VAPOUR–LIQUID EQUILIBRIUM IN TOLUENE–ALIPHATIC C_4 ALCOHOL SYSTEMS*

J. LNĚNIČKOVÁ and I. WICHTERLE

Institute of Chemical Process Fundamentals, Czechoslovak Academy of Sciences, 165 02 Prague 6 - Suchdol

Received May 24th, 1976

The vapour–liquid equilibrium in binary systems containing toluene and butanol, isobutanol sec-butyl alcohol, or tert-butyl alcohol was measured by a recirculation method at 333·31, 343·40, and 353·44 K. The data were correlated by the Barker method considering the correction for the nonideal behaviour of the vapour phase.

As a part of the systematic study of binary mixtures whose components belong to different groups of Ewell's classification, isothermal vapour–liquid equilibria in alcohol–aromate systems were measured. Starting from our preceding work[1] which was dealing with C_4 alcohol–benzene systems, here we report results of our measurements on toluene–aliphatic C_4 alcohol systems.

EXPERIMENTAL

Preparation of pure substances and criteria of purity. As starting products for purification of alcohols we employed commercially available substances of the highest purity grade from Lachema, Brno. Butanol and sec-butyl alcohol were purified by washing with diluted H_2SO_4 and refluxing with 20% NaOH. Then they were twice rectified on a 40-plate column — for the second time with sodium. Isobutanol and tert-butyl alcohol were dried with anhydrous K_2CO_3 and then twice rectified on the 40-plate column. Toluene, A. R. grade (Urx Plants, Valašské Meziříčí) was shaken subsequently with concentrated H_2SO_4, an NaOH solution, water, and finally with mercury. Then it was twice rectified on a 50-plate column. A comparison between measured and literature physicochemical constants is in Table I.

Apparatus and procedure. For our measurements of the vapour–liquid equilibrium we employed the apparatus by Dvořák and Boublík[4] with the total amount of liquid of about 120 ml. The temperature was measured by mercury standards calibrated against a platinum resistance thermometer and a Leeds & Northrup Mueller bridge. The accuracy of these measurements was $\pm 0{\cdot}02$ K. The pressure was measured indirectly as the boiling point of water in a parallelly connected ebulliometer. Samples of equilibrium phases were analyzed refractometrically. Refractive indices were determined at 20°C on an Abbé refractometer with a $\pm 0{\cdot}0001$ accuracy and they were

* Part LXXIV in the series Liquid–Vapour Equilibrium; Part LXXIII: This Journal *41*, 3188 (1976).

TABLE I

Physical Constants of Pure Substances

Substance	Constant	Measured	Literature
Butanol	d_4^{25}, g/cm^3	0·80578	0·8058[2]
	n_D^{20}	1·3992	1·3993[2]
Isobutanol	d_4^{25}, g/cm^3	0·79821	0·79806[2]
	n_D^{20}	1·3959	1·3959[2]
Sec-butyl alcohol	d_4^{25}, g/cm^3	0·80266	0·8023[2]
	n_D^{20}	1·3971	1·3969[2]
Tert-butyl alcohol	d_4^{27}, g/cm^3	0·77849	0·77838[3]
	n_D^{20}	—	1·3878[2]
Toluene	d_4^{25}, g/cm^3	0·86201	0·86231[2]
	n_D^{20}	1·4968	1·49693[2]

TABLE II

Refractive Indices of Mixtures at 20°C and Constants of Eq. (*1*)

Δ is the mean percentual deviation between calculated and experimental refractive indices.

