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Isobaric Vapor–Liquid Equilibria in the System Methyl Propanoate + *n*-Butyl Alcohol

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Isobaric vapor–liquid equilibria were determined at 74.66, 101.32, and 127.99 kPa for binary mixtures containing methyl propanoate + *n*-butyl alcohol by using a dynamic still with vapor and liquid circulation. No azeotrope was detected. The data were found to be thermodynamically consistent according to the point to point test. Application of the group-contribution models ASOG, UNIFAC, and modified UNIFAC to the activity coefficients at the three pressures studied gives average errors of less than 10%, 11%, and 3%, respectively.

Introduction

This paper forms part of a study about vapor–liquid equilibrium (VLE) at constant pressure on binary mixtures of methyl esters with normal alcohols (*1, 2*) and isoalcohols (*3, 4*). Data for this kind of mixtures at pressures different from atmospheric are scarce. In continuation of the series initiated, we report in this paper VLE data for methyl propanoate + *n*-butyl alcohol at 74.66, 101.32, and 127.99 kPa (560, 760, and 960 Torr, respectively). No other isobaric data have been found in the literature for this system, although Fernandez et al. (*5*) have measured isothermal VLE data at 348.15 K.

The experimental values have been compared with those estimated by group-contribution models ASOG (*6*), UNIFAC (*7–9*), and modified UNIFAC (*10*).

Experimental Section

Materials. All chemicals were commercially available (from Fluka AG) and were degassed before use by ultrasound and dried over molecular sieves (reference 69828 from Fluka AG) for several days. The measured physical properties of methyl propanoate did not differ significantly from the values presented previously (*2*). The characteristic properties of *n*-butyl alcohol (puriss pa >99.5 mol %) were density, $\rho/(298.15\ \mathrm{K}) = 805.93\ \mathrm{kg\ m^{-3}}$ (806.0, ref 11; 805.75, ref 12); refractive index, $n(\mathrm{D}, 298.15\mathrm{K}) = 1.3974$ (1.3973, ref 11; 1.397 41, ref 12), and the normal boiling point $T_b = 390.23$ K (390.81, ref 11; 390.875, ref 12).

Apparatus and Procedure. The experimental VLE data at the different pressures were measured using the dynamic recirculating apparatus described previously (*13*).

Vapor and liquid samples were analyzed by densimetry using an Anton-Paar DMA55 vibrating-tube densimeter calibrated with water and *n*-nonane and employing standard curves for the density–concentration of the mixture studied. The estimated accuracies in the mole fractions for the vapor and liquid phases were 0.002 and 0.001, respectively.

Results

Vapor Pressures. The equation used to correlate for the pure component vapor $p_2°$ exerts considerable influence on the thermodynamic treatment of the VLE data, and particularly of the activity coefficients. Therefore, new experimental values for the pairs ($p_i°$, T) were measured for *n*-butyl alcohol. Those corresponding to methyl propanoate were presented previously (*2*). Table I shows the data measured for *n*-butyl alcohol and Table II the constants *A*, *B*, and *C* of the compounds used herein for the Antoine equation.

Table I. Vapor Pressures of *n*-Butyl Alcohol as a Function of Temperature *T*

T/K	$p_i°$/kPa	T/K	$p_i°$/kPa
402.57	154.31	388.02	93.76
401.71	150.00	387.00	90.44
400.21	142.73	385.79	86.49
399.60	139.79	384.64	82.98
398.84	136.30	383.81	80.49
398.00	132.46	382.68	77.18
397.65	130.95	381.87	74.66
397.02	127.99	381.37	73.48
396.69	126.79	380.11	70.01
395.86	123.21	379.05	67.31
394.94	119.34	377.94	64.46
394.35	116.99	376.44	60.93
393.42	113.35	374.61	56.85
392.39	109.36	373.40	54.15
391.58	106.23	371.81	50.90
390.85	103.61	369.82	46.90
390.23	101.32	368.03	43.71
389.72	99.61	366.43	40.87
388.86	96.63	363.61	36.29

Table II. Antoine Equation[a] Coefficients *A*, *B*, and *C* Used in This Work, Temperature Range, and Standard Deviation, $s(p_i°)$

	A	B	C	T/K Range	$s(p_i°)$/kPa	ref
methyl propanoate	6.5888	1469.36	30.99	300–380	0.04	2
n-butyl alcohol	6.9170	1572.51	70.04	350–410	0.04	this work
	6.6017	1362.39	94.38			10
	6.7250	1439.57	85.68			13

[a] Antoine equation: $\log(p_i°/\mathrm{kPa}) = A - B/[(T/\mathrm{K}) - C)$.

