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Isobaric Vapor–Liquid Equilibria for Methyl Propanoate + Isobutyl Alcohol

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Vapor–liquid equilibrium data are reported for methyl propanoate + isobutyl alcohol at pressures of 74.66, 101.32, and 127.99 kPa. No azeotropic points have been found. All the experimental data are thermodynamically consistent according to the point-to-point test. The data agree with the values predicted from ASOG, UNIFAC, and SUPERFAC group contribution models, with an average error of less than 15%.

Introduction

As a continuation of our studies on vapor–liquid equilibria (VLE) of binary mixtures of a methyl ester + alkanols (*1–3*), herein we present the VLE measurements for methyl propanoate + isobutyl alcohol (2-methyl-1-propanol) at three different pressures of 74.66, 101.32, and 127.99 kPa (560, 760, and 960 Torr, respectively). No VLE data have been found in the literature for this system.

The experimental data are compared with those predicted by several group contribution models of interest in chemical engineering: ASOG (*4*), UNIFAC with different alkanol/ester interaction parameters (*5–7*), and SUPERFAC (*8*).

Experimental Section

Materials. All compounds used in this study were from Fluka AG. The source of methyl propanoate was the same as in a previous paper (*2*). Isobutyl alcohol was a puriss p.a. product of >99.5 mol % purity. The liquids were degassed ultrasonically before use and stored in the dark for several days over molecular sieves (Union Carbide, type 4Å, from Fluka AG).

After these treatments, the physical properties of the pure substances were determined experimentally. The characteristics of methyl propanoate did not differ significantly from the values published earlier (*2*). For isobutyl alcohol, we found a density ρ(298.15K) = 798.13 kg m^{-3} (797.8, ref 9), refractive index n(D,298.15K) = 1.3950 (1.3939, ref 9), and normal boiling point T_b = 380.3 K (380.81, ref 9).

Apparatus and Procedure. The ebulliometric equipment and the experimental method of operation have been described previously (*1, 10*). The equilibrium compositions of the liquid phase, x, and the vapor phase, y, were determined by densimetry by using a previously obtained calibration curve. The accuracies in mole fraction of the liquid and vapor phase compositions were, respectively, 0.001 and 0.002.

Experimental Results and Treatment of Data

Table I. Experimental Vapor Pressure $p_i°$ of Isobutyl Alcohol (2-Methyl-1-propanol) as a Function of Temperature T

T/K	$p_i°$/kPa	T/K	$p_i°$/kPa
392.72	154.84	379.66	98.49
392.12	151.79	378.63	94.87
391.41	148.26	377.93	92.46
390.49	143.76	377.02	89.39
389.73	140.01	376.07	86.26
388.94	136.33	374.99	82.70
388.14	132.65	373.88	79.27
387.27	128.79	372.87	76.26
387.12	127.99	372.27	74.66
386.57	125.71	371.65	72.71
385.74	122.16	370.41	69.27
385.00	118.99	369.09	65.76
384.26	115.98	367.73	62.30
383.36	112.35	366.23	58.61
382.35	108.46	364.59	54.90
381.46	104.98	363.15	51.74
380.81	102.53	361.61	48.58
380.39	101.32		

Table II. Antoine Coefficients A, B, and C, Equation 1, Used in the Treatment of VLE Data, Temperature Range, T/K, and Standard Deviations, $s(p_i°)$

component	A	B	C	T/K range	$s(p_i°)$/kPa	ref
methyl propanoate	6.588 81	1469.36	30.99	300–380	0.04	11
isobutyl alcohol	6.069 98	1049.74	122.18	350–400	0.05	this work
	6.345 05	1190.38	106.48			9

Pure Compounds. The vapor pressure $p_i°$ of the pure liquids have an important effect on the computation of the vapor–liquid equilibrium data. Therefore, new experimental $p_i°$ data were taken in the same equilibrium still. The vapor pressures of methyl propanoate agreed with those published in a previous paper (*11*). Table I lists the data obtained for isobutyl alcohol. The values so obtained were correlated through the Antoine equation

$$\log(p_i°/\text{kPa}) = A - B/[(T/\text{K}) - C] \qquad (1)$$

with constants A, B, and C and standard deviations $s(p_i°)$ calculated by a nonlinear regression procedure (*12*) (Table II).

Mixtures. The experimental isobaric VLE data for methyl propanoate (1) + isobutyl alcohol (2) at the pressures p of 74.66 ± 0.02, 101.32 ± 0.02, and 127.99 ± 0.2 kPa are presented in Table III and Figure 1. The activity coefficients, γ_i, in the liquid phase were calculated using the equation

$$\gamma_i = \left(\frac{\phi_i y_i p}{x_i \phi_i° p_i°}\right) \exp[(p_i° - p)v_i^L/RT] \qquad (2)$$

The fugacity coefficients, ϕ_i and $\phi_i°$, were calculated for each equilibrium temperature in terms of the pure and cross second virial coefficients estimated from the Hayden and O'Connell method (*13*). The molar volumes, v_i^L, were calculated using the Yen–Woods equation (*14*).

