ISOTHERMAL AND ISOBARIC VAPOUR–LIQUID EQUILIBRIUM DATA IN THE TETRACHLOROMETHANE–ISOBUTYL ALCOHOL SYSTEM*

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Dedicated to Professor E. Hála on the occasion of his 60th birthday.

Isothermal vapour–liquid equilibrium data at 65, 75 and 83°C and isobaric ones at 101·325 kPa have been measured in the tetrachloromethane–isobutyl alcohol system. A modified circulation still of the Gillespie type has been used for the measurements. The experimental data have been correlated by the Margules 3rd and 4th order equations.

As part of a systematic study of vapour–liquid equilibria of systems consisting of components of different groups of Ewell's classification of liquids[1], the equilibrium data in the title system have been measured at various conditions.

EXPERIMENTAL

Substances used. Tetrachloromethane, analytical reagent grade (Lachema, Brno, Czechoslovakia), has been twice rectified on a fifty-plate bubble-cup column. Its physical constants have been as follows: n.b.p. 76·83°C (ref.[2,3] 76·7—76·76), d_4^{20} 1·5939 g/cm^3 (ref.[2,3] 1·5939—1·59404), n_D^{20} 1·4601 (ref.[2,3] 1·46005—1·46036). Isobutyl alcohol, analytical reagent grade (Lachema, Brno, Czechoslovakia) has been dried with anhydrous K_2CO_3, filtered and rectified on a fifty-plate bubble-cup column[4]. The found values of physical constants of the isobutyl alcohol used have been as follows: n.b.p. 107·75°C (ref.[2] 107·89—108·10), d_4^{20} 0·80187 g/cm^3 (ref.[2] 0·80196), n_D^{20} 1·3959 (ref.[2] 1·3959).

Analytical method. The samples of the equilibrium vapour and liquid phases have been analyzed refractometrically at 20°C. To this purpose an Abbe-type refractometer (Zeiss, Jena) has been used allowing to measure refractive indices with an accuracy of ±0·0001. On the basis of calibration binary mixtures, the constants of the relation

$$n_D = x_1 n_{D1} + x_2 n_{D2} + x_1 x_2 (x_1 A_1 + x_2 A_2 - x_1 x_2 A_3) \qquad (1)$$

have been 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

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constants evaluated from calibration samples by the least-squares method ($A_1 = -0.00506$, $A_2 = 0.00254$, $A_3 = -0.00699$). Eq. (1) represents the experimental points with an average absolute deviation in n_D 0·00005 and a mean per cent deviation 0·07%. Then calibration interpolation tables have been computed for direct reading of the sample composition from measured n_D values.

Apparatus and procedure. The equilibrium measurements have been carried out in a modified Gillespie still. The description of the apparatus and measuring procedure can be found in the literature[1]. The pressure in the system has been established by measuring the boiling point of water in an ebulliometer connected parallel to the equilibrium still. Temperature has been measured by mercury-in-glass calorimetric standards calibrated by means of a Mueller bridge with platinum resistance thermometer (Leeds and Northrup). The equilibrium samples have been taken for analysis only if the boiling point in the still has not been changing for 30 minutes.

TABLE I

Isothermal Vapour–Liquid Equilibrium in the Tetrachloromethane(1)–Isobutyl Alcohol(2) System at 65°C

x_1	y_1	P, kPa	$(y_{1,\mathrm{calc}} - y_{1,\mathrm{exp}})^a$	
			Marg. 3	Marg. 4
0·0775	0·4910	28·70	−0·0291	0·0095
0·1192	0·5881	34·26	−0·0065	0·0014
0·1526	0·6438	38·43	0·0041	−0·0060
0·2111	0·7070	44·16	0·0194	−0·0085
0·2935	0·7665	51·75	0·0247	−0·0088
0·3579	0·7981	56·06	0·0232	−0·0059
0·3911	0·8122	57·99	0·0203	−0·0051
0·5101	0·8410	63·32	0·0159	0·0070
0·6100	0·8671	66·62	−0·0011	0·0029
0·6371	0·8671	67·15	0·0004	0·0072
0·6880	0·8802	68·58	−0·0103	0·0008
0·7230	0·8840	69·40	−0·0124	0·0007
0·9400	0·9400	72·24	−0·0123	−0·0125
0·9557	0·9473	72·11	−0·0060	−0·0080
0·9695	0·9578	71·65	−0·0019	−0·0048
0·9990	0·9971	70·59	0·0011	0·0009
Mean			*0·0118*	*0·0056*