Vapor–Liquid Equilibrium Data. The temperature and compositions of the vapor and liquid phases for methyl propanoate (1) + *n*-butyl alcohol (2) at the pressures p of 74.66, 101.32, and 127.99 kPa are given in Table III along with the activity coefficients, γ_i, calculated for each equilibrium stage using the following expression:

$$\phi_i p y_i = (\gamma_i p_i° x_i \Phi_i°) \exp[v_i^{\mathrm{L}}(p - p_i°)/RT] \qquad (1)$$

The molar volumes of the pure liquids, v_i^{L}, were calculated by the Yen–Woods equation (*15*); the values so obtained did not show significant differences from those calculated through a modified version of the Rackett equation; see ref 16. The fugacity coefficients, ϕ_i and $\phi_i°$, were calculated by using a

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Table III. Experimental Vapor–Liquid Equilibrium Data for the System Methyl Propanoate (1) + *n*-Butyl Alcohol (2) at Pressure *p*, Temperature *T*, Liquid-Phase Mole Fraction x_1, Vapor-Phase Mole Fraction y_1, and Calculated Activity Coefficients γ_1 and γ_2

T/K	x_1	y_1	γ_1	γ_2	T/K	x_1	y_1	γ_1	γ_2
p = 74.66 kPa									
381.87	0.0000	0.0000		1.000	355.66	0.4309	0.7793	1.170	1.129
381.14	0.0061	0.0377	1.888	0.992	354.71	0.4601	0.7954	1.153	1.151
380.12	0.0159	0.0822	1.624	0.993	353.91	0.4857	0.8095	1.141	1.167
378.92	0.0283	0.1335	1.531	0.994	352.84	0.5273	0.8272	1.112	1.210
377.71	0.0411	0.1824	1.490	0.995	352.04	0.5576	0.8411	1.097	1.233
376.72	0.0524	0.2216	1.459	0.995	351.29	0.5890	0.8536	1.080	1.266
375.24	0.0684	0.2774	1.479	0.996	350.53	0.6211	0.8651	1.064	1.311
374.04	0.0827	0.3203	1.441	0.997	350.25	0.6340	0.8706	1.059	1.320
371.27	0.1169	0.4115	1.418	1.000	349.56	0.6662	0.8824	1.045	1.358
370.09	0.1290	0.4377	1.414	1.016	348.83	0.7000	0.8943	1.033	1.406
368.70	0.1519	0.4897	1.399	1.002	348.13	0.7339	0.9057	1.021	1.462
367.34	0.1715	0.5226	1.377	1.015	347.55	0.7650	0.9166	1.011	1.506
365.94	0.1960	0.5614	1.349	1.018	346.91	0.7986	0.9280	1.002	1.564
364.55	0.2195	0.5962	1.334	1.023	346.31	0.8303	0.9388	0.995	1.625
363.42	0.2406	0.6223	1.315	1.032	345.77	0.8597	0.9491	0.990	1.678
363.19	0.2440	0.6277	1.317	1.032	345.20	0.8901	0.9595	0.985	1.753
361.65	0.2734	0.6613	1.298	1.043	344.56	0.9211	0.9704	0.984	1.842
361.23	0.2865	0.6731	1.277	1.044	344.02	0.9488	0.9807	0.984	1.900
360.22	0.3088	0.6929	1.258	1.057	343.60	0.9707	0.9887	0.983	1.986
359.06	0.3316	0.7123	1.249	1.077	343.31	0.9866	0.9947	0.983	2.066
358.20	0.3530	0.7306	1.236	1.082	342.27	1.0000	1.0000	1.000	
356.71	0.3983	0.7584	1.192	1.115					
p = 101.32 kPa									
390.23	0.0000	0.0000		1.000	364.43	0.4548	0.7680	1.128	1.151
