

MEASUREMENTS AND PREDICTION OF VLE OF METHYL PROPANOATE/ETHANOL/PROPAN-1-OL AT 114.16 AND 127.99 kPa

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Isobaric vapor-liquid equilibria for binary mixtures of methyl propanoate with ethanol and propan-1-ol are obtained by using a small-capacity recirculating still at 114.66 and 127.99 kPa. In the thermodynamic treatment of the data, the vapor phase is considered nonideal and all systems show positive deviations of ideality. Predictions carried out by using group contribution methods UNIFAC and ASOG are in good agreement with the experimental results, with errors less than 7% in all cases.

Introduction

The present paper is part of a larger research program designed to gather information about the thermodynamic behavior of systems composed of binary mixtures of esters and *n*-alkanols. After discussing isobaric equilibria of ethyl ester and *n*-alkanols in previous papers,¹⁰⁻¹² we have now begun to study methyl esters. An earlier paper¹⁹ set out vapor-liquid equilibrium data for methyl propanoate/ethanol and methyl propanoate/propan-1-ol at 101.32 kPa. In the present study, in contrast, isobaric equilibrium data for these two systems are determined experimentally at pressures of 114.66 kPa (860 Torr) and 127.99 kPa (960 Torr). Data on equilibria at various pressures are useful for studying a number of aspects, such as the determination of isothermal excess free energies, which in turn are useful in verifying models of state, and of variations in equilibria, the presence of azeotropes in particular, with pressure.

No isobaric equilibrium data for these two binary systems have been uncovered in the literature. However, the isothermal behavior of methyl propanoate/ethanol systems at 298.15 K has been studied by Polak and Lu.¹⁵

The usefulness of the two most widely used group contribution methods for predicting vapor-liquid equilibrium data, the UNIFAC and ASOG models, was demonstrated in a previous paper.¹⁹ Additional estimates achieved by use of these two models will be forthcoming; and as in the past, the parameters will continue to be contrasted with the parameter values

for ester/alkanol interactions reported in the literature. It is interesting to apply the models to different possible cases of such interactions. Thus, the pair OH/COO⁸) was used to study ester/alkanol interactions with the ASOG model, while expanded groups were used with the UNIFAC model, by considering the alkyl groups closest to the functional group. Ester/alkanol interactions have up to now almost always been represented in the literature by three pairs: COH/COO,¹⁾ COH/COOC,¹⁷⁾ and CCOH/COOC.²⁾ Application of the models should provide further verification of their usefulness for such systems, so that, even though experimental determination will in many cases remain essential, they can be used to predict equilibrium data as long as the components of the mixture are known.

1. Experimental Section

The characteristics of the chemicals used in this study were as described earlier.¹⁹⁾

The equilibrium still employed previously¹⁰⁾ was used to obtain the isobaric equilibrium composition of the binary mixtures and the vapor pressures of the pure components. The equipment and methods employed have been thoroughly described in previous papers.^{10,11)} Density values were used to determine the compositions of the liquid phases, *x*, and the vapor phases, *y*, employing density-composition correlations previously obtained for each system.¹³⁾ The degree of precision for the concentration of the liquid phase was ± 0.001 , that for the concentration of the vapor phase ± 0.002 .

Table 1 sets out the experimental values (T, p_i°) obtained for methyl propanoate, in view of the marked

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Table 1. Vapor Pressures of Methyl Propanoate obtained experimentally

Temperature [K]	Vapor Pressure p_i^o /[kPa]	Temperature [K]	Vapor Pressure p_i^o /[kPa]
330.66	48.5	352.16	103.24
331.79	50.56	353.23	106.92
333.11	53.03	354.16	110.15
335.50	57.89	355.16	113.80
336.38	59.94	355.88	116.38
338.01	63.55	356.85	120.16
339.23	66.42	357.45	122.43
340.46	69.29	358.60	126.88
341.68	72.34	360.13	133.21
343.09	76.01	360.69	135.52
344.30	79.26	360.76	135.93
345.56	82.75	360.79	135.99
346.92	86.66	361.61	139.39
347.93	89.62	362.71	144.20
349.08	93.11	363.28	146.84
350.13	96.46	364.00	150.09
351.73	101.78	364.30	151.51

