ISOTHERMAL AND ISOBARIC VAPOUR–LIQUID EQUILIBRIUM DATA IN THE TETRACHLOROMETHANE–SEC-BUTYL ALCOHOL SYSTEM*

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Isothermal vapour–liquid equilibrium data at 65, 73 and 80°C and isobaric ones at 101·3 kPa were measured in the tetrachloromethane–sec-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[1] of vapour–liquid equilibria in the tetrachloromethane–tert-butyl alcohol system, the equilibrium data in the tetrachloromethane–sec-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. Sec-butyl alcohol, analytical reagent grade (Reanal Budapest, Hungary), was dried with anhydrous potassium carbonate, and distilled twice on a fifty-plate bubble-cup column[4,5]. No impurities in the sec-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

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

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 20°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, contants of the relation

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

were computed. Here x_1 is the mole fraction of tetrachloromethane, $x_2 = 1 - x_2$, 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 (at 20°C) calibration samples by the least-squares method ($A_1 = -0.00639$, $A_2 = -0.00633$, $A_3 = 0.01032$). Eq. (2) with the constants represents the experimental points with an average absolute deviation in n_D 0.00005 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[6]. The pressure in the system was established by measuring boiling point of redistilled water in an ebuliometer 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 65, 73 and 80°C are given in Tables II, III and IV, respectively. The values for the isobaric condition if 101.3 kPa are presented in Table V.

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

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

TABLE I

Physical properties of pure substances and Antoine vapour pressure constants

Property	Tetrachloromethane			Sec-butyl alcohol		
	measured	literature	ref.	measured	literature	ref.
Density, d_4^{20}	1.5939	1.5939 — 1.59404	2,3	0.8067	0.8069	2,3
Refractive index, n_D^{20}	1.4601	1.46005 — 1.46036	2,3	1.39705	1.3970 — 1.3972	2,3
Boiling point, °C	76.83	76.65 — 76.76	2,3	99.515	99.5 — 99.52	2,3
Antoine vapour pressure constants[4]						
A		6.00416			6.32621	
B		1 212.021			1 157.000	
C		226.409			168.279	

which is derived for the standard state of pure component 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), γ_i is the activity coefficient, x_i and y_i are the mole fraction 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 cross virial coefficient and R the gas constant. The second virial coefficients required for calculations were estimated by the method of Hayden and O'Connell[7], and are given at the bottom of Tables II–IV. For

TABLE II

Isothermal vapour–liquid equilibrium data in the tetrachloromethane(1)–sec-butyl alcohol(2) system at 65°C and their comparison with calculated values

Experimental			Calculated deviations[a]			
x	y	P, kPa	Δx	Δy	ΔP, kPa	ΔT, K
0·0450	0·2460	30·28	−0·0011	−0·0103	0·23	−0·04
0·0720	0·3515	34·20	−0·0039	−0·0096	0·18	−0·04
0·1390	0·5113	40·60	0·0054	0·0136	−0·19	0·05
0·1740	0·5676	46·13	−0·0081	−0·0055	0·11	−0·03
0·2560	0·6540	53·06	−0·0050	−0·0024	0·06	−0·02
0·3245	0·6940	57·22	0·0050	−0·0054	−0·02	0·00
0·3530	0·7130	59·42	0·0006	−0·0060	0·03	−0·01
0·4173	0·7473	62·79	0·0025	−0·0027	−0·02	0·01
0·4761	0·7721	65·51	0·0018	−0·0016	−0·02	0·01
0·5530	0·7970	68·17	0·0032	−0·0013	−0·06	0·02
0·5923	0·8060	69·48	0·0013	−0·0038	0·00	0·00
0·6492	0·8227	70·86	0·0006	−0·0017	−0·01	0·00
0·6990	0·8380	71·78	0·0002	0·0018	−0·02	0·01
0·7676	0·8560	72·74	−0·0004	0·0039	−0·04	0·01
0·8105	0·8695	73·15	−0·0012	0·0067	−0·05	0·02
0·8545	0·8890	73·93	−0·0050	0·0127	0·20	−0·07
0·9303	0·9244	73·48	−0·0061	0·0120	0·11	−0·04
0·9740	0·9610	72·16	−0·0026	0·0076	0·11	−0·04
Mean absolute:			0·0030	0·0060	0·08	0·02
Root mean square:			0·0038	0·0072	0·11	0·03
Standard:			0·0040	0·0077	0·11	0·03

[a] Constants of the Wilson equation: $\Lambda_{12} = 0.9210$, $\Lambda_{21} = 0.1346$; virial coefficient: $B_{11} = -1\,180.4$ ml/mol, $B_{22} = -2\,012.7$ ml/mol, $B_{12} = -904.8$ ml/mol; liquid molar volumes: $V_1 = 102.1$ ml/mol, $V_2 = 97.6$ ml/mol.

isobaric data, the temperature dependence in the form

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

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[2], and their temperature dependence was calculated

