

LIQUID-VAPOUR EQUILIBRIUM. LVIII.*

THE SYSTEMS BENZENE-2-BUTANOL, BENZENE-ISOBUTANOL AND BENZENE-TERT-BUTANOL

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Results of vapour-liquid equilibrium measurements are presented on systems benzene-2-butanol, benzene-isobutanol at the temperature 60, 70 and 80°C and benzene-tert-butanol at the temperatures 60, 70 and 75°C. The modified circulation still of Gillespie's type was used for the measurements and the data were correlated by means of several equations expressing the dependence of activity coefficients of components on composition of the liquid phase.

As part of a systematic study of thermodynamic properties of binary mixtures belonging to various groups of Ewell's classification of liquids¹, the isothermal vapour-liquid equilibria have been measured for binary systems of aromatic hydrocarbons with alcohols.

EXPERIMENTAL

Preparation of pure substances. Benzene (standard from Urxovy závody, Valašské Meziříčí, 99.99% purity) was used without any further purifications. 2-Butanol (Fluka, better than 99% purity) was rectified on a fifty-plate laboratory distillation column. Isobutanol (Fluka, 99.5% purity) was rectified on a forty-plate laboratory distillation column. Tert-butanol (Fluka, 99.7% purity) was rectified on a fifty-plate laboratory distillation column and after that on an 1 m long packed column (~ 50 TP). The comparison of the measured and published values of physical constants of the used substances is given in Table I.

Analytical procedure. Different mixtures of known concentration were prepared for each system and their refractive indices were measured by an Abbe-type refractometer with an accuracy of ± 0.0001 . Refractive indices of calibration mixtures were expressed by the equation

$$n_D = x_1 n_{D1} + x_2 n_{D2} + x_1 x_2 a_{12}, \quad (I)$$

where x_1 , x_2 are mole fractions; n_{D1} , n_{D2} the refractive indices of the pure components 1 and 2 and a_{12} is an empirical constant determined from the experimental data. The measured values of refractive indices are presented in Table II.

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Measurement of vapour-liquid equilibrium. For measuring the vapour-liquid equilibria, a modified equilibrium still of Gillespie's type was used (Fig. 1). Prior to starting an experiment, the reservoirs *P* and *K* and the flask *B* are filled with the solution whose equilibrium data are measured. The central part of the flask *B*, which is sintered so as to provide for smooth evolution of bubbles, is heated electrically. The droplets sprayed over from the flask, pass with the vapour through the Cottrell's tube into the equilibrium chamber *R*. From this chamber the heterogeneous mixture flows down into the separator where liquid and vapour are separated. The liquid returns to the

TABLE I
Physical Constants of Pure Compounds

Compound	Constant	Measured	Literature
Benzene	d_4^{20} g/cm ³	0.87903	0.87906 ⁵
	n_D^{20}	1.5009	1.5009–1.5011 ⁵
2-Butanol	d_4^{20} g/cm ³	0.8085	0.8080 ⁵
	n_D^{20}	1.3969	1.3969 ⁵
Isobutanol	d_4^{20} g/cm ³	0.8015	0.80196 ⁵
	n_D^{20}	1.3954	1.3959 ⁵
Tert-butyl alcohol	d_4^{30} g/cm ³	0.7766	0.7762 ⁵
	$n_D^{25,50}$	1.3848	1.3851 ⁶

TABLE II
Refractive Indices of the Binary Solutions of Butanols with Benzene

Benzene(1)–2-butanol(2)		Benzene(1)–isobutanol(2)		Benzene(1)–tert-butanol(2)	
x_1	n_D^{20}	x_1	n_D^{20}	x_1	n_D^{30}
0.18502	1.4118	0.1041	1.4049	0.1368	1.3943
0.32014	1.4243	0.1985	1.4140	0.2255	1.4032
0.37157	1.4295	0.3075	1.4228	0.3321	1.4125
0.50414	1.4440	0.4076	1.4342	0.3920	1.4202
0.66389	1.4606	0.5130	1.4458	0.6244	1.4465
0.71552	1.4660	0.6105	1.4561	0.7218	1.4582
0.81171	1.4779	0.7168	1.4679	0.8232	1.4709
0.89165	1.4869	0.8766	1.4860	0.9129	1.4824

boiling flask *via* the reservoir *K*. The vapour leaving the separator passes into the condenser *H*. The condensate flows through the reservoir *P* into the drop counter *D*, beyond which it combines with the equilibrium liquid and returns into the boiling flask. The process is kept running until the system attains steady state. It can be proved that in the steady state the composition of the vapour and the composition of the liquid is the same as the equilibrium composition of the boiling system. In the apparatus of the type described, steady state is safely attained after one hour's circulation. The magnetic stirrers (M_1 , M_2 , M_3) ensure perfect homogenization. The construction prevents the newly coming portions, whose composition does not correspond to the stationary state during the sampling, from getting into the samples being withdrawn. By connection to a sufficiently large reservoir of constant pressure the apparatus is prepared for work under defined pressure. The temperature of boiling was measured with a mercury thermometer. The total pressure of the system was measured indirectly with a standard ebullimeter filled with water. The boiling point of water was measured too with a mercury thermometer and the corresponding total pressure was read from tables of water vapour pressures. If the temperature of boiling is determined within $\pm 0.02^\circ\text{C}$ the pressure is measured with an accuracy of $\pm 0.11\%$ relative.

