

# ISOTHERMAL AND ISOBARIC VAPOUR-LIQUID EQUILIBRIUM DATA IN THE TETRACHLOROMETHANE-TERT-BUTYL ALCOHOL SYSTEM\*

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Isothermal vapour-liquid equilibrium data at 55, 63 and 70°C and isobaric ones at 101.3 kPa were measured in the tetrachloromethane-tert-butyl alcohol system. A modified circulation still of the Gillespie type was used for the measurements. Under the conditions of measurement, the system exhibits positive deviations from Raoult's law and minimum boiling-point azeotropes. The experimental data were fitted to a number of correlation equations, the most suitable being the Wilson equation.

As continuation of our previous study<sup>1</sup> of vapour-liquid equilibria in the tetrachloromethane-isobutyl alcohol system, the equilibrium data in the tetrachloromethane-tert-butyl alcohol system have been measured isothermally at three temperatures and isobarically at normal atmospheric pressure.

## EXPERIMENTAL

*Substances used.* Tetrachloromethane, analytical reagent grade (Lachema Brno, Czechoslovakia), was twice rectified on a fifty-plate bubble-cup column. Tert-butyl alcohol, analytical reagent grade (Reanal Budapest, Hungary), was dried with, and distilled from sodium twice on a fifty-plate bubble-cup column<sup>2,3,5</sup>. No impurities in the tert-butyl alcohol used were detected by gas chromatographic analysis. The water content was less than 0.02%. The measured values of physical constants (density and refractive index) and their comparison with the literature values are given in Table I along with the used values of constants of the Antoine vapour pressure equation

$$\log P^s = A - B/(t + C), \quad (1)$$

where  $P^s$  is in kPa and  $t$  in °C.

*Analytical method.* The samples of the equilibrium vapour and liquid phases were analyzed refractometrically at 25°C. To this purpose, an Abbe-type refractometer (Carl Zeiss, Jena) was used allowing to measure refractive indices with an accuracy of  $\pm 0.0001$ . Using a set of calibration binary mixtures, constants of the relation

$$n_D = x_1 n_{D1} + x_2 n_{D2} + x_1 x_2 (x_1 A_1 + x_2 A_2 - x_1 x_2 A_3) \quad (2)$$

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were computed. Here  $x_1$  is the mole fraction of tetrachloromethane,  $x_2 = 1 - x_1$ ,  $n_D$  is the refractive index of mixture,  $n_{D1}$ ,  $n_{D2}$  those of pure components and  $A_1$ ,  $A_2$ ,  $A_3$  are the constants evaluated from the measured calibration samples by the least-squares method ( $A_1 = -0.01226$ ,  $A_2 = -0.01695$ ,  $A_3 = -0.01353$ ). Eq. (2) with the constants represents the experimental points with an average absolute deviation in  $n_D$  0.00006 and a mean per cent deviation 0.08%. Calibration interpolation tables were computed for direct reading the sample composition from measured  $n_D$  values.

*Apparatus and procedure.* The measurements of vapour-liquid equilibrium were carried out in a modified Gillespie still. The description of the apparatus and measuring procedure can be found in the literature<sup>6</sup>. The pressure in the system was established by measuring boiling point of redistilled water in an ebulliometer connected in parallel to the equilibrium still. Temperature was measured by mercury-in-glass calorimetric standards calibrated by means of a Mueller bridge with platinum resistance thermometer (Leeds and Northrup). The equilibrium samples were taken for analysis only if the boiling point in the still was not changing for 30 minutes.

## RESULTS AND DISCUSSION

The experimental vapour-liquid equilibrium data for the isothermal conditions of 55, 63 and 70°C are given in Tables II, III and IV, respectively. The values for the isobaric condition of 101.3 kPa are presented in Table V.

The equation of vapour-liquid equilibrium in a binary system can be written in the form

$$y_i P = \gamma_i x_i P_i^s \exp \left\{ \left[ (B_{ii} - V_i) (P_i^s - P) - P \left( 2 \sum_{j=1}^2 y_j B_{ij} - B_{ii} - B \right) \right] / RT \right\} \quad (3)$$

TABLE I

Physical properties of pure substances and Antoine vapour pressure constants

Property	Tetrachloromethane			Tert-butyl alcohol		
	measured	literature	ref.	measured	literature	ref.
Density, $d_4^{25}$	1.5842	1.5841 — 1.58437	2	0.7806	0.7812	3
Refractive index, $n_D^{25}$	1.4572	1.45704 — 1.4576	2	1.3850	1.3851	3
Antoine vapour pressure constants <sup>4</sup>						
<i>A</i>	6.00416			6.32830		
<i>B</i>	1 212.021			1 092.971		
<i>C</i>	226.409			170.503		

which is derived for the standard state of pure components at temperature  $T$  and pressure  $P$  of the system, assuming pressure independent pure component liquid molar volumes  $V_i$  and the validity of the volume explicit virial expansion truncated after the second term for the vapour phase. In Eq. (3),  $x_i$  and  $y_i$  are the mole fractions of the liquid and vapour phase, respectively,  $B_{ii}$  and  $P_i^s$  are the second virial coefficient and saturated vapour pressure of pure  $i$ -th component, respectively,  $B_{ij}$  is the second cross virial coefficient and  $R$  the gas constant. The second virial coefficients required for calculations were estimated by the method of Hayden and O'Con-