effect of the pure-liquid vapor pressure data or their corresponding empirical correlations on the analysis of vapor-liquid equilibrium data. The experimental values and correlations for ethanol and propan-1-ol were presented earlier,¹⁴⁾ and therefore only the correlations will be considered herein. The data contained in Table 1 fit the classic Antoine equation:

$$\log p_i^o = A - B/(A - C) \quad (1)$$

in which the parameters A , B and C were calculated by Marquardt's method of non-linear regression.⁹⁾ Table 2 gives the values obtained using Marquardt's equation.

2. Results and VLE Data Analysis

The composition of the vapor and liquid phases, together with equilibrium temperatures, at pressures of 114.66 ± 0.02 kPa (860 ± 0.15 Torr) and 127.99 ± 0.02 kPa (960 ± 0.15 Torr) were obtained for the methyl propanoate/ethanol and methyl propanoate/propan-1-ol systems. Although equilibrium concentrations are customarily presented in terms of the more volatile component, in the present case all values have been presented in terms of the ester, which was common to both systems, making analytical and graphical comparison of the data more meaningful. Table 3 shows these values, along with the activity coefficients, γ_i , calculated for each point using the following equilibrium equation:

$$\phi_i y_i p = \gamma_i x_i \phi_i^o p_i^o \exp[(p - p_i^o)v_i^L/RT] \quad (2)$$

where ϕ_i is the fugacity coefficient for the vapor phase, γ_i is the activity coefficient for the liquid phase, both at T and p , R is the universal gas constant, x and y are the mole fractions of the vapor and liquid phases,

Table 2. Constants of Antoine equation for compounds utilized in this work and standard deviations, $s(p_i^o)$, obtained in the fitting of (T, p_i^o) for methyl propanoate

Compound	Ref.	A	B	C	$s(p_i^o)$ [kPa]
Methyl Propanoate this work		6.6042	1478.55	30.07	0.05
	(14)	6.06734	1170.236	64.40	
Ethanol	(11)	7.1130	1513.02	55.15	0.02
	(13)	7.16879	1552.601	50.731	
Propan-1-ol	(11)	6.8698	1434.94	74.98	0.04
	(13)	6.87613	1441.705	74.291	

Table 3. Vapor-liquid equilibrium measurements and activity coefficients for the systems methyl propanoate(1) + ethanol(2) and methyl propanoate(1) + propan-1-ol(2) at 114.66 and 127.99 kPa

p/kPa	T/K	x_1	y_1	γ_1	γ_2
x_1 Methyl Propanoate + x_2 Ethanol					
114.66	353.55	0.0299	0.0604	2.193	1.007
	353.10	0.0439	0.0855	2.144	1.012
	352.22	0.0794	0.1433	2.042	1.017
	351.81	0.0988	0.1723	1.999	1.020
	351.44	0.1194	0.1989	1.932	1.024
	351.11	0.1395	0.2227	1.871	1.030
	350.77	0.1639	0.2493	1.802	1.037
	350.48	0.1859	0.2717	1.747	1.045
	350.21	0.2089	0.2931	1.692	1.054
	350.01	0.2321	0.3142	1.643	1.062
	349.78	0.2595	0.3364	1.585	1.075
	349.58	0.2839	0.3557	1.542	1.087
	349.53	0.3003	0.3672	1.507	1.095
	349.39	0.3252	0.3852	1.466	1.109
	349.30	0.3322	0.3898	1.457	1.116
	349.28	0.3500	0.4018	1.426	1.125
	349.17	0.3735	0.4171	1.392	1.142
	349.09	0.3981	0.4328	1.359	1.160
	349.04	0.4174	0.4449	1.335	1.175
	349.01	0.4348	0.4564	1.316	1.187
	348.98	0.4401	0.4599	1.311	1.192
	348.95	0.4638	0.4741	1.284	1.214
	348.93	0.4789	0.4833	1.268	1.228
	348.92	0.4943	0.4926	1.253	1.243
	348.95	0.5088	0.5015	1.238	1.256
	348.97	0.5177	0.5068	1.229	1.264
	348.98	0.5229	0.5076	1.218	1.275
	349.02	0.5480	0.5229	1.196	1.302
	349.09	0.5762	0.5407	1.174	1.333
	349.14	0.5911	0.5502	1.162	1.351
	349.28	0.6314	0.5758	1.134	1.405
	349.53	0.6776	0.6080	1.107	1.470
	349.77	0.7232	0.6429	1.089	1.545
	350.20	0.7639	0.6775	1.072	1.609
	350.66	0.8018	0.7123	1.058	1.680
	351.20	0.8370	0.7515	1.052	1.728
	351.80	0.8735	0.7962	1.048	1.785
	352.55	0.9049	0.8396	1.042	1.813
	353.40	0.9308	0.8799	1.035	1.814
127.99	357.13	0.0074	0.0156	2.279	1.004
	356.86	0.0167	0.0340	2.219	1.004
	356.47	0.0301	0.0591	2.166	1.006
	356.08	0.0448	0.0853	2.125	1.007