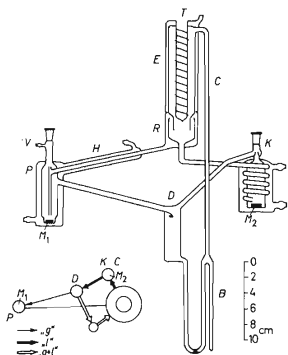


FIG. 1
Modified Gillespie's Still

RESULTS

For vapour-liquid equilibrium in a system at low pressure, the mutual dependence of the equilibrium compositions can be expressed by the following expressions¹:

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

$$\alpha_{12} = P_1^0 \gamma_1 / P_2^0 \gamma_2, \quad (3)$$

where x_1 , x_2 are the mole fractions of the components 1, 2 in the liquid phase, y_1 is

the mole fraction of the component 1 in the vapour phase, α_{12} is the relative volatility, P_1^0, P_2^0 are the vapour pressures of the pure components 1 and 2 at a given temperature, γ_1, γ_2 are the activity coefficients of each component.

The vapour pressures of the pure components were calculated using the Antoine equation

$$\log P^0 = A - B/(t + C). \quad (4)$$

The values of the constants A, B and C were taken from the literature².

TABLE III
Vapour-Liquid Equilibrium in the Benzene(1)-2-Butanol(2) System

60°C			70°C			80°C		
<i>x</i>	<i>y</i>	<i>P</i>	<i>x</i>	<i>y</i>	<i>P</i>	<i>x</i>	<i>y</i>	<i>P</i>
0.0775	0.3130	203.30	0.0760	0.2770	289.20	0.0770	0.2770	435.32
0.2110	0.5830	288.00	0.2050	0.5100	385.06	0.1420	0.3940	500.46
0.2410	0.6150	307.80	0.3340	0.6220	456.19	0.2050	0.4630	548.26
0.2630	0.6350	323.50	0.4830	0.7180	512.07	0.2460	0.5150	582.19
0.4620	0.7460	374.40	0.5540	0.7510	529.91	0.2970	0.5550	617.85
0.6020	0.7850	394.40	0.6250	0.7760	546.20	0.3300	0.5910	643.41
0.7360	0.8350	408.70	0.6950	0.8130	560.79	0.3800	0.6160	664.97
0.8650	0.8800	412.00	0.8050	0.8400	569.27	0.4200	0.6430	682.15
0.9550	0.9400	410.40	0.8770	0.8850	571.41	0.4550	0.6670	697.16
			0.9120	0.8960	569.27	0.4900	0.6900	715.03

Equation	Order	Temperature	A_{12}	A_{21}	D_{12}	Dev ^a
van Laar	3	60	0.3841	0.5758	—	0.0084
		70	0.3393	0.4926	—	0.0104
		80	0.3321	0.3553	—	0.0061
Margules	3	60	0.3607	0.5517	—	0.0081
		70	0.3291	0.4697	—	0.0102
		80	0.3323	0.3543	—	0.0061
Margules	4	60	0.3534	0.5442	-0.0235	0.0081
		70	0.4381	0.5697	0.3480	0.0103
		80	0.4106	0.4819	0.3273	0.0033
Alpha	2	60	6.2381	0.6553	—	0.0073
		70	4.3674	0.4536	—	0.0068
		80	3.5749	0.5292	—	0.0067

^a Mean deviation in the vapour phase composition.

The concentration dependence of the activity coefficients was expressed by the following relations:

