VAPOUR–LIQUID EQUILIBRIUM IN THE ISOBUTYL FORMATE–ISOBUTYL ALCOHOL AND n-BUTYL FORMATE–ISOBUTYL ALCOHOL SYSTEMS AT ATMOSPHERIC PRESSURE*

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

Isobaric vapour–liquid equilibria in the isobutyl formate–isobutyl alcohol and n-butyl formate–isobutyl alcohol systems have been measured at atmospheric pressure. A modified circulation still of the Gillespie type has been used for the measurements. The experimental data have been correlated by means of the third- and fourth-order Margules equations.

The knowledge of vapour–liquid equilibrium data in the alcohol–ester systems is required for the separation of mixtures produced by esterification of the alcohol with the acid. Since the title systems needed have not been found in the literature we have been made to carry out the experimental determination.

EXPERIMENTAL

Substances used. Isobutyl and n-butyl formates have been synthetized and purified in the Department of Heterogeneous Reactions of our Institute. Briefly, the raw product has been prepared by esterification of excess isobutyl alcohol (n-butyl alcohol) with formic acid in the presence of concentrated H_2SO_4, then water has been distilled off azeotropically, the mixture has been neutralized and distilled. The excess of the alcohol in ester has been removed by boiling with acetic anhydride, the reaction mixture has been distilled, neutralized and finally the ester fraction has been thoroughly distilled on a packed column filled with the Dixon rings (≈40 TP). The purity of the fractions of the final ester has been checked during distillation by gas chromatography, the products being found not to contain either free alcohols or acids. The water content determined by the method of K. Fischer has been lower than 0·002%. The physico-chemical constants of the esters have been as follows: isobutyl formate, n.b.p. 98·54°C (ref.[1-3] 98·4), d_4^{20} 0·8858 g/cm^3 (ref.[2,3] 0·88535), n_D^{20} 1·3854 (ref.[1-3] 1·38546); n-butyl formate, n.b.p. 107·32°C (ref.[1,3] 106·6, ref.[2] 106·8), d_4^{20} 0·9027 g/cm^3 (ref.[3] 0·8917), n_D^{20} 1·3882 (ref.[1,3] 1·38903). Isobutyl

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alcohol, analytical reagent grade (Lachema, Brno, Czechoslovakia) has been dried with anhydrous K_2CO_3, filtered and distilled on a fifty-plate bubble-cup column[1]. The water content in the pure product has been lower than 0·01% as determined by titrating with the K. Fischer reagent. The found values of physico-chemical constants of the isobutyl alcohol used have been: n.b.p. 107·75°C (ref.[4] 107·9–108·1), d_4^{20} 0·8019 (ref.[4,5] 0·8020–0·8021), n_D^{20} 1·3959 (ref.[4] 1·3959).

Analytical method. The analysis of the equilibrium vapour and liquid samples has been made by means of a Paar digital densimeter DMA 02C. The dependence of the sample compositions on the measured value of period has been expressed by the relation

$$(x_1M_1 + x_2M_2)/T = x_1M_1/T_1 + x_2M_2/T_2 + x_1x_2(x_1A_1 + x_2A_2 - x_1x_2A_3)\,, \tag{1}$$

where T is the measured value of oscillation period of mixture, M_1 and M_2 are molecular masses, T_1 and T_2 periods, x_1, $x_2 = 1 - x_1$ mole fractions of pure components 1 and 2, respectively, A_1, A_2, A_3 are constants evaluated from calibration measurements by the least-square method. Eq. (*1*) has represented the calibration data with mean deviation lower than 0·2%. In terms of the constants A_1, A_2, A_3, the interpolation table has been computed (with a step $\Delta x = 0.001$) for direct reading of sample compositions.

Saturated vapour pressures of all three substances have been measured using a Swietoslawski ebulliometer[6]. The measured values of saturated vapour pressures of pure components have been correlated by the Antoine equation

$$\log P^0 = A - B/(t + C)\,, \tag{2}$$

where A, B, C are the adjustable parameters evaluated from the experimental data, P^0 is the saturated vapour pressure (kPa) and t temperature (°C).