TABLE II

Isothermal vapour-liquid equilibrium data in the tetrachloromethane(1)-tert-butyl alcohol(2) system at 55°C and their comparison with calculated values

Experimental			Calculated deviations <sup>a</sup>			
$x$	$y$	$P$ , kPa	$\Delta x$	$\Delta y$	$\Delta P$ , kPa	$\Delta T$ , K
0.0745	0.2387	37.46	0.0002	-0.0018	0.22	-0.02
0.1155	0.3174	40.43	0.0033	-0.0038	0.23	-0.02
0.1379	0.3700	42.40	-0.0027	-0.0003	0.21	-0.02
0.1410	0.3700	42.58	-0.0008	-0.0022	0.28	-0.03
0.1875	0.4383	45.28	-0.0014	-0.0001	0.09	-0.01
0.2534	0.4973	48.69	0.0034	-0.0067	0.27	-0.03
0.3474	0.5704	52.16	0.0040	-0.0069	0.06	-0.01
0.3854	0.5986	53.19	0.0023	-0.0031	-0.09	0.01
0.4796	0.6465	55.41	0.0017	-0.0030	-0.10	0.01
0.5906	0.6939	57.13	0.0000	0.0000	0.00	0.00
0.6319	0.7096	57.56	-0.0005	0.0013	0.05	-0.01
0.7017	0.7358	57.97	-0.0014	0.0038	0.09	-0.01
0.8001	0.7719	57.90	-0.0017	0.0044	0.08	-0.01
0.8696	0.8065	57.34	-0.0023	0.0045	0.16	-0.02
0.9167	0.8420	56.26	-0.0022	0.0037	0.18	-0.02
0.9449	0.8696	55.10	0.0000	0.0010	0.12	-0.01
0.9630	0.8982	54.02	0.0003	0.0011	0.14	-0.01
Mean absolute:			0.0017	0.0028	0.14	0.01
Root mean square:			0.0021	0.0035	0.16	0.02
Standard:			0.0022	0.0037	0.17	0.02

<sup>a</sup> Constants of the Wilson equation:  $A_{12} = 0.8474$ ,  $A_{21} = 0.1724$ ; virial coefficients:  $B_{11} = -1.283.4$  ml/mol,  $B_{22} = -1.468.5$  ml/mol,  $B_{12} = -966.8$  ml/mol; liquid molar volumes:  $V_1 = 100.8$  ml/mol,  $V_2 = 98.9$  ml/mol.

nell<sup>7</sup>, and are given at the bottom of Tables II–IV. For isobaric data, the temperature dependence in the form

$$\log(-B_{mn}) = k_1 + k_2/T \quad (4)$$

was used in Table V, where  $k_1$ ,  $k_2$  are adjustable parameters,  $B_{mn}$  is in ml/mol and  $T$  in K. The liquid molar volumes (densities) of pure components were found for several temperatures in the literature<sup>2</sup>, and their temperature dependence was

TABLE III

Isothermal vapour–liquid equilibrium data in the tetrachloromethane(1)–tert-butyl alcohol(2) system at 63°C and their comparison with calculated values

Experimental			Calculated deviations <sup>a</sup>			
<i>x</i>	<i>y</i>	<i>P</i> , kPa	$\Delta x$	$\Delta y$	$\Delta P$ , kPa	$\Delta T$ , K
0.0160	0.0526	46.45	0.0011	−0.0013	0.13	−0.01
0.0745	0.2207	53.25	−0.0011	−0.0005	0.09	−0.01
0.1171	0.3044	57.40	−0.0012	−0.0009	0.13	−0.02
0.1410	0.3417	59.32	−0.0003	−0.0010	0.09	−0.01
0.1567	0.3643	60.40	0.0006	−0.0003	−0.01	0.00
0.1967	0.4148	63.49	0.0005	−0.0017	0.09	−0.01
0.2564	0.4646	67.16	0.0054	−0.0091	0.24	−0.04
0.3587	0.5530	71.92	0.0013	−0.0030	0.07	−0.01
0.4037	0.5771	73.07	0.0037	−0.0046	−0.16	0.02
0.4796	0.6187	75.24	0.0017	−0.0028	−0.08	0.01
0.6013	0.6717	77.24	0.0003	−0.0007	−0.02	0.00
0.6385	0.6860	77.53	0.0001	−0.0003	−0.02	0.00
0.7123	0.7200	77.85	−0.0021	0.0058	0.03	0.00
0.8053	0.7474	77.44	0.0016	−0.0033	0.04	−0.01
0.8721	0.7899	76.38	0.0002	0.0009	0.14	−0.02
0.9136	0.8357	74.62	−0.0049	0.0065	0.16	−0.02
0.9449	0.8659	73.10	0.0002	0.0032	0.28	−0.04
0.9642	0.8982	71.54	0.0011	0.0038	0.37	−0.05
Mean absolute:			0.0015	0.0028	0.12	0.02
Root mean square:			0.0022	0.0037	0.15	0.02
Standard:			0.0023	0.0039	0.16	0.02