van Laar 3rd order:^{1,3}

$$\log \gamma_1 = A_{12}x_2^2/[x_1(A_{12}/A_{21}) + x_2]^2, \quad (5)$$

$$\log \gamma_2 = A_{21}x_1^2/[x_2(A_{21}/A_{12}) + x_1]^2, \quad (6)$$

TABLE IV

Vapour-Liquid Equilibrium in the Benzene(1)-Isobutanol(2) System

60°C			70°C			80°C		
<i>x</i>	<i>y</i>	<i>P</i>	<i>x</i>	<i>y</i>	<i>P</i>	<i>x</i>	<i>y</i>	<i>P</i>
0.1400	0.5580	202.38	0.1170	0.4940	282.02	0.0840	0.3640	362.54
0.3280	0.7430	290.41	0.1940	0.6190	365.48	0.1650	0.5270	461.54
0.3730	0.7550	316.88	0.3180	0.7060	430.23	0.2400	0.6180	540.04
0.4960	0.8120	343.93	0.3500	0.7230	473.03	0.3530	0.6940	611.03
0.5690	0.8360	361.08	0.4250	0.7640	468.75	0.4130	0.7270	643.41
0.6770	0.8560	372.91	0.5050	0.7850	496.64	0.4490	0.7460	662.55
0.7600	0.8750	383.52	0.6450	0.8330	523.91	0.5000	0.7630	679.67
0.8130	0.8850	386.60	0.7600	0.8650	546.20	0.5180	0.7640	687.12
0.9450	0.9440	397.54	0.8570	0.8930	554.49	0.5610	0.7870	704.76
0.9500	0.9460	396.96	0.9530	0.9450	558.68	0.6040	0.8030	712.45

Equation	Order	Temperature	<i>A</i> ₁₂	<i>A</i> ₂₁	<i>D</i> ₁₂	Dev. ^a
Van Laar	3	60	0.4378	0.5223	—	0.0143
		70	0.4266	0.5045	—	0.0078
		80	0.3691	0.4492	—	0.0025
Margules	3	60	0.4385	0.5137	—	0.0143
		70	0.4265	0.4975	—	0.0079
		80	0.3638	0.4438	—	0.0024
Margules	4	60	0.5873	0.6641	0.4792	0.0130
		70	0.5237	0.6184	0.3516	0.0080
		80	0.3516	0.4282	—0.0453	0.0021
Alpha	2	60	8.6328	0.5018	—	0.0034
		70	7.7254	0.6055	—	0.0037
		80	6.1237	0.5129	—	0.0025

^a See Table III.

Margules 3rd order:^{1,3}

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

Margules 4th order:^{1,3}

$$\log(\gamma_1/\gamma_2) = x_2^2 A_{12} + x_1^2 A_{21} - 2x_1 x_2 [A_{12} - A_{21} + (x_2 - x_1) D_{12}], \quad (8)$$

TABLE V
Vapour-Liquid Equilibrium in the Benzene(1)-tert-Butanol(2) System

60°C			70°C			75°C		
<i>x</i>	<i>y</i>	<i>P</i>	<i>x</i>	<i>y</i>	<i>P</i>	<i>x</i>	<i>y</i>	<i>P</i>
0.0710	0.2050	346.74	0.1430	0.2900	565.01	0.0580	0.1240	620.14
0.1940	0.3770	400.71	0.2750	0.4200	620.14	0.1260	0.2430	667.40
0.3000	0.4730	433.62	0.3600	0.4770	641.05	0.1900	0.3070	704.78
0.4020	0.5320	452.65	0.4520	0.5350	658.50	0.2370	0.3850	730.64
0.5500	0.6170	468.75	0.5410	0.5850	672.29	0.9150	0.8250	733.27
0.6280	0.6550	470.57	0.6360	0.6330	669.84	0.9250	0.8370	728.02
0.6840	0.6800	470.57	0.6970	0.6640	667.40	0.9350	0.8500	722.80
0.7460	0.7080	470.57	0.7400	0.6900	662.55	0.9460	0.8700	711.17
0.8330	0.7640	461.54	0.7970	0.7270	657.72			
0.8830	0.8000	452.66	0.8250	0.7470	652.92			

Equation	Order	Temperature	<i>A</i> ₁₂	<i>A</i> ₂₁	<i>D</i> ₁₂	Dev. ^a
Van Laar	3	60	0.3277	1.0007	—	0.0264
		70	0.3938	0.4583	—	0.0030
		75	0.3050	0.6168	—	0.0045
Margules	3	60	0.2177	0.6703	—	0.0320
		70	0.3913	0.4539	—	0.0031
		75	0.2586	0.5681	—	0.0060
Margules	4	60	0.3539	0.8086	0.4090	0.0312
		70	0.4587	0.5226	0.1934	0.0020
		75	0.3097	0.5988	0.1723	0.0045
Alpha	2	60	2.9005	1.4597	—	0.0059
		70	2.3148	1.4144	—	0.0031
		75	2.1422	1.8681	—	0.0101

^a See Table III.

the expansion of relative volatility 2nd order¹:

$$\alpha_{12} = (1 + A_{12}x_2)/(1 + A_{21}x_1), \quad (9)$$

A_{12} , A_{21} , D_{12} are constants characteristic for the given binary mixture and evaluated by means of the weighted least square method for the correlation equation

$$\log(\gamma_1/\gamma_2) = F(x_1).$$

The statistical weight was calculated by the relation⁴

$$w = [(1/2 \cdot 303^2)(1/x_1^2 x_2^2 + 1/y_1^2 y_2^2) + (dF(x_1)/dx_1)^2]^{-1}. \quad (10)$$

The values of the constants of each one of the former equations, just as the comparison of the experimental and calculated vapour-liquid equilibrium data are summarized in Tables III–V.

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