Table 3. (continued)

p/kPa	T/K	x_1	y_1	γ_1	γ_2
	355.62	0.0640	0.1163	2.057	1.010
	355.08	0.0892	0.1534	1.983	1.014
	354.64	0.1129	0.1859	1.920	1.018
	354.23	0.1373	0.2154	1.853	1.024
	353.84	0.1657	0.2458	1.773	1.033
	353.52	0.1926	0.2717	1.703	1.043
	353.26	0.2175	0.2948	1.650	1.052
	353.02	0.2445	0.3181	1.595	1.063
	352.83	0.2680	0.3372	1.552	1.074
	352.66	0.2947	0.3572	1.503	1.088
	352.52	0.3200	0.3758	1.463	1.102
	352.42	0.3443	0.3925	1.424	1.116
	352.33	0.3684	0.4086	1.390	1.132
	352.28	0.3863	0.4187	1.360	1.147
	352.23	0.4106	0.4342	1.329	1.164
	352.19	0.4346	0.4489	1.300	1.184
	352.17	0.4562	0.4621	1.276	1.202
	352.15	0.4765	0.4750	1.257	1.220
	352.16	0.4921	0.4842	1.240	1.235
	352.17	0.5069	0.4933	1.226	1.249
	352.20	0.5364	0.5109	1.199	1.281
	352.27	0.5706	0.5329	1.173	1.317
	352.40	0.6082	0.5579	1.148	1.359
	352.53	0.6414	0.5795	1.126	1.405
	352.75	0.6770	0.6047	1.106	1.455
	352.04	0.7135	0.6327	1.088	1.507
	353.33	0.7477	0.6609	1.075	1.563
	353.67	0.7792	0.6903	1.067	1.610
	354.10	0.8111	0.7224	1.058	1.660
	354.48	0.8362	0.7490	1.052	1.706
	354.88	0.8587	0.7769	1.050	1.732
	355.30	0.8814	0.8068	1.049	1.759
	355.90	0.9076	0.8456	1.048	1.765
	356.63	0.9348	0.8862	1.041	1.788
x_1 Methyl Propanoate + x_2 Propan-1-ol					
114.66	372.04	0.0210	0.0620	1.893	1.013
	370.53	0.0539	0.1391	1.724	1.016
	369.83	0.0717	0.1764	1.675	1.017
	369.04	0.0907	0.2093	1.604	1.025
	368.34	0.1086	0.2466	1.610	1.023
	366.43	0.1631	0.3399	1.558	1.025
	365.88	0.1786	0.3590	1.526	1.035
	365.13	0.2046	0.3931	1.490	1.041
	364.29	0.2335	0.4281	1.456	1.051
	363.49	0.2674	0.4635	1.408	1.064
	361.98	0.3383	0.5294	1.327	1.095
	361.55	0.3596	0.5488	1.310	1.103
	361.19	0.3815	0.5650	1.285	1.117
	360.59	0.4143	0.5908	1.259	1.135
	360.54	0.4198	0.5946	1.252	1.138
	360.26	0.4388	0.6059	1.231	1.156
	360.04	0.4503	0.6159	1.227	1.160
	359.75	0.4863	0.6331	1.178	1.199
	359.38	0.5100	0.6514	1.168	1.212
	395.00	0.5396	0.6709	1.150	1.236
	358.62	0.5681	0.6883	1.133	1.267
	358.17	0.6146	0.7158	1.104	1.318
	357.83	0.6502	0.7375	1.086	1.360
	357.54	0.6744	0.7551	1.081	1.379
	357.25	0.7008	0.7744	1.077	1.398
	356.95	0.7364	0.7940	1.060	1.467
	356.62	0.7708	0.8198	1.056	1.495
	356.48	0.7958	0.8369	1.048	1.527
	356.27	0.8298	0.8602	1.040	1.584

