Vapour—liquid equilibrium of some binary systems containing 1,1-dichloroethylene

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The isobaric vapour—liquid equilibrium data were measured in binary systems containing 1,1-dichloroethylene with *trans*-1,2-dichloroethylene, methanol or ethanol at the pressure of 101.3 kPa. The experimental data were interpreted by using equations with two or three constants. The dependence of pressure on temperature of the saturated vapour of 1,1-dichloroethylene was measured in the range 100—311 kPa and the results were expressed by the Antoine equation.

При давлении 101,3 кПа измерены изобарические равновесные параметры пары—жидкость в бинарных системах 1,1-дихлорэтилена с транс-1,2-дихлорэтиленом, метанолом и этанолом. Для интерпретации экспериментальных данных использованы уравнения с двумя или тремя постоянными. Изучена также зависимость давления от температуры насыщенных паров 1,1-дихлорэтилена в промежутке 100—311 кПа, и результаты были представлены в форме уравнения Антуана.

trans-1,2-Dichloroethylene is one of the main impurities in the important monomer, *i.e.* 1,1-dichloroethylene prepared by dehydrochlorination of 1,1,2-trichloroethane. Sometimes, the azeotropic distillation with methanol [1] is applied to purification of 1,1-dichloroethylene (vinylidene chloride). The isobaric equilibria in the systems vinylidene chloride—*trans*-1,2-dichloroethylene, vinylidene chloride—methanol or vinylidene chloride—ethanol are interesting in this connection. They are described in this paper.

Experimental

Chemicals

1,1-Dichloroethylene was prepared by dehydrochlorination of 1,1,2-trichloroethane with 5 % molal excess of NaOH (with respect to the substance amount of 1,1,2-trichloroethane) in 10 mass % aqueous solution at 70 °C [2]. The obtained vinylidene chloride was purified by rectification in nitrogen atmosphere and stabilized by *p*-methoxyphenol (200 mass ppm).

trans-1,2-Dichloroethylene was prepared by repeated distillation of its mixture with cis-isomer which was obtained by dehydrochlorination of 1,1,2,2-tetrachloroethane in aqueous suspension of powdered zinc at 90 °C.

Methanol and ethanol were distilled from commercial anal. grade products. Before distillation, ethanol was dried with molecular sieve Calsit 5A (J. Dimitrov Chemical Works, Bratislava). It was found by the K. Fischer method [3] that the purified methanol contained, 0.01 mass % of water while the content of water in ethanol amounted to 0.08 mass %.

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

Table 1

Physical constants of the used substances

Substance	n(D, 20 °C)		ϱ(20 °C)/(g cm^{-3})		B.p.(101.3 kPa)/°C	
	Found	Ref. [4]	Found	Ref. [4]	Found	Ref. [8]
1,1-Dichloroethylene	1.4247	1.42468[a]	1.2129	1.2132[a]	31.4	31.56
trans-1,2-Dichloroethylene	1.4458	1.4454	1.2567	1.2565	47.3	47.67
Methanol	1.3288	1.3288	0.7911	0.7914	64.3	64.55
Ethanol	1.3610	1.3611	0.7894	0.7893	78.3	78.30

a) Ref. [1].

Apparatus and working procedure

The equilibrium data were measured with a Gillespie apparatus constructed in the modification put forward by Otsuki and Williams. This apparatus has been described in literature [5]. The measurements were performed in nitrogen atmosphere at the pressure of 101.3 kPa.

The dependence of pressure on temperature of the saturated vapour of 1,1-dichloroethylene was measured with a Swietoslawski ebulliometer which was made of stainless steel. A formation of polymer during measurement was not observed. Apparatus and working procedure have been described in literature [5].