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[6]. The pressure in the system has been maintained at 101·3 kPa by means of manostat and nitrogen overpressure and checked by measuring the boiling point of water in an ebulliometer connected parallel to the equilibrium still. The temperature has been measured by mercury-in-glass calorimetric standards calibrated by means of a Mueller bridge with a platinum resistance thermometer (Leeds and Northrup). The equilibrium samples have been taken for analysis only when the boiling point in the still has not changed for 30 minutes.

RESULTS

The experimental values of saturated vapour pressures, the evaluated constants A, B, C of the Antoine equation (*2*) and the comparison of measured and calculated values are given in Tables I (isobutyl alcohol), II (n-butyl formate) and III (isobutyl formate).

The relations for the description of dependence of equilibrium variables in a binary system with non-ideal vapour phase can be written in the form

$$\ln \gamma_1 = \ln (y_1P/x_1P_1^0) + ((B_{11} - V_1)(P - P_1^0) + P\delta_{12}y_2^2)/RT, \tag{3a}$$

$$\ln \gamma_2 = \ln (y_2 P / x_2 P_2^0) + ((B_{22} - V_2)(P - P_2^0) + P\delta_{12} y_1^2)/RT\,, \qquad (3b)$$

where

$$\delta_{12} = 2B_{12} - B_{11} - B_{22}\,, \qquad (4)$$

TABLE I

Saturated Vapour Pressures of Isobutyl Alcohol

t, °C	P, kPa		Deviation	
	exptl.	calc.[a]	kPa	%
51·350	7·834	7·822	−0·012	−0·16
52·980	8·579	8·570	−0·001	−0·11
54·990	9·581	9·575	−0·005	−0·06
56·160	10·208	10·204	−0·004	−0·04
58·460	11·531	11·544	0·013	0·12
60·025	12·543	12·539	−0·004	−0·03
60·805	13·043	13·060	0·017	0·14
61·000	13·191	13·194	0·003	0·02
62·030	13·927	13·917	−0·009	−0·07
63·645	15·131	15·117	−0·013	−0·09
64·260	15·604	15·597	−0·007	−0·04
64·700	15·952	15·948	−0·004	−0·02
66·680	17·599	17·611	0·013	0·07
66·980	17·857	17·874	0·017	0·10
68·870	19·606	19·614	0·008	0·04
70·190	20·896	20·913	0·017	0·08
72·240	23·059	23·070	0·011	0·05
75·580	26·982	26·982	0·000	0·00
75·815	27·270	27·276	0·007	0·02
77·710	29·756	29·752	−0·004	−0·01
78·710	31·156	31·132	−0·024	−0·08
80·330	33·477	33·481	0·004	0·01
80·680	33·996	34·006	0·011	0·03
83·600	38·686	38·669	−0·017	−0·04
83·780	38·995	38·975	−0·023	−0·06
87·585	45·891	45·873	−0·017	−0·04
92·910	57·225	57·190	−0·033	−0·06
95·430	63·293	63·293	0·000	0·00
97·750	69·425	69·374	−0·051	−0·07
102·690	83·820	83·916	0·096	0·11
Standard deviation			*0·025*	

[a] Antoine vapour pressure constants: $A = 6{\cdot}58646$, $B = 1322{\cdot}416$, $C = 180{\cdot}931$.

TABLE II

Saturated Vapour Pressures of n-Butyl Formate

t, °C	P, kPa		Deviation	
	exptl.	calc.[a]	kPa	%
80·530	42·090	42·108	0·018	0·04
83·440	46·625	46·692	0·068	0·14
84·820	49·101	49·002	−0·099	−0·02
87·260	53·402	53·307	−0·095	−0·18
90·120	58·654	58·734	0·079	0·14
93·190	65·054	65·037	−0·017	−0·03
96·180	71·646	71·683	0·037	0·05
98·780	77·880	77·888	0·008	0·01
101·450	84·622	84·695	0·073	0·09
103·780	90·978	91·011	0·032	0·04
105·890	96·991	97·044	0·053	0·05
106·580	99·245	99·084	−0·161	−0·16
Standard deviation			*0·086*	

[a] Antoine vapour pressure constants: $A = 6{\cdot}03014$, $B = 1245{\cdot}850$, $C = 202{\cdot}247$.