Table 3. (continued)

p/kPa	T/K	x_1	y_1	γ_1	γ_2
	355.95	0.8890	0.9065	1.033	1.646
	355.85	0.9077	0.9218	1.032	1.662
	355.79	0.9203	0.9335	1.029	1.687
	355.75	0.9362	0.9452	1.028	1.690
127.99	375.32	0.0182	0.0511	1.834	1.011
	374.58	0.0334	0.0890	1.775	1.012
	372.81	0.0745	0.1795	1.681	1.013
	370.87	0.1254	0.2717	1.593	1.021
	370.04	0.1494	0.3106	1.563	1.024
	369.19	0.1751	0.3484	1.531	1.029
	368.36	0.2051	0.3864	1.483	1.037
	367.51	0.2365	0.4245	1.446	1.045
	366.71	0.2708	0.4601	1.399	1.058
	366.04	0.3012	0.4912	1.369	1.067
	365.79	0.3131	0.5016	1.354	1.073
	365.30	0.3381	0.5234	1.326	1.084
	364.87	0.3612	0.5436	1.305	1.094
	364.43	0.3878	0.5636	1.276	1.110
	363.94	0.4165	0.5867	1.254	1.123
	363.43	0.4490	0.6101	1.227	1.144
	362.99	0.4803	0.6315	1.203	1.166
	362.57	0.5107	0.6516	1.181	1.190
	362.17	0.5445	0.6738	1.159	1.215
	361.79	0.5771	0.6950	1.140	1.242
	361.40	0.6124	0.7181	1.123	1.271
	361.08	0.6457	0.7387	1.105	1.305
	360.74	0.6813	0.7604	1.089	1.348
	360.41	0.7152	0.7837	1.079	1.380
	360.12	0.7510	0.8065	1.067	1.428
	359.87	0.7815	0.8288	1.061	1.454
	359.69	0.8077	0.8472	1.055	1.485
	359.53	0.8329	0.8654	1.050	1.515
	359.37	0.8566	0.8841	1.048	1.529
	359.24	0.8803	0.9026	1.045	1.547
	359.09	0.9054	0.9231	1.044	1.554
	358.95	0.9365	0.9476	1.037	1.581

and the superscripts refer to saturation values. The fugacity coefficient values were in turn calculated using the virial equation, truncated after the second term:

$$\phi_i = \exp \left[(p/RT) \left(2 \sum_j y_j B_{ij} - \sum_i \sum_j y_i y_j B_{ij} \right) \right] \quad (3)$$

The second virial coefficients were calculated by use of the correlations reported by Tsonopoulos²⁰⁾ for the case where $k_{ij} = 0.05$, suggested by Tsonopoulos when one of the components is an alkanol. The molar volumes for the saturated liquid, v_i^L , in Eq. (2) were treated as independent of pressure and were determined by use of a modified version of Rackett's equation.¹⁸⁾