Analytical methods

The composition of mixtures of 1,1-dichloroethylene with trans-1,2-dichloroethylene was determined chromatographically [6]. A Perkin—Elmer instrument, type Sigma 3 equipped with a flame ionization detector, a stainless steel column of 400 cm length and 3 mm diameter and packing consisting of 10 mass % of UCON LB-550 X on Chromaton NAW 0.2—0.4 mm were used for this purpose. The temperature of column was 60 °C. Rates of flow of gases: v(H$_2$) = 25 cm^3 min^{-1}, v(air) = 250 cm^3 min^{-1}, v(carrier gas − N$_2$) = 30 cm^3 min^{-1}.

The composition of mixtures of 1,1-dichloroethylene with *trans*-1,2-dichloroethylene was measured with a relative precision ± 2 %.

The systems of 1,1-dichloroethylene with alcohols were analyzed by means of the index of refraction by using the calibration curve

$$n(D, 20\ ^\circ C) = a_0 + a_1\{w\} + a_2\{w\}^2 \qquad (1)$$

where $\{w\}$ is the numerical value of mass fraction (mass percentage) of 1,1-dichloroethylene in a mixture with alcohol. The parameters in eqn (1) calculated by the method of least squares for the system 1,1-dichloroethylene—methanol are $a_0 = 1.3298$, $a_1 = 3.368 \times 10^{-4}$, $a_2 = 6.28 \times 10^{-6}$, the standard deviation $s = 2.47 \times 10^{-3}$, and the mean relative deviation referred to the difference of experimental values found for pure substances $d_r = 1.47$ %. The corresponding values for the system 1,1-dichloroethylene—ethanol are $a_0 = 1.3611$, $a_1 = 2.743 \times 10^{-4}$, $a_2 = 3.61 \times 10^{-6}$, $s = 3.46 \times 10^{-4}$, and $d_r = 0.26$ %.

Results

In correlating the results of measurements obtained for the binary equilibria of 1,1-dichloroethylene, we expressed the dependence of pressure p (kPa) on temperature θ of the saturated vapour of pure components in terms of the Antoine equation

$$\log\{p^0\} = A - B/(C + \{\theta\}) \qquad (2)$$

For 1,1-dichloroethylene the parameters of eqn (2) were calculated in the temperature range 31 °C—68 °C by nonlinear regression (Gauss—Newton method) [7] on the basis of the minimum sum of squared deviations $\Delta\theta = \theta_{exp} - \theta_{calc}$ of the experimental temperatures corresponding to the values of measured pressure. The experimental results expressing the relationship between pressure and temperature of the saturated vapour of 1,1-dichloroethylene as well as the deviations are given in Table 2. The parameters of the Antoine equation calculated for 1,1-dichloroethylene are given in Table 3. This table also contains the Antoine constants [8] for other substances used for our investigation of the binary vapour—liquid equilibria. The temperature θ of saturated vapour was measured with a precision ± 0.1 °C while the precision of measurement of the pressure of the saturated vapour of 1,1-dichloroethylene was ± 0.3 kPa.

Our measurements of the pressure and temperature of the saturated vapour near to the normal boiling temperature are fairly consistent with the known data [8] concerning the medium-pressure region. The results of this study fit in earlier results [9] obtained for the range 10 °C—61 °C or 17 °C—59 °C.

It is valid for the composition of the vapour and liquid phase of binary systems [5]

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

Table 2

Variation of pressure with temperature of the saturated vapour of 1,1-dichloroethylene

Experiment	p/kPa	$\theta/°\text{C}$	$\Delta\theta^a/°\text{C}$
1	100.8	31.4	0.00
2	116.4	35.6	−0.03
3	147.9	42.9	−0.06
4	160.4	45.6	0.08
5	174.5	48.3	0.07
6	203.4	53.3	0.02
7	226.2	56.8	−0.09
8	268.8	62.9	−0.01
9	310.7	68.2	0.04
10	209.5	54.2	−0.08
11	173.8	48.2	0.10
12	140.0	41.2	−0.05
13	116.4	35.6	−0.03
14	114.6	35.2	0.03
15	100.8	31.4	0.00

a) $\Delta\theta = \theta_{exp} - \theta_{calc}$ from eqn (2), $A = 6.37386$, $B = 1275.497$, $C = 260.452$.

