

# Vapour—liquid equilibrium of some binary systems containing 1,1,2-trichloroethane

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The isobaric binary vapour—liquid equilibria in the systems containing 1,1,2-trichloroethane with 1,1-dichloroethane, 1,1,2,2-tetrachloroethane or 1,1,1,2-tetrachloroethane were measured with a modified Gillespie apparatus at the pressure of 101.3 kPa. The experimental data were correlated by using equations with two or three constants.

На модифицированном приборе Гиллеспи при давлении 101,3 кПа изучались изобарические бинарные равновесия пары—жидкость в системах 1,1,2-трихлорэтана с 1,1-дихлорэтаном, 1,1,2,2-тетрахлорэтаном и 1,1,1,2-тетрахлорэтаном. Экспериментальные данные были взаимно коррелированы с использованием уравнений с двумя или тремя постоянными.

1,1,2-Trichloroethane produced by chlorination of vinyl chloride contains other chlorinated hydrocarbons. The equilibrium data for some binary systems which come into consideration from the view-point of purification of 1,1,2-trichloroethane by rectification are not known from available literature. In this paper, we present the results obtained by measuring the vapour—liquid equilibria in the systems 1,1-dichloroethane—1,1,2-trichloroethane, 1,1,2-trichloroethane—1,1,1,2-tetrachloroethane, and 1,1,2-trichloroethane—1,1,2,2-tetrachloroethane at the pressure of 101.3 kPa.

## Experimental

### Chemicals

1,1-Dichloroethane was isolated from the residues remaining after distillation of vinyl chloride (Wilhelm Pieck Chemical Works, Nováky). The present 1,2-dichloroethylenes were quantitatively transformed into tetrachloroethanes by chlorination. Then 1,1-dichloroethane was obtained by repeated rectification.

1,1,2-Trichloroethane was prepared by chlorination of vinyl chloride in an iron reactor in the medium of liquid product at 36 °C [1]. The crude product was washed with a solution of Na<sub>2</sub>CO<sub>3</sub> and water. After drying, it was purified by repeated rectification. The last

rectification was carried out at the pressure of 40 kPa. The purified product was stabilized with 0.01 mass % of hydroquinone.

1,1,1,2-Tetrachloroethane was obtained by chlorination of 1,1-dichloroethylene in the presence of  $\text{FeCl}_3$  at 40 °C. It was purified by rectification on a column the efficiency of which corresponded to fifty theoretical plates.

1,1,2,2-Tetrachloroethane was isolated from crude tetrachloroethane (Wilhelm Pieck Chemical Works, Nováky) by rectification at the pressure of 2.7 kPa.

The physical constants of the prepared substances as well as the respective literature data are given in Table 1.

Table 1

Physical constants of the used substances

Substance	$n(D, 20\text{ °C})$		$\rho(20\text{ °C})/\text{g cm}^{-3}$		B.p.(101.3 kPa)/°C	
	Found	Ref. [2]	Found	Ref. [2]	Found	Ref. [2]
1,1-Dichloroethane	1.4166	1.4164	1.1723	1.1757	57.1	57.28
1,1,2-Trichloroethane	1.4709	1.4714	1.4409	1.4397	113.7	113.77
1,1,1,2-Tetrachloroethane	1.4819	1.4821	1.5535	1.5406 <sup>a</sup>	129.8	130.5
1,1,2,2-Tetrachloroethane	1.4939	1.4940	1.5958	1.5953	145.9	146.2

a) 1.5532 according to Ref. [3].

### Apparatus and working procedure

The equilibrium data were measured with a Gillespie apparatus made according to the modification put forward by Otsuki and Williams. This apparatus has been described in literature [4]. The measurements were performed in nitrogen atmosphere at the pressure of 101.3 kPa.

### Analytical methods

The system 1,1,2-trichloroethane—1,1,1,2-tetrachloroethane was analyzed chromatographically [5]. The conditions settled for an instrument Chrom 4 with flame-ionization detector (Laboratorní přístroje, Prague) were: Stainless column of 300 cm length and 3 mm diameter, packing 10 % UCON LB-550 X on Chromaton NAW 0.16 mm—0.20 mm. Temperature regime in the column: 60 °C—10 min, from 60 °C to 140 °C—1 °C/min. Rates of gas flow:  $v(\text{H}_2) = 30\text{ cm}^3\text{ min}^{-1}$ ,  $v(\text{air}) = 300\text{ cm}^3\text{ min}^{-1}$ ,  $v(\text{carrier gas — N}_2) = 30\text{ cm}^3\text{ min}^{-1}$ . Temperature of injector 150 °C, temperature of detector 200 °C, feed 1 mm<sup>3</sup>, and internal standard n-nonane.