<sup>a</sup> Constants of the Wilson equation:  $A_{12} = 0.8429$ ,  $A_{21} = 0.1927$ ; virial coefficients:  $B_{11} = -1.199.9$  ml/mol,  $B_{22} = -1.355.2$  ml/mol,  $B_{12} = -910.1$  ml/mol; liquid molar volumes:  $V_1 = 101.8$  ml/mol,  $V_2 = 100.0$  ml/mol.

calculated from the relation

$$V_i = K_1/(1 - K_2T), \quad (5)$$

where  $K_1$  and  $K_2$  are adjustable parameters and  $V_i$  is in ml/mol.

The experimental data were fitted to the following correlation relations<sup>8</sup>: Redlich-Kister equation of the 3rd, 4th and 5th order, van Laar-Null equation, the Wilson

TABLE IV

Isothermal vapour-liquid equilibrium data in the tetrachloromethane(1)-tert-butyl alcohol(2) system at 70°C and their comparison with calculated values

Experimental			Calculated deviations <sup>a</sup>			
<i>x</i>	<i>y</i>	<i>P</i> , kPa	$\Delta x$	$\Delta y$	$\Delta P$ , kPa	$\Delta T$ , K
0.0160	0.0526	63.37	-0.0007	-0.0009	0.10	-0.01
0.0745	0.2057	71.62	-0.0037	-0.0014	0.24	-0.04
0.1219	0.2914	76.72	-0.0030	-0.0010	0.20	-0.03
0.1441	0.3217	76.64	-0.0009	-0.0015	0.14	-0.02
0.1676	0.3530	80.74	-0.0002	-0.0019	0.13	-0.02
0.2071	0.3994	83.78	0.0012	-0.0017	0.04	-0.01
0.2579	0.4590	87.62	-0.0028	0.0028	0.02	0.00
0.3073	0.4919	90.29	0.0015	-0.0021	0.01	0.00
0.3643	0.5340	93.15	0.0004	-0.0012	0.04	-0.01
0.4023	0.5543	94.40	0.0024	-0.0031	-0.06	0.01
0.4837	0.6013	96.71	0.0009	-0.0002	-0.16	0.03
0.6053	0.6556	98.93	-0.0002	0.0006	-0.02	0.00
0.6439	0.6716	99.17	-0.0004	0.0011	-0.03	0.00
0.7175	0.7044	99.28	-0.0017	0.0040	0.01	0.00
0.8065	0.7486	98.32	-0.0035	0.0069	0.02	0.00
0.8721	0.7873	96.71	-0.0023	0.0051	0.17	-0.03
0.9216	0.8306	93.83	-0.0008	0.0021	0.09	-0.01
0.9449	0.8634	91.91	-0.0002	0.0033	0.20	-0.03
0.9617	0.8995	89.14	-0.0035	0.0022	0.03	0.00
Mean absolute:			0.0016	0.0023	0.09	0.01
Root mean square:			0.0020	0.0028	0.12	0.02
Standard:			0.0021	0.0029	0.12	0.02

<sup>a</sup> Constants of the Wilson equation:  $A_{12} = 0.8578$ ,  $A_{B1} = 0.2073$ ; virial coefficients:  $B_{11} = -1.134.0$  ml/mol,  $B_{22} = -1.267.2$  ml/mol,  $B_{12} = -864.8$  ml/mol; liquid molar volumes:  $V_1 = 102.7$  ml/mol,  $V_2 = 100.9$  ml/mol.

equation and the Renon–Prausnitz (NRTL) equation. As a results of computations, the Wilson equation

$$\ln \gamma_1 = 1 - \ln(x_1 + x_2 A_{12}) - \frac{x_1}{x_1 + x_2 A_{12}} - \frac{x_2 A_{21}}{x_2 + x_1 A_{21}}, \quad (6a)$$

TABLE V

Isobaric vapour–liquid equilibrium data in the tetrachloromethane(1)–tert-butyl alcohol(2) system at 101.3 kPa and their comparison with calculated values