Standard deviation $s = 0.062$, the mean absolute deviation is 0.045. Calculated b.p.(101.3 kPa) = 31.54 °C.

Table 3

Parameters [8] of the Antoine equation for the used substances

Substance	A	B	C
1,1-Dichloroethylene[a]	6.37386	1275.497	260.452
trans-1,2-Dichloroethylene	6.09003	1141.984	231.930
Methanol	7.20587	1582.271	239.726
Ethanol	7.23710	1592.864	226.184

a) This paper.

where x_1, $x_2 = 1 - x_1$ and y_1, $y_2 = 1 - y_1$ are mole fractions of components 1 and 2 in the liquid or vapour phase, respectively.

Assuming real behaviour of the liquid solution and ideal behaviour of the vapour phase (in the region of low pressures), it is valid for relative volatility

$$\alpha_{1,2} = (y_1/y_2)/(x_1/x_2) \tag{4}$$

or

$$\alpha_{1,2} = (\gamma_1/\gamma_2)(p_1^0/p_2^0) \tag{5}$$

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where p_1^0 and p_2^0 are the pressures (kPa) of the saturated vapour of pure components at the temperature of measurement.

For expressing the relationship between activity coefficients γ_1, γ_2 of components and composition of the liquid phase, we used the following equations [5, 10]:

the Wilson equation

$$\ln\,(\gamma_1/\gamma_2) = \ln\frac{x_2 + A_{2,1}x_1}{x_1 + A_{1,2}x_2} + \left[\frac{A_{1,2}}{x_1 + A_{1,2}x_2} - \frac{A_{2,1}}{x_2 + A_{2,1}x_1}\right] \tag{6}$$

the van Laar equation

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

the Margules equation (third order)

$$\log\,(\gamma_1/\gamma_2) = x_2^2 A_{1,2} - x_1^2 A_{2,1} - 2x_1 x_2 (A_{1,2} - A_{2,1}) \tag{8}$$

the Margules equation (fourth order)

$$\log\,(\gamma_1/\gamma_2) = x_2^2 A_{1,2} - x_1^2 A_{2,1} - 2x_1 x_2 [A_{1,2} - A_{2,1} + (x_2 - x_1)\,D_{1,2}] \tag{9}$$

The parameters $A_{1,2}$, $A_{2,1}$, and $D_{1,2}$ of eqns (6—9) for the given functional form were calculated by the method of least squares. For equations with nonlinear parameters the *Marquardt* method was used [11]. By means of the mean absolute deviation of the experimental and calculated composition of the vapour phase

$$d = \frac{1}{n}\sum_{i=1}^{n}|y_{1,\text{exp}} - y_{1,\text{calc}}|_i \tag{10}$$

we characterized reproduction of experimental data by the mentioned correlation equations for experimental temperatures and compositions x_1 of the liquid phase.

The experimental data as well as the composition of the vapour phase calculated from the most suited equation (according to d) for individual binary systems are presented in Tables 4—6. The parameters of eqns (6—9) and corresponding mean absolute deviations are given in Table 7.

The system 1,1-dichloroethylene—*trans*-1,2-dichloroethylene is almost ideal. Supposing $\gamma_1 = \gamma_2 = 1$, the mean absolute deviation is $d = 0.0032$. By using the Margules equation of the third order or the Wilson equation, we can very precisely express the experimental data of this system (Tables 4 and 7).

The experimental data of the systems 1,1-dichloroethylene—methanol and 1,1-dichloroethylene—ethanol are thermodynamically consistent according to the Herington integral criterion [5]. These systems exhibit considerable deviations from ideal behaviour, form azeotropic mixtures and their description by means of correlation eqns (6—9) is rather less successful than it is for the system 1,1-dichlo-

Table 4

Vapour—liquid equilibrium in the system 1,1-dichloroethylene (1)—*trans*-1,2-dichloroethylene (2) at 101.3 kPa

$\theta/°C$	x_1	$y_{1,exp}$	$y_{1,calc}{}^a$
46.3	0.060	0.102	0.102
45.7	0.117	0.190	0.188
44.1	0.190	0.290	0.288
42.3	0.280	0.400	0.399
41.1	0.360	0.490	0.487
39.3	0.460	0.592	0.590
36.0	0.685	0.890	0.789
33.0	0.895	0.940	0.939

a) From the Margules equation (*8*).