389.92	0.0044	0.0199	1.482	0.995	363.65	0.4816	0.7838	1.113	1.166
388.56	0.0182	0.0787	1.468	0.995	362.46	0.5235	0.8049	1.090	1.205
387.65	0.0280	0.1168	1.450	0.995	361.66	0.5548	0.8205	1.075	1.228
385.67	0.0513	0.1920	1.371	1.002	360.90	0.5861	0.8338	1.058	1.264
384.45	0.0662	0.2382	1.361	1.004	360.07	0.6165	0.8486	1.051	1.288
383.38	0.0799	0.2780	1.355	1.004	359.35	0.6483	0.8611	1.037	1.330
381.96	0.0969	0.3231	1.349	1.011	358.68	0.6779	0.8732	1.027	1.366
380.12	0.1263	0.3888	1.309	1.011	358.01	0.7092	0.8862	1.017	1.399
378.62	0.1480	0.4367	1.308	1.011	357.38	0.7379	0.8968	1.009	1.448
376.88	0.1725	0.4802	1.295	1.027	356.69	0.7716	0.9098	1.001	1.498
375.86	0.1898	0.5104	1.287	1.028	356.10	0.8012	0.9214	0.994	1.540
374.56	0.2146	0.5478	1.267	1.031	355.32	0.8376	0.9349	0.990	1.618
373.62	0.2297	0.5678	1.261	1.042	354.77	0.8656	0.9457	0.986	1.672
372.18	0.2598	0.6048	1.237	1.050	354.23	0.8931	0.9563	0.983	1.734
371.09	0.2846	0.6337	1.221	1.052	353.80	0.9150	0.9655	0.982	1.756
369.90	0.3097	0.6589	1.208	1.065	353.32	0.9385	0.9746	0.982	1.827
368.45	0.3440	0.6882	1.185	1.087	352.99	0.9560	0.9818	0.982	1.858
367.35	0.3737	0.7128	1.167	1.098	352.66	0.9738	0.9893	0.981	1.863
366.53	0.3972	0.7304	1.153	1.108	352.41	0.9872	0.9948	0.981	1.876
365.30	0.4283	0.7531	1.144	1.126	351.77	1.0000	1.0000	1.000	
p = 127.99 kPa									
397.02	0.0000	0.0000		1.000	371.57	0.4887	0.7682	1.072	1.157
396.48	0.0048	0.0228	1.662	0.998	370.37	0.5248	0.7892	1.062	1.188
395.89	0.0117	0.0488	1.480	0.998	369.29	0.5609	0.8083	1.051	1.222
395.28	0.0201	0.0745	1.336	1.000	368.39	0.5908	0.8232	1.043	1.255
394.24	0.0332	0.1188	1.324	1.000	367.36	0.6311	0.8435	1.031	1.286
393.39	0.0436	0.1523	1.320	1.002	366.69	0.6588	0.8556	1.022	1.319
392.24	0.0597	0.1989	1.297	1.002	365.99	0.6878	0.8693	1.016	1.344
390.90	0.0788	0.2482	1.269	1.006	365.13	0.7266	0.8856	1.005	1.393
389.63	0.0963	0.2926	1.264	1.009	364.39	0.7636	0.9009	0.995	1.440
388.26	0.1169	0.3415	1.260	1.009	363.67	0.7941	0.9137	0.992	1.485
386.04	0.1519	0.4142	1.247	1.013	362.85	0.8286	0.9280	0.990	1.542
384.59	0.1766	0.4555	1.226	1.022	362.03	0.8635	0.9423	0.989	1.608
383.30	0.1976	0.4901	1.220	1.030	361.34	0.8939	0.9547	0.989	1.674
381.45	0.2335	0.5445	1.206	1.032	360.80	0.9196	0.9656	0.988	1.718
379.47	0.2762	0.5954	1.177	1.047	360.34	0.9416	0.9747	0.988	1.775
378.41	0.3033	0.6230	1.155	1.055	360.05	0.9566	0.9814	0.988	1.778
377.24	0.3294	0.6499	1.146	1.065	359.75	0.9720	0.9879	0.988	1.817
375.86	0.3645	0.6820	1.129	1.077	359.48	0.9863	0.9941	0.988	1.833
373.70	0.4241	0.7264	1.099	1.113	358.83	1.0000	1.0000	1.000	
372.56	0.4524	0.7478	1.096	1.129					