TABLE III

Isothermal vapour–liquid equilibrium data in the tetrachloromethane(1)–sec-butylalcohol(2) system at 73°C and their comparison with calculated values

Experimental			Calculated deviations[a]			
x	y	P, kPa	Δx	Δy	ΔP, kPa	ΔT, K
0·0255	0·1261	38·65	0·0015	−0·0087	0·16	−0·04
0·0570	0·2493	44·02	0·0023	−0·0120	0·17	−0·05
0·1026	0·4005	52·10	−0·0040	−0·0065	0·09	−0·03
0·1595	0·5113	60·16	−0·0061	−0·0034	0·07	−0·02
0·2080	0·5810	66·32	−0·0095	0·0000	0·06	−0·02
0·2760	0·6346	72·44	−0·0018	−0·0035	0·03	−0·01
0·3735	0·6970	79·73	0·0052	−0·0021	−0·04	0·01
0·4055	0·7223	82·68	−0·0042	0·0017	0·04	−0·02
0·4996	0·7566	87·02	0·0057	0·0002	−0·08	0·04
0·5495	0·7770	89·50	0·0009	0·0017	−0·03	0·01
0·6021	0·7921	91·28	0·0016	0·0009	−0·04	0·02
0·6460	0·8060	92·54	0·0012	0·0023	−0·05	0·02
0·7096	0·8260	93·93	0·0006	0·0052	−0·07	0·03
0·7676	0·8455	95·16	−0·0029	0·0085	0·03	−0·01
0·8150	0·8590	95·43	−0·0019	0·0085	−0·06	0·03
0·8575	0·8814	96·43	−0·0062	0·0150	0·25	−0·11
0·9290	0·9214	95·16	−0·0088	0·0134	0·05	−0·02
0·9770	0·9624	93·01	−0·0021	0·0064	0·06	−0·03
Man absolute:			0·0037	0·0056	0·08	0·03
Root mean square:			0·0045	0·0071	0·10	0·04
Standard:			0·0048	0·0076	0·10	0·04

[a] Constants of the Wilson equation: $\Lambda_{12} = 0.9193$, $\Lambda_{21} = 0.1529$; virial coefficients: $B_{11} = -1\,107.6$ ml/mol, $B_{22} = -1\,767.8$ ml/mol, $B_{12} = -853.6$ ml/mol; liquid molar volumes: $V_1 = 103.1$ ml/mol, $V_2 = 98.6$ ml/mol.

from the relation

$$V_i = K_1/(1 - K_2 T) \qquad (5)$$

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[8]: Redlich-–Kister equation of the 3rd, 4th and 5th order, van Laar–Null equation, the Wilson equation and the Renon–Prausnitz (NRTL) equation. As a results of computations,

TABLE IV

Isothermal vapour–liquid equilibrium data in the tetrachloromethane(1)–sec-butyl alcohol(2) system at 80°C and their comparison with calculated values

Experimental			Calculated deviations[a]			
x	y	P, kPa	Δx	Δy	ΔP, kPa	ΔT, K
0·0226	0·1105	51·58	−0·0007	−0·0063	0·10	−0·03
0·0463	0·2163	57·07	−0·0040	−0·0052	0·08	−0·03
0·0765	0·3161	63·42	−0·0071	−0·0046	0·07	−0·03
0·1200	0·4080	70·54	−0·0045	−0·0045	0·06	−0·02
0·1515	0·4730	76·21	−0·0088	−0·0015	0·05	−0·02
0·2330	0·5710	86·44	−0·0023	0·0017	0·00	0·00
0·3044	0·6361	94·30	−0·0009	0·0049	−0·02	0·01
0·3836	0·6811	100·60	0·0084	0·0034	−0·09	0·04
0·4580	0·7240	107·02	−0·0018	0·0034	0·01	0·00
0·5396	0·7536	111·72	−0·0032	−0·0001	0·05	−0·02
0·6135	0·7814	114·02	0·0041	0·0049	−0·10	0·06
0·6460	0·7753	116·02	−0·0017	−0·0128	0·13	−0·07
0·6667	0·7953	115·94	0·0019	0·0018	−0·06	0·03
0·7065	0·8151	117·41	−0·0039	0·0082	0·05	−0·02
0·7675	0·8350	118·31	−0·0027	0·0099	−0·02	0·01
0·8273	0·8590	119·22	−0·0054	0·0127	0·07	−0·04
0·8334	0·8590	119·22	−0·0046	0·0106	0·06	−0·03
0·8830	0·8815	118·88	−0·0055	0·0100	−0·01	0·01
0·9331	0·9080	117·32	−0·0072	0·0001	−0·11	0·06
0·9726	0·9580	114·98	−0·0054	0·0035	0·00	0·00
Mean absolute:			0·0042	0·0055	0·06	0·03
Root mean square:			0·0048	0·0067	0·07	0·03
Standard:			0·0051	0·0071	0·07	0·03