Other systems were analyzed according to density  $\rho(20\text{ °C})/\text{g cm}^{-3}$  by using the following calibration curve

$$\{\rho(20\text{ °C})\} = a_0 + a_1\{w\} + a_2\{w\}^2 \quad (1)$$

where  $w$  stands for the mass percentage of 1,1-dichloroethane or 1,1,2,2-tetrachloroethane in a mixture with 1,1,2-trichloroethane. The parameters of eqn (1) calculated by the method of least squares for the system 1,1-dichloroethane—1,1,2-trichloroethane are  $a_0 = 1.1735$ ,  $a_1 = 2.241 \times 10^{-3}$ ,  $a_2 = 4.20 \times 10^{-6}$ , standard deviation  $s = 5.2 \times 10^{-3}$ , and mean relative deviation referred to the difference between experimental values found for pure substances  $d_r = 0.29\%$ . The corresponding values for the system 1,1,2-trichloroethane—1,1,2,2-tetrachloroethane are  $a_0 = 1.4410$ ,  $a_1 = 1.393 \times 10^{-3}$ ,  $a_2 = 1.52 \times 10^{-6}$ ,  $s = 1.06 \times 10^{-3}$ , and  $d_r = 0.20\%$ .

### Results

The measurements of binary equilibria were evaluated on the basis of known relationships [4]. It results from the definition of relative volatility

$$\alpha_{1,2} = (y_1/y_2)/(x_1/x_2) \quad (2)$$

that it is valid for equilibrium composition of the vapour and liquid phase

$$y_1 = \alpha_{1,2}(x_1/x_2)/[1 + \alpha_{1,2}(x_1/x_2)] \quad (3)$$

where  $x_1$ ,  $x_2 = 1 - x_1$  or  $y_1$ ,  $y_2 = 1 - y_1$  are mole fractions of components 1 and 2 in the liquid or vapour phase. Assuming the behaviour of the liquid solution is real and the behaviour of the vapour phase is ideal, we may write for the relative volatility

$$\alpha_{1,2} = (\gamma_1/\gamma_2) (p_1^0/p_2^0) \quad (4)$$

where  $\gamma_1$  and  $\gamma_2$  are the activity coefficient of components in the liquid phase. The pressures (kPa) of the saturated vapour of pure components  $p_1^0$ ,  $p_2^0$  were calculated from the Antoine equation

$$\log \{p^0\} = A - B/(C + \{\theta\}) \quad (5)$$

where  $\theta$  is temperature ( $^{\circ}\text{C}$ ). The used values of constants  $A$ ,  $B$ ,  $C$  [6] are given in Table 2.

Table 2

Constants [6] of the Antoine equation

Substance	A	B	C
1,1-Dichloroethane	6.10192	1174.022	229.060
1,1,2-Trichloroethane	6.07675	1314.410	209.197
1,1,1,2-Tetrachloroethane	6.02365	1365.876	209.744
1,1,2,2-Tetrachloroethane	5.75658	1228.062	179.942

The dependence of relative volatility and activity coefficients on composition was correlated [4, 7, 8] with the equations in the following form

$$\alpha_{1,2} = (1 + ax_1)/(b + cx_1) \quad (6)$$

the Margules equation (third order)

$$\log (\gamma_1/\gamma_2) = x_2^2 A_{1,2} - x_1^2 A_{2,1} - 2x_1 x_2 (A_{1,2} - A_{2,1}) \quad (7)$$

the Wilson equation

$$\ln (\gamma_1/\gamma_2) = \ln \frac{x_2 + A_{2,1}x_1}{x_1 + A_{1,2}x_2} + \left[ \frac{A_{1,2}}{x_1 + A_{1,2}x_2} - \frac{A_{2,1}}{x_2 + A_{2,1}x_1} \right] \quad (8)$$

The parameters  $a$ ,  $b$ ,  $c$  or  $A_{1,2}$ ,  $A_{2,1}$  characteristic of a given binary mixture were calculated by the method of least squares for the correlation equations in the above functional form. The *Marquardt* method [9] was applied to equations nonlinear in parameters. The approximation of experimental data obtained by individual equations was characterized by mean absolute deviation of the calculated and experimental values of composition of the vapour phase

$$d = \frac{1}{n} \sum_{i=1}^n |y_{1,\text{calc}} - y_{1,\text{exp}}|_i \quad (9)$$

The values of  $d$  and parameters of the correlation equations are given in Table 6 for individual systems. In some cases, the parameters of eqns (6—8) have been brought in close correlation.