The consistency test proposed by Fredenslund et al. (*15*) was applied to each system using the physical properties

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Table III. Experimental Vapor–Liquid Equilibrium Data for Methyl Propanoate (1) + Isobutyl Alcohol (2) at Constant Pressure p, Temperature T, Liquid-Phase Mole Fraction x_1, Vapor-Phase Mole Fraction y_1, and Calculated Activity Coefficients γ_i

T/K	x_1	y_1	γ_1	γ_2	T/K	x_1	y_1	γ_1	γ_2
p = 74.66 kPa									
372.27	0.0000	0.0000		1.000	353.68	0.4069	0.7026	1.191	1.093
370.06	0.0220	0.1063	2.017	0.997	352.82	0.4374	0.7247	1.175	1.109
369.32	0.0337	0.1409	1.783	0.999	352.06	0.4686	0.7441	1.154	1.130
368.51	0.0462	0.1768	1.671	1.001	351.45	0.4970	0.7611	1.136	1.147
367.66	0.0591	0.2108	1.597	1.007	350.64	0.5351	0.7829	1.114	1.171
366.88	0.0731	0.2465	1.545	1.007	350.00	0.5640	0.7991	1.102	1.190
366.15	0.0852	0.2761	1.518	1.010	349.37	0.5981	0.8167	1.084	1.214
365.41	0.1004	0.3078	1.469	1.012	348.73	0.6311	0.8327	1.070	1.244
364.55	0.1152	0.3424	1.460	1.012	348.15	0.6676	0.8497	1.053	1.275
363.72	0.1332	0.3768	1.425	1.013	347.56	0.6988	0.8639	1.043	1.311
362.99	0.1486	0.4031	1.397	1.019	347.02	0.7313	0.8790	1.033	1.341
361.96	0.1701	0.4412	1.379	1.022	346.60	0.7575	0.8898	1.024	1.381
361.06	0.1910	0.4741	1.356	1.025	346.01	0.7972	0.9089	1.014	1.405
360.11	0.2134	0.5042	1.330	1.035	345.50	0.8293	0.9235	1.007	1.437
359.13	0.2386	0.5384	1.309	1.038	344.98	0.8623	0.9386	1.002	1.467
357.85	0.2691	0.5786	1.298	1.044	344.46	0.8984	0.9554	0.997	1.482
357.28	0.2866	0.5981	1.283	1.045	343.97	0.9305	0.9701	0.994	1.488
356.64	0.3058	0.6176	1.267	1.051	343.55	0.9537	0.9804	0.994	1.495
356.13	0.3232	0.6349	1.252	1.053	343.22	0.9740	0.9892	0.994	1.492
355.58	0.3388	0.6480	1.241	1.065	342.27	1.0000	1.0000	1.000	
354.55	0.3752	0.6796	1.215	1.074					
p = 101.32 kPa									
380.39	0.0000	0.0000		1.000	361.74	0.4532	0.7103	1.136	1.102
378.71	0.0214	0.0884	1.827	0.993	360.98	0.4827	0.7300	1.122	1.122
377.83	0.0362	0.1279	1.601	0.996	360.51	0.5075	0.7468	1.108	1.127
376.87	0.0534	0.1720	1.499	0.998	359.72	0.5427	0.7679	1.092	1.151
376.08	0.0690	0.2081	1.435	1.000	359.03	0.5757	0.7879	1.079	1.168
375.27	0.0840	0.2434	1.411	1.001	358.41	0.6073	0.8043	1.065	1.197
374.50	0.0997	0.2755	1.375	1.004	357.91	0.6357	0.8192	1.052	1.218
373.70	0.1155	0.3090	1.362	1.005	357.42	0.6642	0.8350	1.043	1.232
372.85	0.1347	0.3449	1.335	1.006	356.83	0.6947	0.8501	1.034	1.264
371.97	0.1535	0.3770	1.314	1.012	356.41	0.7191	0.8607	1.025	1.301
371.08	0.1736	0.4100	1.296	1.016	355.76	0.7560	0.8804	1.018	1.324
370.22	0.1935	0.4412	1.283	1.020	355.23	0.7877	0.8960	1.011	1.355
369.30	0.2174	0.4750	1.263	1.024	354.77	0.8210	0.9125	1.003	1.380
368.56	0.2362	0.4999	1.250	1.029	354.17	0.8543	0.9291	1.000	1.412
366.78	0.2794	0.5570	1.241	1.038	353.76	0.8860	0.9446	0.994	1.437
365.72	0.3089	0.5890	1.225	1.048	353.38	0.9125	0.9581	0.991	1.441
364.82	0.3386	0.6177	1.204	1.057	352.92	0.9409	0.9720	0.990	1.456
363.91	0.3673	0.6453	1.192	1.065	352.46	0.9689	0.9853	0.989	1.484
363.14	0.3955	0.6664	1.170	1.082	352.20	0.9844	0.9926	0.989	1.507
362.41	0.4239	0.6890	1.154	1.092	351.77	1.0000	1.0000	1.000	
p = 127.99 kPa									
387.12	0.0000	0.0000		1.000	369.15	0.4593	0.6918	1.103	1.106
385.84	0.0163	0.0662	1.867	0.991	368.58	0.4843	0.7106	1.092	1.114
385.01	0.0317	0.1034	1.533	0.995	367.80	0.5205	0.7377	1.080	1.121
384.28	0.0433	0.1356	1.501	0.996	367.01	0.5530	0.7593	1.071	1.139
383.60	0.0581	0.1644	1.381	1.001	366.39	0.5837	0.7770	1.057	1.162
382.75	0.0786	0.2036	1.294	1.005	365.80	0.6157	0.7933	1.042	1.195
381.81	0.0953	0.2388	1.284	1.012	365.02	0.6514	0.8162	1.037	1.210
381.08	0.1108	0.2702	1.274	1.013	364.38	0.6870	0.8366	1.028	1.230
380.33	0.1285	0.3031	1.258	1.015	363.84	0.7161	0.8505	1.019	1.269
379.64	0.1443	0.3299	1.243	1.019	363.34	0.7488	0.8685	1.010	1.289
378.67	0.1707	0.3720	1.217	1.021	362.76	0.7808	0.8870	1.007	1.300
377.48	0.1997	0.4169	1.205	1.026	362.34	0.8078	0.9006	1.001	1.328
376.58	0.2199	0.4462	1.201	1.034	361.94	0.8301	0.9132	1.000	1.334
375.47	0.2485	0.4879	1.199	1.035	361.57	0.8570	0.9277	0.995	1.342
374.51	0.2712	0.5173	1.196	1.043	361.16	0.8858	0.9429	0.991	1.350
373.70	0.2918	0.5417	1.192	1.051	360.62	0.9162	0.9583	0.990	1.376
372.23	0.3435	0.5951	1.160	1.060	360.19	0.9436	0.9723	0.989	1.383
371.34	0.3749	0.6257	1.146	1.066	359.78	0.9674	0.9842	0.989	1.389
370.61	0.4022	0.6476	1.130	1.080	358.83	1.0000	1.0000	1.000	
369.87	0.4275	0.6691	1.122	1.090					

