{21}) \quad (1)$$

where

$$\Lambda_{ij} = \frac{V_j}{V_i} \exp\left(-\frac{\lambda_{ij} - \lambda_{ii}}{RT}\right) \quad (2)$$

λ_{ij} is the binary energy interaction parameter for the i-j pair; V_i is the liquid molar volume of component i.

NRTL

$$\frac{g^E}{RT} = x_1x_2\left(\frac{\tau_{21}G_{21}}{x_1 + x_2G_{21}} + \frac{\tau_{12}G_{12}}{x_2 + x_1G_{12}}\right) \quad (3)$$

where

$$\tau_{ij} = (g_{ij} - g_{jj})/RT \quad (4)$$

$$G_{ij} = \exp(-\alpha_{ij}\tau_{ij}) \quad (5)$$

g_{ij} is the binary energy interaction parameter for the i-j pair; α_{ij} is the mixture nonrandomness parameter.

Modified UNIQUAC

$$g^E = g^E(\text{combinatorial}) + g^E(\text{residual}) \quad (6)$$

$$\frac{g^E(\text{combinatorial})}{RT} = x_1 \ln \frac{\phi_1}{x_1} + x_2 \ln \frac{\phi_2}{x_2} + \frac{Z}{2}\left[q_1x_1 \ln \frac{\theta_1}{\phi_1} + q_2x_2 \ln \frac{\theta_2}{\phi_2}\right] \quad (7)$$

$$g^E(\text{residual})/RT = -q_1'x_1 \ln (\theta_1' + \theta_2'\tau_{21}) - q_2'x_2 \ln (\theta_2' + \theta_1'\tau_{12}) \quad (8)$$

where the coordination z is set equal to 10 and segment fraction ϕ and area fractions θ and θ' are given by

$$\phi_i = x_i r_i/\sum_j x_j r_j \quad (9)$$

$$\theta_i = x_i q_i/\sum_j x_j q_j \quad (10)$$

$$\theta_i' = x_i q_i'/\sum_j x_j q_j' \quad (11)$$

the parameters r, q, and q' are pure-component molecular structure constants depending on the molecular size and the external surface area.

$$\tau_{ij} = \exp[-(u_{ij} - u_{jj})/RT] \quad (12)$$

where u_{ij} is the binary energy parameter for the i-j pair. When $q = q'$, eq 6 reduces to the original UNIQUAC (*5*).

The fugacity coefficients are calculated by the virial equation of state in terms of pressure, truncated after the second term. Second virial coefficients were calculated by using the correlation of Hayden and O'Connell (*12*). The molar volumes were calculated by using the Rackett equation as modified by Spencer and Danner (*13*). For the liquid phase the standard-state fugacities at zero pressure were calculated by the correlation of Prausnitz et al. (*14*).

The computer program developed by Prausnitz et al. (*14*) was used in the correlation of the binary vapor-liquid equilibrium data. The adjustable binary parameters of the excess Gibbs energy equations were estimated by a nonlinear regression method based on the maximum-likelihood principle (*15*). The following objective function is minimized:

$$s^2 = \sum_{i=1}^{N} \left\{\frac{(P_i - \hat{P}_i)^2}{\sigma_P^2} + \frac{(T_i - \hat{T}_i)^2}{\sigma_T^2} + \frac{(x_{1i} - \hat{x}_{1i})^2}{\sigma_x^2} + \frac{(y_{1i} - \hat{y}_{1i})^2}{\sigma_y^2}\right\} \quad (13)$$

where N is the total experimental points and σ's are the estimated standard deviation for each of the measured variables, i.e., pressure, temperature, and liquid-phase and vapor-phase compositions. A circumflex denotes the calculated variable.

The estimated standard deviations for the measured variables were 0.1 kPa for pressure, 0.1 K for temperature, and 0.001 and 0.010 for liquid-phase and vapor-phase compositions.

The resulting parameters of the Wilson, NRTL, and modified UNIQUAC equations for the binary system cyclohexane-*tert*-butyl alcohol are shown in Table IV. Two alternatives were considered for the NRTL equation depending on whether the α_{12} parameter was fixed or not. As recommended by Renon and Prausnitz (*9*) the α_{12} parameter was set equal to 0.47 for systems formed by aromatic and alcohols.

The compromise between goodness of fit and number of parameters requires some method of discriminating between models. A useful parameter for the comparison is obtained from the sum of the weighted squared residuals (eq 13) divided by the number of data points minus the number of degrees of freedom. This quantity is a measure of the overall fit of the equation to the experimental data and it approximates to the overall variance of errors. These estimated variances are also given in Table IV along with the obtained parameters.