Toluene(1)–butanol(2)		toluene(1)–isobutanol(2)		toluene(1)–sec-butyl alcohol(2)		tert-butyl alcohol(1)–toluene(2)	
A_1 = 0·00421		0·00335		0·00347		0·00463	
A_2 = 0·01260		0·00875		0·01115		0·00035	
A_3 = 0·01378		0·01415		−0·00454		−0·00106	
Δ = 0·07		0·03		0·06		0·11	
x_1	n_D^{20}	x_1	n_D^{20}	x_1	n_2^{20}	x_1	n_D^{20}
0·1281	1·4132	0·1149	1·4085	0·1258	1·4108	0·1118	1·4845
0·2045	1·4212	0·1961	1·4172	0·1883	1·4171	0·2273	1·4721
0·2756	1·4288	0·2653	1·4246	0·2730	1·4259	0·3148	1·4628
0·3692	1·4381	0·3568	1·4342	0·4637	1·4449	0·4298	1·4501
0·4663	1·4477	0·4816	1·4469	0·5780	1·4561	0·5399	1·4380
0·6695	1·4668	0·5700	1·4557	0·6545	1·4636	0·5955	1·4320
0·7937	1·4781	0·7292	1·4710	0·7607	1·4738	0·7929	1·4100
0·8751	1·4853	0·7609	1·4740	0·8540	1·4827	0·9037	1·3980
		0·8878	1·4860				

correlated by the equation

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

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 squares method from experimental values. Relation (*1*) was employed for the calculation of interpolation tables serving for determining the concentration dependence of the refractive index. Experimental values and calculated constants are given in Table II.

TABLE III
The Vapour–Liquid Equilibrium

333·31 K			343·40 K			353·44 K		
x_1	y_1	P, kPa	x_1	y_1	P, kPa	x_1	y_1	P, kPa
				Toluene(1)–butanol(2)				
0·010	0·073	8·764	0·034	0·173	16·18	0·011	0·056	23·42
0·031	0·185	9·747	0·064	0·277	18·03	0·033	0·148	25·40
0·111	0·426	12·97	0·110	0·385	20·37	0·073	0·261	28·47
0·134	0·467	13·70	0·187	0·498	23·32	0·117	0·355	31·31
0·240	0·592	16·26	0·240	0·548	24·94	0·194	0·464	35·11
0·337	0·652	17·87	0·308	0·598	26·47	0·309	0·564	39·08
0·387	0·675	18·45	0·345	0·620	27·17	0·349	0·586	40·07
0·502	0·723	19·50	0·389	0·642	27·89	0·389	0·609	40·89
0·584	0·746	19·95	0·446	0·669	28·63	0·452	0·638	41·95
0·684	0·773	20·33	0·510	0·692	29·42	0·513	0·664	42·98
0·796	0·808	20·51	0·687	0·752	30·40	0·705	0·745	44·11
0·859	0·836	20·46	0·796	0·793	30·58	0·798	0·775	44·06
0·914	0·869	20·18	0·908	0·858	29·91	0·860	0·809	43·57
0·940	0·896	19·94	0·940	0·892	29·45	0·940	0·889	42·12
0·981	0·957	19·20	0·980	0·958	28·26	0·982	0·958	40·30
				Isobutanol(1)–toluene(2)				
0·003	0·009	18·93	0·003	0·009	27·73	0·028	0·081	41·69
0·028	0·082	19·81	0·028	0·081	29·25	0·091	0·206	45·76
0·092	0·195	21·60	0·104	0·216	32·29	0·106	0·220	46·37
0·104	0·205	21·76	0·198	0·282	33·62	0·137	0·252	47·37
0·135	0·231	22·10	0·289	0·328	34·11	0·197	0·300	48·57
0·199	0·270	22·51	0·407	0·375	34·11	0·285	0·345	49·52
0·291	0·304	22·72	0·489	0·407	33·84	0·404	0·398	49·78

TABLE III
(*continued*)