[a] Constants of correlation equations: Marg. 3: $A_{12} = 0.3524$, $A_{21} = 0.8902$; Marg. 4: $A_{12} = 0.5563$, $A_{21} = 0.9541$, $D_{12} = 0.7108$.

RESULTS

The mutual dependence of equilibrium compositions of the liquid and vapour phases in a binary system is given by

$$y_1 = \alpha_{12}(x_1/x_2)/(1 + \alpha_{12}(x_1/x_2))\,, \tag{2a}$$

$$y_2 = 1/(1 + \alpha_{12}(x_1/x_2))\,, \tag{2b}$$

where x_1, x_2 are mole fractions of the components 1 and 2 in the liquid phase and y_1, y_2 those in the vapour phase. The relative volatility α_{12} is defined by

$$\alpha_{12} = (y_1/y_2)/(x_1/x_2)\,, \tag{3}$$

TABLE II

Isothermal Vapour–Liquid Equilibrium in the Tetrachloromethane(1)–Isobutyl Alcohol(2) System at 75°C

x_1	y_1	P, kPa	$(y_{1,\text{calc}} - y_{1,\text{exp}})$[a]	
			Marg. 3	Marg. 4
0·0135	0·1040	28·82	−0·0022	0·0063
0·0594	0·3657	38·24	−0·0228	−0·0158
0·1207	0·5366	49·52	−0·0102	−0·0163
0·2065	0·6661	62·66	−0·0015	−0·0159
0·2296	0·6830	65·58	0·0061	−0·0087
0·2935	0·7276	72·57	0·0130	−0·0004
0·3515	0·7626	78·00	0·0102	0·0001
0·3895	0·7863	80·52	0·0026	−0·0049
0·5061	0·8176	88·12	0·0048	0·0055
0·6083	0·8456	92·61	−0·0051	0·0011
0·6330	0·8573	93·22	−0·0132	−0·0060
0·7261	0·8720	96·26	−0·0141	−0·0056
0·8300	0·8980	98·64	−0·0177	−0·0125
0·9040	0·9151	99·42	−0·0043	−0·0042
0·9250	0·9190	99·14	0·0048	0·0034
0·9400	0·9331	99·32	0·0016	−0·0006
0·9753	0·9650	98·29	0·0031	0·0005
Mean			*0·0081*	*0·0063*

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[a] Constants of correlation equations: Marg. 3: $A_{12} = 0{\cdot}3516$, $A_{21} = 0{\cdot}7349$; Marg. 4: $A_{12} = 0{\cdot}3995$, $A_{21} = 0{\cdot}7863$, $D_{12} = 0{\cdot}2955$.

and for a low pressure region holds

$$\alpha_{12} = (\gamma_1/\gamma_2)\,(P_1^0/P_2^0)\,, \tag{4}$$

where P_1^0 and P_2^0 denote the vapour pressures of pure components at a given temperature and γ_1, γ_2 their activity coefficients. The temperature dependence of the vapour pressures of pure components P^0 (kPa) in the form of the Antoine equation

$$\log P^0 = A - B/(t + C)\,, \tag{5}$$

t is temperature (°C) and A, B, C are constants, has been taken over from the literature (tetrachloromethane: $A_1 = 6{\cdot}05881$, $B_1 = 1242{\cdot}430$, $C_1 = 230{\cdot}00$ (ref.[5]); isobutyl alcohol: $A_2 = 6{\cdot}58646$, $B_2 = 1322{\cdot}416$, $C_2 = 180{\cdot}931$ (ref.[6])).