virial state equation with the coefficients estimated from the Hayden and O'Connell method (*17*).

The experimental p–T–x–y data were tested using the method proposed by Fredenslund et al. (*18*), fitting the g^E/RT function with a fourth-order Legendre polynomial, and found to be thermodynamically consistent.

The experimental VLE data were correlated with the relationship

$$Q = z(1-z)\sum_i A_i[z/(z + k(1-z))]^i \qquad (2)$$

where Q represents the fitting function and z the variable. Q,

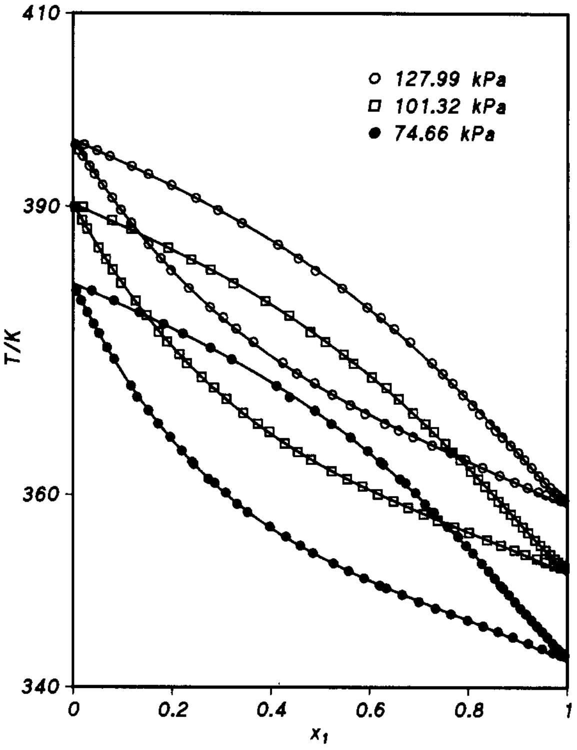

Figure 1. Representation of equilibrium temperature T *vs* liquid-phase x_1 or vapor-phase y_1 mole fractions for methyl propanoate (1) + n-butyl alcohol (2) at different pressures. Experimental points and fitting curves using eq 2 and coefficients of Table IV.

Table IV. Parameters Obtained for Equation 2 and Standard Deviations, $s(Q)$

p/kPa	A_0	A_1	A_2	A_3	k	$s(Q)$
$Q = (y_1 - x_1)$ *vs* $z = x_1$						
74.66	5.454	-8.510	12.878	-9.194	0.07	0.001
101.32	3.852	-3.908	4.545	-3.907	0.11	0.001
127.99	3.438	-4.235	6.231	-4.863	0.10	0.001
$Q = (T - T_1x_1 - T_2x_2)/K$ *vs* $z = x_1$						
74.66	-68.74	52.41			0.56	0.10
101.32	-55.73	41.13			0.70	0.10
127.99	-47.21	33.22			0.66	0.12
$Q = (T - T_1y_1 - T_2y_2)/K$ *vs* $z = y_1$						
74.66	17.04	33.27	-34.34		2.34	0.13
101.32	15.89	25.16	-26.72		2.04	0.13
127.99	14.45	27.62	-26.46		1.93	0.12

z, and the other parameters are shown in Table IV. The A_i parameters were determined by a linear-regression procedure, optimizing the k values in order to get the minimum standard deviation, $s(Q)$, of the function considered. Figure 1 presents the experimental and calculated values of T–x–y at the working pressures.