TABLE III

Saturated Vapour Pressures of Isobutyl Formate

t, °C	P, kPa		Deviation	
	exptl.	calc.[a]	kPa	%
70·320	39·634	39·601	−0·033	−0·08
74·075	45·408	45·398	−0·012	−0·03
77·985	52·101	52·121	0·021	0·04
81·520	58·836	58·854	0·016	0·03
84·420	64·692	64·870	0·178	0·27
87·390	71·727	71·519	−0·208	−0·29
90·340	78·639	78·638	−0·001	−0·00
92·710	84·669	84·745	0·076	0·09
95·220	91·609	91·607	−0·001	−0·00
97·160	97·236	97·199	−0·037	−0·04
Standard deviation			*0·110*	

[a] Antoine vapour pressure constants: $A = 5{\cdot}78268$, $B = 1093{\cdot}134$, $C = 190{\cdot}884$.

γ_1, γ_2 are the activity coefficients, y_1, y_2 mole fractions in the vapour phase of the component 1 and 2, respectively, P is the system pressure, T the system absolute temperature, P_1^0, P_2^0 are the saturated vapour pressures, V_1, V_2 the molar volumes of liquid, B_{11}, B_{22} the second virial coefficients of pure components 1 and 2, B_{12} the second cross virial coefficient and R the gas constant.

The concentration dependence of activity coefficients has been expressed by means of the Margules 3rd order equation[6]

$$\log\left(\gamma_1/\gamma_2\right) = x_2^2A_{12} - x_1^2A_{21} - 2x_1x_2(A_{12} - A_{21}) \qquad (5)$$

TABLE IV

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

x_1	y_1	t, °C	$(y_{1,\mathrm{calc}} - y_{1,\mathrm{exp}})^a$	
			Marg. 3	Marg. 4
0·0110	0·0230	107·35	0·0012	0·0008
0·0192	0·0418	107·07	−0·0003	−0·0008
0·0297	0·0620	106·72	0·0008	0·0003
0·0468	0·0940	106·11	0·0018	0·0013
0·0906	0·1745	104·83	−0·0033	−0·0028
0·1274	0·2356	103·86	−0·0093	−0·0077
0·1792	0·2950	102·81	−0·0013	0·0017
0·2384	0·3664	101·63	−0·0062	−0·0023
0·3322	0·4506	100·35	−0·0016	0·0019
0·4850	0·5677	98·82	0·0018	0·0019
0·5587	0·6190	98·31	0·0038	0·0022
0·6046	0·6532	97·84	0·0029	0·0004
0·6432	0·6802	97·79	0·0035	0·0004
0·7062	0·7250	97·73	0·0049	0·0015
0·7820	0·7854	97·58	0·0035	0·0007
0·8452	0·8432	97·58	−0·0010	−0·0025
0·8942	0·8870	97·70	0·0002	−0·0003
0·8922	0·8897	97·30	−0·0041	−0·0046
0·9394	0·9335	97·79	−0·0011	−0·0008
0·9637	0·9590	97·96	−0·0006	−0·0002
0·9782	0·9737	98·10	0·0009	0·0013
Mean			*0·0026*	*0·0017*

[a] Constants of correlation equations: Marg. 3: $A_{12} = 0{\cdot}2413$, $A_{21} = 0{\cdot}2255$; Marg. 4: $A_{12} = 0{\cdot}2331$, $A_{21} = 0{\cdot}2155$, $D = -0{\cdot}0640$; Second virial coefficients[10]: $B_{11} = -1171{\cdot}00$, $B_{22} = -1230{\cdot}00$, $B_{12} = -1187{\cdot}00$ cm^3/mol.

and the Margules 4th order equation[6]

$$\log(\gamma_1/\gamma_2) = x_2^2 A_{12} - x_1^2 A_{21} - 2x_1x_2(A_{12} - A_{21} + (x_2 - x_1)\,D)\,, \tag{6}$$

where A_{12}, A_{21}, D are constants characteristic of the given mixture and equation.