The concentration dependence of the activity coefficients has been expressed by the Margules 3rd and 4th order equations

$$\log (\gamma_1/\gamma_2) = x_2^2 A_{12} - x_1^2 A_{21} - 2x_1 x_2 (A_{12} - A_{21}) \tag{6}$$

TABLE III

Isothermal Vapour–Liquid Equilibrium in the Tetrachloromethane(1)–Isobutyl Alcohol(2) System at 83°C

x_1	y_1	P, kPa	$(y_{1,\mathrm{calc}} - y_{1,\mathrm{exp}})^a$	
			Marg.3	Marg. 4
0·0890	0·3425	59·09	0·0030	0·0103
0·1360	0·4760	68·58	−0·0050	−0·0072
0·3106	0·7230	95·29	−0·0009	−0·0136
0·4340	0·7863	108·74	0·0091	0·0028
0·5320	0·8130	115·14	0·0140	0·0135
0·7690	0·8750	124·91	−0·0075	−0·0018
0·8301	0·8870	126·20	−0·0066	−0·0025
0·8886	0·9040	126·55	−0·0034	−0·0021
0·9145	0·9145	126·20	−0·0005	−0·0007
0·9160	0·9145	126·00	0·0004	0·0001
0·9370	0·9294	126·05	−0·0003	−0·0016
0·9710	0·9561	126·03	0·0046	0·0025
Mean			*0·0046*	*0·0049*

[a] Constants of correlation equations: Marg. 3: $A_{12} = 0{\cdot}1612$, $A_{21} = 0{\cdot}7236$; Marg. 4: $A_{12} = 0{\cdot}2257$, $A_{21} = 0{\cdot}7611$, $D_{12} = 0{\cdot}2623$.

and

$$\log(\gamma_1/\gamma_2) = x_2^2 A_{12} - x_1^2 A_{21} - 2x_1 x_2 [A_{12} - A_{21} + (x_2 - x_1) D_{12}], \quad (7)$$

where A_{12}, A_{21}, D_{12} are constants characteristic of the given binary mixture. Their values have been computed from the experimental data by minimizing the correlation equations in the form

$$\log(\gamma_1/\gamma_2) = F(x_1) \quad (8)$$

by means of the least squares method.

The experimental vapour–liquid equilibrium data for the isothermal conditions of 65, 75 and 83°C together with the deviations between the calculated and experimental values and with the constants of correlation equations are given in Tables I, II and III,

TABLE IV

Isobaric Vapour–Liquid Equilibrium in the Tetrachloromethane(1)–Isobutyl Alcohol(2) System at 101·3 kPa

x_1	y_1	t, °C	$(y_{1,\text{calc}} - y_{1,\text{exp}})^a$	
			Marg. 3	Marg. 4
0·1482	0·5190	93·07	−0·0138	−0·0122
0·2390	0·6485	87·96	0·0006	−0·0052
0·2965	0·7040	85·27	0·0033	−0·0035
0·3531	0·7390	83·12	0·0095	0·0034
0·3705	0·7483	82·72	0·0100	0·0043
0·4340	0·7840	81·06	0·0044	0·0005
0·4612	0·7987	80·44	−0·0001	−0·0031
0·4820	0·8100	80·13	−0·0048	−0·0070
0·5690	0·8301	78·49	−0·0016	−0·0011
0·6430	0·8465	77·43	−0·0031	−0·0010
0·7388	0·8642	76·59	−0·0034	−0·0008
0·7942	0·8703	76·50	0·0021	0·0040
0·8441	0·8946	75·69	−0·0068	−0·0061
0·8946	0·9114	75·50	−0·0025	−0·0036
0·9250	0·9250	75·47	0·0016	−0·0005
0·9473	0·9390	75·60	0·0039	0·0015
Mean			*0·0045*	*0·0036*

[a] Constants of correlation equations: Marg. 3: $A_{12} = 0·3204$, $A_{21} = 0·7114$; Marg. 4: $A_{12} = 0·3763$, $A_{21} = 0·7489$, $D_{12} = 0·1817$.

respectively. The same values for the isobaric conditions (101·325 kPa) are presented in Table IV.

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