The experimental VLE data were also compared with predictions made using the following group-contribution models: ASOG (*6*), UNIFAC (*7–9*), and modified UNIFAC (*10*). In general, the predictions are better at lower pressures. The best predictions are obtained with modified UNIFAC (*10*) (0.02 for y_1 and 3% for γ_1). The average error in predicting γ_1 is of the order of 0.05 and in predicting the activity coefficients is less than 13%.

Conclusions

Isobaric vapor–liquid equilibrium data for methyl propanoate + n-butyl alcohol at 74.66, 101.32, and 127.99 kPa have been measured. The mixture shows positive deviations from ideality which increase with decreasing pressure. The point-to-point test shows that the VLE data are thermodynamicaly consistent.

ASOG, UNIFAC, and modified UNIFAC reproduce the experimental data fairly well. The best estimates are obtained with the modified UNIFAC (*10*).

Glossary

A_i,k	parameters in eq 2
p_i°	vapor pressure of pure component i, kPa
p	total pressure, kPa
R	universal gas constant, J K^{-1} mol^{-1}
s	standard deviation
T	temperature, K
T_i	boiling point of pure component i, K
x_i	liquid-phase mole fraction of component i
y_i	vapor-phase mole fraction of component i

Greek Letters

γ_i	activity coefficient of component i

Literature Cited

(1) Susial, P.; Ortega, J.; de Alfonso, C. *J. Chem. Eng. Data* **1989**, *31*, 339.

(2) Ortega, J.; Susial, P. *J. Chem. Eng. Jpn.* **1990**, *23*, 349.

(3) Ortega, J.; Susial, P. *Ber. Bunsen-Ges. Phys. Chem.* **1991**, *95*, 1214.

(4) Susial, P.; Ortega, J. *J. Chem. Eng. Data* **1993**, *38*, 434.

(5) Fernandez, J.; Berro, C.; Peneloux, A. *J. Chem. Eng. Data* **1987**, *32*, 17.

(6) Kojima, K.; Tochigi, K. *Prediction of Vapor-Liquid Equilibria by ASOG Method*; Elsevier: Amsterdam, 1979.

(7) Fredenslund, Aa; Gmehling, J.; Michelsen, M. L.; Rasmussen, P.; Prausnitz, J. M. *Ind. Eng. Chem. Process Des. Dev.* **1977**, *16*, 450.

(8) Skjold-Jorgensen, S.; Kolbe, B.; Gmehling, J.; Rasmussen, P. *Ind. Eng. Chem. Process Des. Dev.* **1979**, *18*, 714.

(9) Fredenslund, Aa; Jones, R. L.; Prausnitz, J. M. *AIChE J.* **1975**, *21*, 1086.

(10) Larsen, B. L.; Rasmussen, P.; Fredenslund, Aa. *Phase Equilibria and Separation Process. A Modified UNIFAC Group Contribution Model for Prediction of Phase Equilibria and Heat of Mixing*; Inst. Kem. Danmarks Tek. Hoj.: Lyngby, Denmark, 1986.

(11) *TRC-Thermodynamic Tables-Non Hydrocarbons*; Thermodynamic Research Center, The Texas A&M University Systems: College Station, TX, 1969.

(12) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents*, 4th ed.; Wiley-Interscience: New York, 1986.

(13) Ortega, J.; Peña, J. A.; de Alfonso, C. *J. Chem. Eng. Data* **1986**, *31*, 339.

(14) Venkateswararao, K.; Raviprasad, A.; Chiranjivi, C. *Fluid Phase Equilib.* **1980**, *4*, 293.

(15) Yen, L. C.; Woods, S. S. *AIChE J.* **1966**, *12*, 95.

(16) Spencer, C. F.; Danner, R. P. *J. Chem. Eng. Data* **1972**, *17*, 236.

(17) Hayden, J. G.; O'Connell, J. P. *Ind. Eng. Chem. Process Des. Dev.* **1975**, *14*, 209.

(18) Fredenslund, Aa.; Gmehling, J.; Rasmussen, P. *Vapor-Liquid Equilibria Using UNIFAC. A Group Contribution Method*; Elsevier: Amsterdam, 1977.

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