333·31 K			343·40 K			353·44 K		
x_1	y_1	P, kPa	x_1	y_1	P, kPa	x_1	y_1	P, kPa
0·410	0·347	22·59	0·606	0·459	32·97	0·487	0·435	49·58
0·496	0·377	22·35	0·683	0·498	32·21	0·604	0·488	48·58
0·786	0·537	19·62	0·783	0·573	30·37	0·686	0·537	47·43
0·808	0·560	19·17	0·824	0·617	29·32	0·777	0·606	45·32
0·825	0·577	18·93	0·854	0·657	28·51	0·864	0·705	42·51
0·875	0·645	17·62	0·915	0·749	26·14	0·915	0·776	40·07
0·917	0·721	16·42	0·943	0·816	24·81	0·967	0·897	36·71
0·972	0·883	14·47	0·972	0·898	23·26	0·971	0·906	36·52
Sec-butyl alcohol(1)–toluene(2)								
0·004	0·017	18·94	0·042	0·130	30·97	0·005	0·017	39·70
0·041	0·141	21·07	0·048	0·155	31·41	0·041	0·130	44·04
0·083	0·226	22·71	0·083	0·228	33·46	0·068	0·197	46·14
0·125	0·278	23·74	0·123	0·283	34·97	0·166	0·332	51·96
0·166	0·313	24·34	0·167	0·324	36·13	0·268	0·406	54·62
0·270	0·372	25·14	0·322	0·421	38·14	0·322	0·439	55·45
0·332	0·400	25·37	0·431	0·472	38·70	0·427	0·493	56·64
0·432	0·446	25·58	0·538	0·524	38·75	0·541	0·547	57·00
0·543	0·497	25·50	0·605	0·568	38·56	0·731	0·665	55·91
0·742	0·611	24·31	0·736	0·636	37·62	0·796	0·714	54·93
0·798	0·658	23·59	0·798	0·688	36·65	0·866	0·785	53·09
0·873	0·738	22·27	0·871	0·765	35·04	0·946	0·926	49·72
0·966	0·911	19·76	0·965	0·921	31·88			
Toluene(1)–tert-butyl alcohol(2)								
0·024	0·032	39·41	0·028	0·035	61·99	0·047	0·053	93·52
0·062	0·080	39·93	0·063	0·072	62·45	0·078	0·077	93·59
0·100	0·117	40·28	0·100	0·106	62·66	0·136	0·123	93·35
0·152	0·161	40·53	0·153	0·150	62·71	0·177	0·151	92·95
0·270	0·239	40·42	0·275	0·222	61·92	0·215	0·172	92·41
0·339	0·271	40·13	0·339	0·253	61·22	0·283	0·212	91·14
0·407	0·307	39·55	0·398	0·281	60·40	0·395	0·266	88·56
0·497	0·343	38·77	0·496	0·323	58·65	0·494	0·309	85·78
0·546	0·366	38·27	0·551	0·348	57·65	0·596	0·356	82·37
0·698	0·436	35·74	0·698	0·420	53·51	0·688	0·404	78·06
0·837	0·533	31·81	0·747	0·449	51·56	0·864	0·553	63·99
0·867	0·570	30·49	0·838	0·522	46·85	0·908	0·630	58·02
0·937	0·701	25·83	0·910	0·626	41·01	0·922	0·663	55·74
0·982	0·874	21·19	0·955	0·753	35·16	0·970	0·824	46·49

RESULTS

The vapour–liquid equilibria were measured at three temperature levels: 333·31, 343·40, and 353·44 K. Results of these measurements are summarized in Table III.

The data were correlated according to the Barker's method[5] by the relations

$$P = \gamma_1 P_1 + \gamma_2 P_2 \tag{2}$$

$$P_1 = x_1 P_1^0 \exp\left[(V_1 - B_1)(P - P_1^0)/RT\right] \tag{3}$$

$$P_2 = x_2 P_2^0 \exp\left[(V_2 - B_2)(P - P_2^0)/RT\right], \tag{4}$$

where P is the total pressure, γ_i is the activity coefficient, P_i^0 is the saturated vapour pressure of pure component i, V_i is the molar volume of pure liquid component i, B_i is the second virial coefficient, x_i and y_i are mole fractions of component i in the liquid and vapour phase, respectively, T is temperature, and R gas constant. The numerical values are collected in Table IV. The saturated vapour pressures of pure components were determined experimentally, virial coefficients were extrapolated from data[6] and values of molar liquid volumes were roughly extrapolated from