Thermodynamic analysis of the data was carried out by applying some of the consistency tests published in the literature. All the systems were consistent by the test described by Herington.⁶⁾ However, when the point-to-point test of Van Ness *et al.*²¹⁾ as modified by Fredenslund *et al.*³⁾ was applied, all the systems were consistent except methyl propanoate/propan-1-

ol at 127.99 kPa (960 Torr). The limitations of this consistency test when applied to systems containing *n*-alkanols, chiefly due to association effects, were discussed earlier.^{19,14)} In the present experiments, however, the difficulties were increased by the presence of the ester as the second component. Consequently, to diminish the inflexibility of the test, the method of Van Ness and Fredenslund was modified by calculating the virial coefficients using a subroutine based on Tsonopoulos' empirical coefficients²⁰⁾ rather than the method put forward by Hayden and O'Connell.⁵⁾ With this modification, all the systems were again consistent, with overall mean deviations for the mole fraction of the vapor phase lower than 0.01 in each case. The overall evaluation using the consistency tests notwithstanding, all experimental values 50% greater than 0.01 were discarded and are not included in Table 3.

The experimental concentration data in Table 3 were correlated by use of a polynomial equation proposed in Ref. (10) by one of us which has in the past yielded excellent results in analyzing various thermodynamic magnitudes.

$$y_1 - x_1 = x_1 x_2 \sum_i A_i [(x_1 + kx_2)]^i \quad i=0, 1, 2, \dots \quad (4)$$

where x_1 represents methyl ester concentration. The coefficients A_i were calculated by the method of least squares, with the value of k optimized to the minimum standard deviation value, $s(y_1 - x_1)$. The values so obtained appear in Table 4.

2.1 Azeotropic data

Of the two systems considered in this paper, only the methyl propanoate/ethanol system formed a minimum azeotrope. A previous paper¹⁰⁾ reported VLE data for such a system at 101.32 kPa (760 Torr), with an azeotrope at $x=y=0.483$ (methyl ester composition) and $T=345.58$ K. In the present calculations, azeotropes were estimated at $x=y=0.480$ and $T=348.92$ K at 114.66+0.02 kPa (860 Torr) and at $x=y=0.476$ and $T=352.15$ K at 127.99+0.02 (960 Torr). The azeotropic points obtained by direct experimentation substantiated the graphical method proposed by Horsley⁷⁾ in which singular points for a large number of ester/ethanol systems are plotted. However, it is more appropriate to plot pressure on composition (x or y) as well as on temperature difference, δ , between the azeotrope and the lower-boiling point component. Unlike Horsley's graphical method, such plots call for separate representations for each system. Figure 1 therefore presents the singular points for the methyl propanoate/ethanol system at various pressures, showing the quasi-regular distribution of the azeotropes.

2.2 VLE Prediction using group contribution models

Two of the most commonly used theoretical methods of predicting VLE's, the ASOG and UNIFAC models, were applied to the mixtures in question. Predictions were made on the basis of the activity coefficients and mole fraction values for the vapor phase at various working pressures. The group interaction pair OH/COO, proposed by Kojima and

Table 4. Values of parameters for Eq. (4) and standard deviations, $s(y_1 - x_1)$, in each system

p/kPa	A_0	A_1	A_2	A_3	k	$s(y_1 - x_1)$
<i>x</i> Methyl Propanoate + (1- <i>x</i>)Ethanol						
114.66	1.216	-3.257	3.414	-2.349	0.662	0.0007
127.99	1.132	-3.062	3.036	-2.070	0.694	0.0008
<i>x</i> Methyl Propanoate + (1- <i>x</i>)Propan-1-ol						
114.66	2.594	-4.747	7.512	-5.259	0.114	0.0017
127.99	1.974	-1.745	1.209	-1.315	0.188	0.0008