Since our aim has been to provide data for chemical engineers we have used the recommended[7] objective function F suitable especially for the determination of the number of stages of distillation equipment, *viz.* the difference of the ratios of loga-

TABLE V

Vapour–Liquid Equilibrium Data in the n-Butyl Formate(1)–Isobutyl Alcohol(2) System at 101·3 kPa

x_1	y_1	t, °C	$(y_{1,\mathrm{calc}} - y_{1,\mathrm{exp}})^a$ Marg. 3	Marg. 4
0·0615	0·0912	106·96	−0·0035	0·0024
0·0830	0·1188	106·45	−0·0022	0·0022
0·0828	0·1205	106·71	−0·0043	0·0000
0·1112	0·1590	106·34	−0·0063	−0·0052
0·1370	0·1910	106·01	−0·0064	−0·0089
0·1658	0·2267	105·65	−0·0081	−0·0146
0·2086	0·2698	105·22	−0·0034	−0·0153
0·2530	0·3158	104·86	−0·0032	−0·0189
0·3116	0·3688	104·54	0·0000	−0·0173
0·3712	0·4194	104·29	0·0021	−0·0132
0·4602	0·4830	104·22	0·0101	0·0031
0·5750	0·5772	104·28	0·0011	0·0077
0·7134	0·6955	104·77	−0·0149	−0·0002
0·7768	0·7564	105·08	−0·0244	−0·0118
0·8218	0·7944	105·48	−0·0223	−0·0135
0·8408	0·8096	105·65	−0·0193	−0·0125
0·8698	0·8394	105·84	−0·0192	−0·0161
0·9005	0·8642	106·23	−0·0095	−0·0102
0·9386	0·9072	106·61	−0·0040	−0·0083
0·9860	0·9678	107·03	0·0076	0·0046
Mean			*0·0086*	*0·0093*

[a] Constants of correlation equations: Marg. 3: $A_{12} = 0{\cdot}1688$, $A_{21} = 0{\cdot}2673$; Marg. 4: $A_{12} = 0{\cdot}2470$, $A_{21} = 0{\cdot}3303$, $D = 0{\cdot}3531$; Second virial coefficients[10]: $B_{11} = -1333{\cdot}00$, $B_{22} = -1168{\cdot}00$, $B_{12} = -1230{\cdot}00$ cm^3/mol.

rithms of activity coefficients

$$F = \ln(\gamma_1/\gamma_2)_{\text{exp}} - \ln(\gamma_1/\gamma_2)_{\text{calc}} \,. \qquad (7)$$

The constants of the correlation equations have been computed by least-square minimization of the function F.

Virial coefficients needed to compute activity coefficients in terms of Eqs (*3*) and (*4*) are very limited. Only second virial coefficients of isobutyl alcohol can be found in the literature[8]. For n-butyl formate even the critical constants are not known and have had to be estimated by means of the Lydersen method[9]. This has made us use the Hayden and O'Connell method[10] for predicting the second virial coefficients of pure substances as well as for the mixtures. With regard to small differences in the boiling points of components in the binary systems and an approximate character of the estimated virial coefficients, the temperature dependence of the virial coefficients has not been considered and the values used have been computed for the temperature equal to the average value of normal boiling points of the respective pure components.

The results of the vapour–liquid equilibrium measurements together with the constants of correlation equations, second virial coefficients and the deviations between computed and experimental values of the vapour phase composition are given in Table IV (the isobutyl formate–isobutyl alcohol system) and Table V (the n-butyl formate–isobutyl alcohol system).

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