reported in the literature (*9, 15, 16*), and the Antoine constants calculated by us (Table II) with a third-order Legendre polynomial; the overall mean deviations, $\delta(y_1)$, obtained at each working pressure, for ester vapor-phase mole fraction y_1 were 0.004, 0.005, and 0.008 at, respectively, 74.66, 101.32, and 127.99 kPa. The thermodynamic consistency test of Moon et al. (*17*) gave, for a second-order function of g^E/RT and a fourth-order function of $\ln(\gamma_1/\gamma_2)$ and $\epsilon = 0.03$, the following results: (1) For the point test, $\delta = 3.15$, 2.18, and 2.98 at $p = 74.66$, 101.32, and 127.99 kPa, respectively. (2) For the area test, $A = 2.52$, 1.32, and 0.01 at $p = 74.66$, 101.32, and 127.99 kPa, respectively. (3) For the infinite dilution test, the values of I_1 and I_2 were 9.1 and 5.0 at 74.66 kPa, 12.5 and 3.5 at 101.32 kPa, and 10.4 and 14.8 at 127.99 kPa. Therefore, according to the conditions reported by Moon et al. (*17*), the VLE data are thermodynamically consistent. The area test of Redlich–Kister (*18*) indicates consistency at 74.66 and 101.32 kPa.