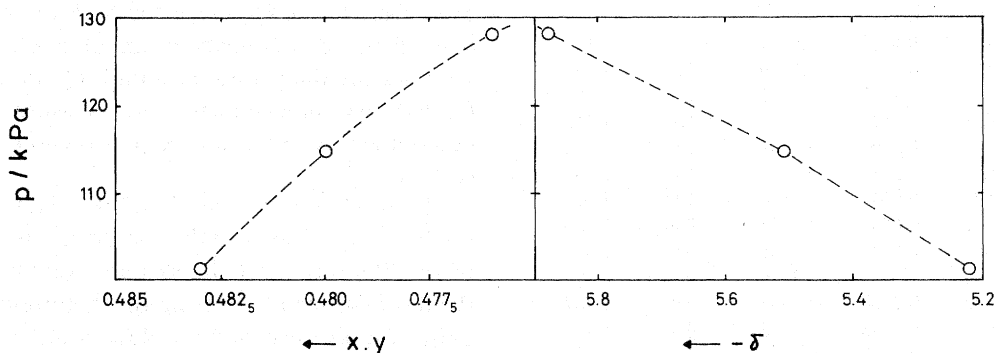


Fig. 1. Plot of total pressure vs azeotrope composition x, y (a) and vs δ (b). δ =boiling point of lower-boiling component minus azeotrope boiling point.

Table 5. Errors calculated in the prediction of vapor-liquid equilibria using the ASOG and UNIFAC models

System	ASOG		UNIFAC	
	COO/OH	COH/COO	OH/COOC	CCOH/COOC
$p = 114.66 \text{ kPa (860 Torr)}$				
Methyl Propanoate/Ethanol				
$\bar{e}(\gamma_i)$, %	3.9	1.3	1.6	2.8
$\bar{e}(\gamma_i)$, %	5.0	4.0	4.5	6.4
azeotrope	0.417	0.509	0.511	0.547
Methyl Propanoate/Propan-1-ol				
$\bar{e}(\gamma_i)$, %	4.7	3.3	2.9	3.0
$\bar{e}(\gamma_i)$, %	2.7	5.8	4.8	1.8
$p = 127.99 \text{ kPa (960 Torr)}$				
Methyl Propanoate/Ethanol				
$\bar{e}(\gamma_i)$, %	4.1	1.4	1.8	3.0
$\bar{e}(\gamma_i)$, %	4.6	4.4	5.5	6.7
azeotrope	0.403	0.500	0.505	0.536
Methyl Propanoate/Propan-1-ol				
$\bar{e}(\gamma_i)$, %	4.9	3.3	3.0	3.2
$\bar{e}(\gamma_i)$, %	3.1	5.5	4.5	1.9

Tochigi,⁸⁾ was used in the ASOG model. In contrast, three pairs used to represent ester/alkanol interactions in the literature, COH/COO, suggested by Fredenslund *et al.*,¹⁾ OH/COOC, proposed by Skjold-Jorgensen *et al.*¹⁷⁾ and CCOH/COOC, put forward by Fredenslund *et al.*,²⁾ were applied in the UNIFAC model.

Table 5 gives the estimation errors for the different interaction groups used to characterize the mixtures studied in this work.

In conclusion, this paper has set out experimental vapor-liquid equilibrium data for the methyl propanoate/ethanol and methyl propanoate/propan-1-ol binary systems at pressures of 114.66 kPa and 127.99 kPa, and methyl ester vapor pressure values as well. Thermodynamic analysis of the data was performed to verify their consistency. Prediction of isobaric equilibrium data for these two systems using the ASOG and UNIFAC models was generally good, with mean errors of less than 7% in all cases. However, the errors in estimates of the azeotropes for the methyl propanoate/ethanol system were higher.

Nomenclature

A, B, C	= constants of Antoine equation	[—]
A_i	= parameter of Eq. (4)	[—]
B_{ii}	= second virial coefficient for component i	[—]
$\bar{e}(z)$	= mean error of z , %	[—]
k	= parameter of Eq. (4)	[—]

p_i°	= vapor pressure component i	[kPa]
p	= total pressure	[kPa]
R	= universal gas constant	[JK ⁻¹ mol ⁻¹]
s	= standard deviation	[—]
T	= temperature	[K]
v_i^L	= molar volume component i	[m ³ mol ⁻¹]
x	= liquid-phase mole fraction	[—]
y	= vapor-phase mole fraction	[—]

γ_i	= activity coefficient component i
Φ_i	= fugacity coefficient component i
Σ	= adding
Δ	= difference between two values

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