Experimental			Calculated deviations <sup>a</sup>			
<i>x</i>	<i>y</i>	T, K	$\Delta x$	$\Delta y$	$\Delta T$ , K	$\Delta P$ , kPa
0.0180	0.0458	81.50	0.0010	−0.0013	−0.01	0.05
0.0302	0.0762	80.99	0.0016	−0.0007	0.00	0.00
0.0560	0.1330	79.95	0.0031	−0.0014	0.00	0.00
0.0745	0.1767	79.17	0.0016	−0.0004	0.00	−0.02
0.1155	0.2476	77.83	0.0041	−0.0013	0.01	−0.07
0.1798	0.3446	75.92	0.0034	−0.0021	0.01	−0.04
0.2520	0.4271	74.33	0.0036	−0.0023	0.02	−0.09
0.3203	0.4834	73.16	0.0051	−0.0062	0.00	−0.03
0.3952	0.5394	72.18	0.0034	−0.0054	0.00	−0.01
0.4411	0.5691	71.72	0.0022	−0.0043	−0.01	0.02
0.5229	0.6027	71.24	0.0059	−0.0114	0.01	−0.13
0.5287	0.6172	71.10	0.0007	−0.0023	−0.01	0.07
0.5946	0.6479	70.79	0.0002	−0.0014	−0.03	0.17
0.6677	0.6781	70.68	0.0005	−0.0014	−0.02	0.13
0.6795	0.6860	70.62	−0.0005	0.0012	−0.04	0.25
0.7370	0.7110	70.72	−0.0008	0.0022	−0.02	0.12
0.7409	0.7123	70.64	−0.0003	0.0019	−0.06	0.31
0.8306	0.7590	71.17	−0.0022	0.0039	0.00	0.03
0.9044	0.8152	72.15	−0.0036	0.0031	0.00	−0.02
0.9509	0.8733	73.46	−0.0020	0.0013	0.00	0.01
0.9918	0.9678	75.87	0.0002	0.0000	0.00	0.00
Mean absolute:			0.0022	0.0026	0.01	0.07
Root mean square:			0.0027	0.0036	0.02	0.11
Standard:			0.0029	0.0038	0.02	0.12

<sup>a</sup> Constants of the Wilson equation:  $A_{12} = 0.8789$ ,  $A_{21} = 0.2097$ ; temperature dependence of virial coefficients:  $\log(-B_{11}) = 1.8691 + 406.84/T$ ,  $\log(-B_{22}) = 1.7017 + 480.82/T$ ,  $\log(-B_{12}) = 1.8549 + 371.31/T$ ; temperature dependence of liquid molar volumes:  $V_1 = 70.601/(1 - 9.1282 \cdot 10^{-4}T)$ ,  $V_2 = 66.790/(1 - 9.9166 \cdot 10^{-4}T)$ .

$$\ln \gamma_2 = 1 - \ln(x_2 + x_1 A_{21}) - \frac{x_2}{x_2 + x_1 A_{21}} - \frac{x_1 A_{12}}{x_1 + x_2 A_{12}} \quad (6b)$$

was used to represent the composition dependence of liquid-phase activity coefficients in Tables II–V. Despite only two constants, it gives practically the same deviations as the other equations containing three or four constants.

The parameters of the correlation relations were evaluated using the maximum likelihood method. The minimized objective function has the form

$$S = \sum_{n=1}^N \left[ \frac{(x_n^e - x_n^t)^2}{\sigma_{x_n}^2} + \frac{(y_n^e - y_n^t)^2}{\sigma_{y_n}^2} + \frac{(T_n^e - T_n^t)^2}{\sigma_{T_n}^2} + \frac{(P_n^e - P_n^t)^2}{\sigma_{P_n}^2} \right], \quad (7)$$

where  $n$  denotes the  $n$ -th experimental point,  $N$  is the total number of experimental points,  $\sigma^2$  are estimated variances of respective variables and the superscripts  $e$  and  $t$  denote the experimental and "true" values, respectively, of the variable corresponding to the given experimental point. The estimated uncertainties in measured quantities are as follows:  $\Delta x = \Delta y = 0.002$ ,  $\Delta P = 0.13$  kPa,  $\Delta T = 0.03$  K. The simplex method by Nelder and Mead<sup>9</sup> was used to minimize the objective function (7).

As it can be seen from Tables II–V, the system tetrachloromethane–tert-butyl alcohol exhibits positive deviations from ideal behaviour of the liquid phase with a minimum-boiling azeotrope. At normal atmospheric pressure (101.325 kPa), the coordinates of the azeotropic point evaluated from our data are 69.5 mol% tetrachloromethane and 70.62°C, which is in fair agreement with the literature value reported by Horsley<sup>10</sup>, viz., 70.2 mol% tetrachloromethane and 71.1°C.

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