[a] Constants of the Wilson equation: $\Lambda_{12} = 0.9335$, $\Lambda_{21} = 0.1716$; virial coefficients: $B_{11} = -1\,049.8$ ml/mol, $B_{22} = -1\,589.7$ ml/mol, $B_{12} = -812.5$ ml/mol; liquid molar volumes: $V_1 = 104.0$ ml/mol, $V_2 = 99.5$ ml/mol.

the Wilson equation

$$\ln \gamma_1 = 1 - \ln\left(x_1 + x_2\Lambda_{12}\right) - \frac{x_1}{x_1 + x_1\Lambda_{12}} - \frac{x_2\Lambda_{21}}{x_2 + x_1\Lambda_{21}}, \qquad (6a)$$

$$\ln \gamma_2 = 1 - \ln\left(x_2 + x_1\Lambda_{21}\right) - \frac{x_2}{x_2 + x_1\Lambda_{21}} - \frac{x_1\Lambda_{12}}{x_1 + x_2\Lambda_{12}} \qquad (6b)$$

TABLE V

Isobaric vapour–liquid equilibrium data in the tetrachloromethane(1)–sec-butyl alcohol(2) system at 101·3 kPa and their comparison with calculated values

	Experimental			Calculated deviations[a]		
x	y	T, K	Δx	Δy	ΔT, K	ΔP, kPa
0·0226	0·0811	97·41	0·0002	−0·0101	−0·04	0·08
0·0540	0·1951	94·73	−0·0013	−0·0085	−0·03	0·07
0·0857	0·2910	92·36	−0·0025	−0·0048	−0·02	0·05
0·1183	0·3751	90·12	−0·0049	−0·0016	−0·01	0·02
0·1563	0·4526	87·79	−0·0083	−0·0017	−0·02	0·04
0·2033	0·5146	85·90	−0·0009	0·0001	0·00	0·00
0·2743	0·6021	82·85	−0·0060	−0·0007	−0·02	0·04
0·3920	0·6906	79·69	0·0003	0·0006	0·00	0·00
0·4745	0·7350	77·99	−0·0007	−0·0004	0·00	0·01
0·5580	0·7676	76·95	0·0070	0·0001	0·05	−0·11
0·6491	0·8030	75·91	0·0026	0·0028	0·04	−0·08
0·7195	0·8260	75·33	−0·0006	0·0040	0·01	−0·02
0·7644	0·8440	75·08	−0·0024	0·0085	0·00	0·00
0·7753	0·8485	75·04	−0·0026	0·0098	0·01	−0·01
0·8151	0·8605	74·87	−0·0034	0·0093	−0·01	0·03
0·8680	0·8830	74·78	−0·0049	0·0120	−0·03	0·06
0·9200	0·9081	74·92	−0·0048	0·0096	−0·03	0·06
0·9361	0·9230	75·04	−0·0057	0·0115	−0·04	0·09
0·9667	0·9521	75·47	−0·0030	0·0106	−0·05	0·11
0·9880	0·9740	76·12	−0·0002	0·0017	−0·01	0·02
Mean absolute:			0·0031	0·0054	0·02	0·05
Root mean square:			0·0039	0·0069	0·03	0·06
Standard:			0·0041	0·0073	0·03	0·06

[a] Constants of the Wilson equation: $\Lambda_{12} = 0·9687$, $\Lambda_{21} = 0·1491$; temperature dependence of virial coefficients: $\log(-B_{11}) = 1·8597 + 410·15/T$, $\log(-B_{22}) = 0·98575 + 782·55/T$, $\log(-B_{12}) = 1·8312 + 380·87/T$; temperature dependence of liquid molar volumes: $V_1 = 70·601/(1 - 9·1292 . 10^{-4}T)$, $V_2 = 71·262/(1 - 7·6502 . 10^{-4}T)$.

was used to represent the composition dependence of liquid-phase activity coefficients in Tables II—V. Despite only two constants (A_{12}, A_{21}), it gives practically the same deviations as the other equations containing three or four constant.

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

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

where n denotes the n-th experimental point, N is the total number of experimental points, σ^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: $\Delta x = \Delta y = 0.005$, $\Delta P = 0.13$ kPa, $\Delta T = 0.05$ K. The simplex method by Nelder and Mead[9] was used to minimize the objective function (7).

The higher values of estimated uncertainties in the experimental data, compared to our previous paper on the tetrachloromethane–tert-butyl alcohol system, allow for a detectable unstability of the tetrachloromethane–sec-butyl alcohol mixtures on boiling in the equilibrium still (slight temperature increase), which was proved by gas chromatographic analysis of equilibrium samples, too.

As it can be seen from Tables II—V, the system tetrachloromethane–sec-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 87·0 mol% tetrachloromethane and 74·8°C, which is in reasonable agreement with two literature values reported by Horsely[10], viz., 85·4 and 84·7 mol% tetrachloromethane and 74·6 and 74°C.

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Translated by the author.