TABLE IV
Some Physicochemical Constants of the Pure Components

Substance	T, K	P^0, kPa	B, cm^3/mol	V, cm^3/mol
Butanol	333·31	8·215	−1·9	0·096
	343·40	13·70	−1·8	0·097
	353·44	22·40	−1·7	0·099
Isobutanol	333·31	13·24	−1·3	0·096
	343·40	21·44	−1·2	0·097
	353·44	34·11	−1·1	0·099
Sec-butyl alcohol	333·31	18·49	−1·3	0·096
	343·40	30·24	−1·2	0·097
	353·44	47·27	−1·1	0·099
Tert-butyl alcohol	333·31	38·95	−1·2	0·100
	343·40	61·56	−1·1	0·101
	353·44	92·95	−1·0	0·102
Toluene	333·31	18·64	−1·8	0·111
	343·40	27·42	−1·7	0·112
	353·44	39·22	−1·6	0·114

available data. The activity coefficient was approximated by the Redlich–Kister 4th-order equation

$$\log \gamma_1 = x_2^2[b + c(3x_1 - x_2) + d(x_1 - x_2)(5x_1 - x_2)],$$

$$\log \gamma_2 = x_1^2[b + c(3x_2 - x_1) + d(x_2 - x_1)(5x_2 - x_1)], \qquad (5)$$

where b, c, d are constants. Relations (3)–(5) were substituted into Eq. (2) wherefrom coefficients b, c, and d, which characterize the system at a given temperature, were evaluated by the least squares method (minimization of pressure deviations). Together with standard deviations in the vapour phase composition and pressure they are given in Table V.

The employed correlation method satisfies automatically the consistency test[7], which possesses several advantages over the commonly used Herrington equal area test.

TABLE V

Constants in the Redlich–Kister Expansion and Standard Deviations in Pressure and the Vapour Phase Composition

System	T, K	b	c	d	σ_p, kPa	σ_y
Toluene(1)–butanol(2)	333·31	0·5925	0·1246	0·0729	0·035	0·0048
	343·40	0·5715	0·1010	0·0699	0·035	0·0055
	353·44	0·5312	0·0898	0·0496	0·055	0·0050
Isobutanol(1)–toluene(2)	333·31	0·5638	−0·1042	0·0578	0·073	0·0162
	343·40	0·5467	−0·0808	0·0632	0·067	0·0085
	353·44	0·5053	−0·0726	0·0636	0·085	0·0081
Sec-butyl alcohol(1)–toluene(2)	333·31	0·5456	−0·0946	0·0624	0·041	0·0055
	343·40	0·5089	−0·0799	0·0497	0·053	0·0086
	353·44	0·4726	−0·0703	0·0139	0·154	0·0107
Toluene(1)–tert-butyl alcohol(2)	333·31	0·5264	0·0629	0·0406	0·054	0·0094
	343·40	0·4895	0·0575	0·0316	0·082	0·0033
	353·44	0·4591	0·0492	0·0106	0·085	0·0037

REFERENCES

1. Ruiz Echevarria H.: This Journal *38*, 1295 (1973).
2. *Selected Values of Properties of Hydrocarbons and Related Compounds.* Amer. Petrol. Inst. Res. Proj. 44, extant 1972.
3. Brown I., Fock W., Smith F.: J. Chem. Thermodyn. *1*, 273 (1969).
4. Dvořák K., Boublík T.: This Journal *28*, 1249 (1963).
5. Barker J. A.: Aust. J. Chem. *6*, 207 (1953).
6. Dymond J. H., Smith E. B.: *The Virial Coefficients of Gases.* Clarendon Press, Oxford 1969.
7. Van Ness H. C., Byer S. M., Gibbs R. E.: AIChE J. *19*, 238 (1973).

Translated by K. Hlavatý.