Table IV. Wilson, NRTL, and UNIQUAC Parameters for the Binary System Cyclohexane (1)–*tert*-Butyl Alcohol (2)

eq	temp/K	$(\Delta_{12}/R)^a$/ K	$(\Delta_{21}/R)^a$/ K	α_{12}	$\mathbf{s}^{2\,b}$
Wilson	328.2	1148 ± 67	235 ± 33		0.40
	343.3	1295 ± 69	118 ± 28		0.39
NRTL[c]	328.2	970 ± 55	354 ± 31	0.47	0.49
	343.3	1095 ± 59	240 ± 29	0.47	0.50
NRTL	328.2	1185 ± 68	522 ± 43	0.71 ± 0.02	0.20
	343.3	1187 ± 65	512 ± 56	0.71 ± 0.03	0.23
UNIQUAC[d]	328.2	937 ± 41	−193 ± 6		0.50
	343.3	1027 ± 40	−226 ± 6		0.48

[a] Δ_{ij} is $\lambda_{ij} - \lambda_{ii}$ for the Wilson equation, $g_{ij} - g_{jj}$ for the NRTL equation, and $u_{ij} - u_{jj}$ for the UNIQUAC equation. [b] $\mathbf{s}^2$ is the estimated variance of the fit. [c] α_{12} was fixed. [d] $r_1 = 3.97$, $q_1 = q_1' = 3.01$; $r_2 = 3.45$, $q_2 = 3.05$, $q_2' = 0.88$.

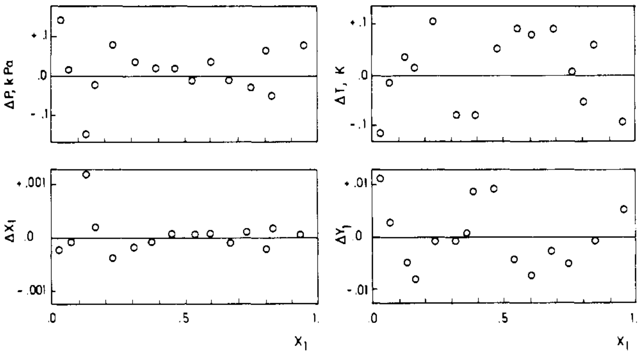

Figure 2. Residuals for the three-parameter NRTL fit to the VLE data for the system cyclohexane (1)–*tert*-butyl alcohol (2) at 328.2 K.

The analysis of variances shows that the Wilson equation gives the best fit for two-parameter models while the UNIQUAC and NRTL ($\alpha_{12} = 0.47$) show a similar fit. The three-parameter NRTL equation gives the best fit for the models considered here.

An analysis of residuals for the variables (i.e., pressure, temperature, vapor and liquid mole fractions) can be used to detect any lack of fit.

Figure 2 shows the obtained residuals when the three-parameter NRTL equation was used to correlate the equilibrium data at 328.2 K. A similar behavior was obtained for the data at 343.3 K.

Since these plots show a random distribution of the residuals, the three-parameter NRTL equation was considered suitable to represent the data.

Glossary

g^E	excess Gibbs energy, J mol^{-1}
g_{ij}	NRTL binary parameter for the i–j pair interaction, J mol^{-1}
G_{ij}	defined by eq 5
N	total experimental points
P	pressure, kPa
q_i	molecular-geometric area parameter for the pure component i
q_i'	molecular-interaction area parameter for the pure component i
r_i	molecular-volume parameter for the pure component i
R	gas constant, J mol^{-1} K^{-1}
s^2	sum of the weighted squared residuals defined by eq 13
$\mathbf{s}^2$	estimated variance of the fit
T	absolute temperature, K
u_{ij}	UNIQUAC binary parameter for the i–j pair interaction, J mol^{-1}
v_i	liquid molar volume for the component i, cm^3 mol^{-1}
x_i	liquid mole fraction for the component i
y_i	vapor mole fraction for the component i
z	coordination number

Greek Letters

α_{ij}	NRTL nonrandomness parameter
λ_{ij}	Wilson binary parameter for the i–j pair interaction, J mol^{-1}
Λ_{ij}	defined by eq 2
τ_{ij}	defined by eq 4 and 12
ϕ_i	volume fraction defined by eq 9
θ_i	area fraction defined by eq 10
θ_i	area fraction defined by eq 11
σ	estimated standard deviation

Registry No. Cyclohexane, 110-82-7; *tert*-butyl alcohol, 75-65-0.

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