VAPOUR-LIQUID EQUILIBRIUM IN TETRACHLOROMETHANE-ISOBUTYL ALCOHOL SYSTEM*

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The isobaric vapour–liquid equilibrium in the tetrachloromethane–isobutyl alcohol was measured by a recirculation method at 101·325 kPa. The data were correlated by the NRTL and the Margules equations.

As a part of the systematic study of binary systems whose components belong to different groups of Ewell's classification, isobaric vapour–liquid equilibrium of a system containing polar and non-polar compound was measured. In continuation of this work, we report here the results of our measurements on tetrachloromethane–isobutyl alcohol system.

EXPERIMENTAL

Substances used. Tetrachloromethane, analytical reagent grade was twice rectified on 50-plate bubble cap column. Its determined values of physical constants were: normal boiling point 76·75°C (lit. 76·75°C), density d_4^{20}, g/cm^3 1·5939 (lit. 1·5939—1·5941), refractive index n_D^{20} 1·4601 (lit. 1·4601—1·4604). Isobutyl alcohol, analytical reagent grade was dried with anhydrous K_2CO_3 and rectified on 50-plate bubble cap column. Its determined values of physical constants were: normal boiling point 108·0°C (lit. 107·9—108·1°C), density d_4^{20}, g/cm^3 0·8018 (lit. 0·80196 to 0·80210), refractive index n_D^{20} 1·3959 (lit. 1·3959). All literature data are taken from Timmermans[1].

Apparatus and procedure. The vapour–liquid equilibrium was measured by employing a recirculation still as described by Dvořák and Boublík[2] with about 70 ml of total amount of liquid mixture. The temperature was measured by mercury thermometer calibrated against a platinum resistance thermometer and a Leeds and Northrup Mueller bridge. The accuracy of the temperature measurements was ±0·1 K. The pressure in the system was maintained at 101·325 kPa and checked by measuring boiling point of water in an ebulliometer connected parallelly to the equilibrium still. The equilibrium samples were taken for refractometrical analysis only if the boiling point in the still did not change for 20 minutes. The refractive indices were determined

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at 20°C on an Abbé refractometer with ±0·0001 accuracy and they were correlated by the equation

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

where x_1 and x_2 are mole fractions, n_{D1} and n_{D2} are refractive indices of pure substance 1 and 2, n_D is the refractive index of the mixture and A_1, A_2, A_3 are empirical constants determined by the least square method from experimental values. This equation was employed for the calculation of interpolation tables serving for determining the concentration dependence of the refractive index. The experimental values are given in Table I; the evaluated parameters of Eq. (*1*) are $A_1 = -0{\cdot}00611$, $A_2 = 0{\cdot}00059$, $A_3 = -0{\cdot}01107$ yielding average per cent deviation equal to 0·04.

TABLE I

Refractive Indices of CCl_4(1)–Isobutyl Alcohol(2) Mixtures at 20°C

x_1	0·1075	0·2556	0·3565	0·6900	0·7909	0·8929
n_C^{20}	1·4029	1·4125	1·4189	1·4399	1·4462	1·4528

TABLE II

Vapour–Liquid Equilibrium in the CCl_4(1)–Isobutyl Alcohol(2) System at 101·325 kPa

Experimental			Calculated	
x_1	y_1	T	y(M4)	y(NRTL)
0·013	0·094	105·6	—0·015	—0·017
0·035	0·172	103·6	0·017	0·014
0·082	0·326	99·2	0·029	0·032
0·127	0·441	95·5	0·022	0·031
0·272	0·667	86·8	—0·003	0·007
0·357	0·745	83·4	—0·013	—0·009
0·445	0·780	81·1	0·003	0·001
0·550	0·816	79·1	0·009	0·003
0·618	0·837	78·1	0·007	0·001
0·711	0·862	77·1	0·002	—0·002
0·794	0·877	76·5	0·003	0·002
0·866	0·894	76·1	0·004	0·005
0·914	0·917	76·0	0·000	0·002
0·962	0·952	76·3	—0·001	—0·001
0·988	0·981	76·6	0·000	0·000
		Mean	*0·0084*	*0·0085*

RESULTS

The vapour–liquid equilibrium was measured at a constant pressure of 101·325 kPa and the experimental results are summarized in Table II. The data were correlated using the following three-parameter equations:

1) The 4-suffix Margules equation

$$\log \gamma_1/\gamma_2 = A_{12}x_2(1 - 3x_1) - A_{21}x_1(1 - 3x_2) - 2x_1x_2(x_2 - x_1)\,D\,, \tag{2}$$

where $A_{12} = 0{\cdot}4470$, $A_{21} = 0{\cdot}7876$ and $D = 0{\cdot}4532$;

2) The NRTL equation with adjusted parameter α

$$\log \gamma_1/\gamma_2 = \frac{\tau_{21}G_2(x_2^2G_2 - x_1^2)}{(x_1 + x_2G_2)^2} - \frac{\tau_{12}G_1(x_1^2G_1 - x_2^2)}{(x_2 + x_1G_1)^2}\,, \tag{3}$$

where $G_1 = \exp(-\alpha\tau_{12})$, $G_2 = \exp(-\alpha\tau_{21})$, $\tau_{12} = 1{\cdot}5386$, $\tau_{21} = 0{\cdot}3984$, $\alpha = 0{\cdot}6378$.

The adjustments were carried out by minimizing the sum of square deviations in logarithm of activity coefficients ratio ($\log \gamma_1/\gamma_2$). The deviations between vapour phase compositions calculated by means of smoothed parameters and experimental values are presented in Table II ($\Delta y = y_{\mathrm{calc}} - y_{\mathrm{exp}}$).

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