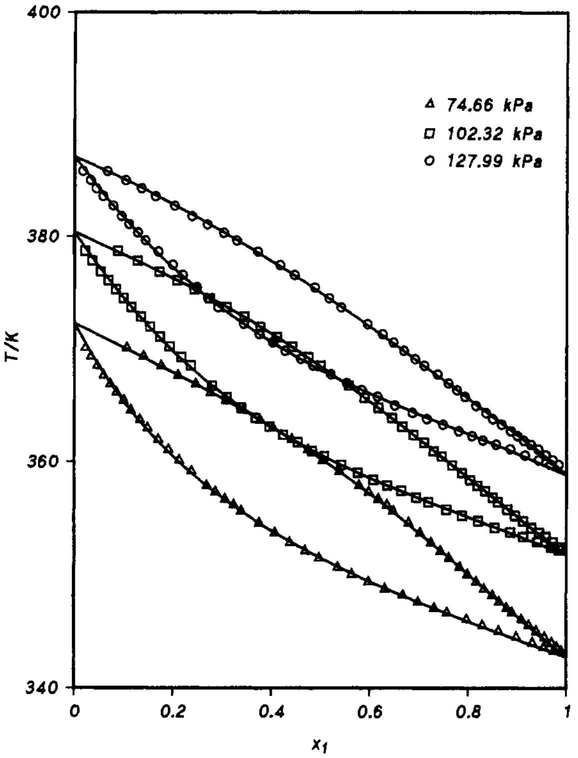

Figure 1. Representation of equilibrium temperature T *vs* liquid-phase x_1 or vapor-phase mole fractions y_1. Experimental points and fitting curves using eq 3 and coefficients of Table IV for methyl propanoate (1) + isobutyl alcohol (2).

Table IV. Parameters A_i and k in Equation 3 and Standard Deviation, $s(Q)$, at Constant Pressure P (T_i is the Boiling Temperature of Pure Component i)

p/kPa	A_0	A_1	A_2	A_3	k	s(Q)
		$Q = (y_1 - x_1)$ *vs* $z = x_1$				
74.66	5.691	−12.391	16.242	−9.005	0.93	0.001
101.32	4.315	9.132	12.367	−7.054	0.11	0.001
127.99	4.312	−11.078	15.974	−8.729	0.10	0.002
		$Q = (T - T_1x_1 - T_2x_2)/K$ *vs* $z = x_1$				
74.66	−53.78	39.45			0.33	0.15
101.32	−36.86	25.85			0.72	0.12
127.99	−31.38	23.50			0.93	0.15
		$Q = (T - T_1y_1 - T_2y_2)/K$ *vs* $z = y_1$				
74.66	7.77	16.49	−19.79		1.30	0.09
101.32	8.40	10.24	−14.12		0.76	0.08
127.99	9.42	−12.40	18.67		6.22	0.12

The experimental T–x_1–y_1 data were correlated with a polynomial equation of the form

$$Q = z(1-z)\sum_i A_i[z/(z + k(1-z)]^i \qquad (3)$$

where Q represents the fitting function (see Table IV) and z the variable x_1 or y_1. The parameters A_i were obtained by a linear-regression method optimizing the k values in order to get the best standard deviation values, $s(Q)$ (see ref 19). The results presented in Table IV and Figure 1 show the pressure influence on the VLE data.

Prediction of VLE with Group Contribution Models

The ASOG, UNIFAC, and SUPERFAC models were applied to the mixture studied considering the three working pressures and using different interaction group pairs. The prediction of the vapor-phase mole fractions, y_1, was carried out, and the overall mean deviations obtained in each of three cases were, with the ASOG model and using the pair OH/COO (*4*), $\delta(y_1)$ = 0.029, 0.038, and 0.048 (giving a mean error of less than 9%); with the UNIFAC model and the pair CCOH/COOC (*5*), $\delta(y_1)$ = 0.005, 0.012, and 0.023 (<4%); with the pair OH/COOC (*6*), $\delta(y_1)$ = 0.044, 0.050, and 0.058, (<11%); and with the pair COH/COO (*7*), $\delta(y_1)$ = 0.047, 0.055, and 0.064, (<12%); and with the temperature-dependent parameter in the SUPERFAC model, with the pair OH/COOC (*8*), $\delta(y_1)$ = 0.012, 0.014, and 0.020 (<4%).

Conclusions

The VLE data reported in this paper for methyl propanoate + isobutyl alcohol at 74.66, 101.32, and 127.99 kPa are thermodynamically consistent. No azeotropic points have been found. The data show that the ester vapor-phase mole fraction increases with decreasing pressure. The mixture presents slight positive deviations from ideality, especially at higher alkanol concentrations.

The group contribution methods ASOG, with the pair OH/COO, and UNIFAC, with the pairs OH/COOC and COH/COO, predict the VLE data with a mean error of 10%. The best predictions were obtained with the pair CCOH/COOC in the UNIFAC model and OH/COOC in the SUPERFAC model, with a mean error smaller than 4%.

Glossary

A_i,k	parameters in eq 3
p_i°	vapor pressure of pure component i, kPa
p	total pressure, kPa
R	universal molar gas constant, J K^{-1} mol^{-1}
s	standard deviation
T	temperature, K
T_i	boiling point of pure component i, K
x	liquid-phase mole fraction
y	vapor-phase mole fraction

Greek Letters

γ_i	activity coefficient of component i
δ	mean deviation
ρ	liquid density, kg m^{-3}

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