Table 5

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

$\theta/°C$	x_1	$y_{1,exp}$	$y_{1,calc}{}^a$
60.9	0.010	0.147	0.148
58.0	0.025	0.305	0.299
52.5	0.046	0.445	0.441
48.8	0.084	0.585	0.575
43.9	0.116	0.670	0.648
39.6	0.158	0.723	0.708
34.8	0.252	0.809	0.780
32.4	0.367	0.844	0.823
30.4	0.522	0.857	0.852
30.0	0.551	0.863	0.855
29.3	0.675	0.888	0.858
29.0	0.935	0.9uö	0.877
28.9	0.956	0.915	0.898
29.5	0.984	0.935	0.949

a) From the Margules equation (*9*).

roethylene—*trans*-1,2-dichloroethylene. The use of other more complicated equation NRTL [10] does not change the situation, either.

The valuation according to the mean absolute deviation d shows that eqns (*6—9*) are almost equivalent for description of the system 1,1-dichloroethylene—methanol. In the proximity of the azeotropic point, the Wilson equation is

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Table 6

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

$\theta/°C$	x_1	$y_{1,exp}$	$y_{1,calc}$[a]
76.9	0.010	0.066	0.107
74.8	0.020	0.173	0.197
68.5	0.042	0.367	0.361
61.9	0.091	0.575	0.573
45.4	0.215	0.811	0.804
37.4	0.354	0.882	0.884
34.6	0.520	0.910	0.920
31.6	0.753	0.930	0.945
30.8	0.919	0.949	0.955
30.8	0.930	0.949	0.956
30.7	0.939	0.949	0.956
30.7	0.950	0.950	0.958
30.7	0.969	0.959	0.961
30.8	0.985	0.970	0.968

a) From the Wilson equation (6).

Table 7

Parameters of correlation equations of binary systems with 1,1-dichloroethylene at 101.3 kPa

System	Equation	$A_{1,2}$	$A_{2,1}$	$D_{1,2}$	d
1,1-Dichloroethylene (1)—	Wilson (6)	0.3791	1.8839		0.0015
—trans-1,2-dichloroethylene (2)	Margules (8)	0.0295	−0.0216		0.0015
1,1-Dichloroethylene (1)—	Wilson (6)	0.4312	0.0673		0.0159
—methanol (2)	van Laar (7)	0.7264	1.2106		0.0156
	Margules (8)	0.7165	1.1619		0.0157
	Margules (9)	0.7933	1.2379	0.6562	0.0153
1,1-Dichloroethylene (1)—	Wilson (6)	0.9090	0.0237		0.0099
—ethanol (2)	van Laar (7)	0.3970	1.3353		0.0111
	Margules (8)	0.3380	1.1384		0.0139
	Margules (9)	0.3860	1.2001	0.5351	0.0127

relatively the most satisfactory one. Provided the total pressure of 101.3 kPa is constant, its application gives for azeotropic composition $x_1 = y_1 = 0.872$ at 28.98 °C. According to the experimental plot y_1 vs. x_1 and θ vs. x_1 or y_1 the azeotropic data may be $x_1 = y_1 = 0.905$ and $\theta = 29.0$ °C even if the lowest measured temperature has been 28.9 °C.

According to the value of d, the Wilson equation is most suited for the system 1,1-dichloroethylene—ethanol. In the proximity of the azeotropic point, the van Laar equation is, however, more convenient. By using this equation, we calculated for constant total pressure of 101.3 kPa $x_1 = y_1 = 0.950$ and $\theta = 30.95$ °C while the corresponding experimental values were $x_1 = y_1 = 0.950$ and $\theta = 30.7$ °C.

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