The values of  $y_1$  calculated from the equation which interprets the measured data best with respect to  $d$  as well as the experimental results are presented in Tables

Table 3

Vapour—liquid equilibrium in the system 1,1-dichloroethane (1)—1,1,2-trichloroethane (2)  
at 101.3 kPa

$\theta/^\circ\text{C}$	$x_1$	$y_{1,\text{exp}}$	$y_{1,\text{calc}}^a$
103.3	0.048	0.194	0.192
100.8	0.118	0.393	0.394
94.6	0.200	0.553	0.557
89.4	0.260	0.642	0.645
84.0	0.352	0.746	0.745
76.0	0.500	0.853	0.851
70.3	0.597	0.901	0.898
64.8	0.745	0.945	0.948
59.7	0.906	0.985	0.985

a) From eqn (6).

Table 4

Vapour—liquid equilibrium in the system 1,1,2-trichloroethane (1)—1,1,2,2-tetrachloroethane (2)  
at 101.3 kPa

$\theta/^\circ\text{C}$	$x_1$	$y_{1,\text{exp}}$	$y_{1,\text{calc}}^a$
145.1	0.023	0.051	0.050
142.9	0.067	0.138	0.140
141.2	0.110	0.221	0.222
137.5	0.195	0.356	0.363
132.6	0.337	0.552	0.551
128.2	0.463	0.687	0.678
122.6	0.656	0.828	0.826
120.2	0.772	0.893	0.894
117.6	0.854	0.935	0.936

a) From eqn (6).

Table 5

Vapour—liquid equilibrium in the system 1,1,2-trichloroethane (1)—1,1,1,2-tetrachloroethane (2)  
at 101.3 kPa

$\theta/^\circ\text{C}$	$x_1$	$y_{1,\text{exp}}$	$y_{1,\text{calc}}^a$
129.8	0.031	0.049	0.049
127.3	0.140	0.207	0.204
126.6	0.185	0.260	0.262
125.2	0.290	0.387	0.388
123.5	0.339	0.443	0.443
121.9	0.445	0.555	0.553
120.5	0.526	0.627	0.631
118.7	0.661	0.751	0.749
117.4	0.709	0.779	0.789
116.6	0.806	0.866	0.864
115.5	0.868	0.914	0.910
114.7	0.950	0.966	0.967

a) From eqn (6).

3—5. The best agreement of the measured and calculated values of  $y_1$  (according to *d*) was, in all cases, obtained by means of eqn (6) for the relative volatility. The use of the Margules equation of the fourth order [4, 7] for the correlation of activity coefficients with composition did not clearly improve (according to *d*) the expression of experimental data when compared with the equation of the third order.

Table 6

Parameters of the correlation equations of binary systems containing 1,1,2-trichloroethane at 101.3 kPa

System	Equation	$a$ , resp. $A_{1,2}$	$b$ , resp. $A_{2,1}$	$c$	$d$
1,1-Dichloroethane (1)—	(6)	0.3275	0.2165	- 0.0245	0.0023
- 1,1,2-trichloroethane (2)	Margules (7)	0.0072	- 0.0262		0.0070
	Wilson (8)	0.3552	1.9876		0.0067
1,1,2-Trichloroethane (1)—	(6)	2.9016	0.4527	1.0922	0.0029
- 1,1,2,2-tetrachloroethane (2)	Margules (7)	- 0.0347	0.0135		0.0078
	Wilson (8)	1.8225	0.4464		0.0070
1,1,2-Trichloroethane (1)—	(6)	6.7409	0.6103	4.4585	0.0026
- 1,1,1,2-tetrachloroethane (2)	Margules (7)	0.0226	0.0023		0.0050
	Wilson (8)	0.5164	1.6019		0.0050

The investigated systems resemble ideal systems by their behaviour. Provided  $y_1 = y_2 = 1$ , the calculated values of  $y_1$  are slightly higher than the experimental ones and the values of  $d$  for the systems 1,1-dichloroethane—1,1,2-trichloroethane, 1,1,2-trichloroethane—1,1,2,2-tetrachloroethane, and 1,1,2-trichloroethane—1,1,1,2-tetrachloroethane are 0.0084, 0.0087, and 0.0055, respectively.

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