VAPOR-LIQUID EQUILIBRIA BEHAVIOR OF METHYL ESTERS AND PROPAN-2-OL AT 74.66, 101.32 AND 127.99 kPa*[1]

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Isobaric vapor-liquid equilibrium data were measured at 74.66, 101.32 and 127.99 kPa for binary mixtures composed of methyl ethanoate or methyl propanoate and propan-2-ol using a dynamic method. In thermodynamic calcutions using the data, the vapor phase was considered to be non-ideal, and all the systems studied exhibit positive deviations from ideal solution behavior. At 74.66 kPa, the binary system (x_1 methyl propanoate $+x_2$ propan-2-ol) presents an azeotrope at $x_1 = 0.666$, $T = 340.47$ K.; as pressure increased, azeotrope concentration decreased quasi-regularly towards regions richer in propan-2-ol. After reduction of the data by fitting with a suitable equation and verification of thermodynamic consistency, various group-contribution models were applied to estimate the isobaric VLE data. The mean error in prediction of the activity coefficients for each system in no case exceeded 7%.

Introduction

This paper is part of a larger study of the isobaric vapor-liquid equilibrium behavior of binary mixtures composed of the first components in the alkyl ester and n-alkanol series, in the context of an ambitious research project into the thermodynamic properties of mixtures of alkyl esters and n-alkanes, n-alkanols, and 1-chloroalkanes that has been under way for some years now. Work under this project commenced on methyl esters + n-alkanols with a view to systematizing the study of VLE data, and several papers on such mixtures have already appeared, e.g. Susial et al.[22] and Ortega et al.[15, 16] for atmospheric pressure and Ortega and Susial[17, 18, 19] for higher pressures. In line with the ultimate objectives of this research project, we have felt that it would be interesting to present values for systems containing alkanol isomers for which insufficient data are available in the literature, which sets out isothermal VLE values only for the system consisting of methyl ethanoate + propan-2-ol by Gmehling et al.[5]. Consequently, the VLE values for binary mixtures of methyl ethanoate (*ME*) or methyl propanoate (*MP*) and propan-2-ol (*PR-2*) were measured at 74.66 kPa (560 Torr), 101.32 kPa (760 Torr), and 127.99 kPa(960 Torr), effectively expanding the range of pressures considered in earlier papers.

There were a variety of reasons for carrying out the determinations of the VLE values for these mixtures at different pressures. Apart from the interest in such data from an engineering standpoint, there is also a need to observe the changes taking place in the behavior of such systems at different pressures, particularly as regards the

presence of singular points, which are an important aspect with respect to purification of the components as well as for modelling VLE behavior with the aid of various theoretical models.

The literature has reported data for the binary system methyl ethanoate + propan-2-ol as isothermal by Nagata et al.[12], and as isobaric at atmospheric pressure by Nagata[11]. However, no VLE data for (methyl propanoate + propan-2-ol) have been published, although Horsley[8] reported the existence of an azeotrope at intermediate concentrations, and we intended to try to corroborate this work.

Previous work achieved good results by applying different group-contribution models [ASOG and UNIFAC, including the version(UNIFAX-2) put forward by Larsen et al.[10]], and overall mean errors smaller than 7% were obtained. Nevertheless, considerable difficulties are still encountered when trying to make precise predictions of the azeotropes. We consider it important to broaden the available data base as a means of seeking new proposals regarding alkanol/ester interactions. Up to now, calculation of the virial coefficients using the expressions published by Tsonopoulos[24] both to verify the consistency of the VLE data and to determine the concentrations of the vapor phase when applying theoretical models has been both effective and interesting. However, the difficulties entailed in performing computations with the VLE data for components that exhibit association effects, which are quite appreciable in the case of alkanols and certain esters, has made it impossible to draw generalizations on the basis of some of the results obtained.

Table 1. *VLE* data for x_1 methyl esters = x_2 propan-2-ol at different pressures

p/kPa	T/K	x_1	y_1	γ_1	γ_2
	x_1 Methyl ethanoate + x_2 Propan-2-ol				
74.66	347.65	0.0000	0.0000	–	1.000
	343.08	0.0588	0.2170	1.820	1.004
	342.02	0.0742	0.2645	1.814	1.003
	341.12	0.0886	0.3022	1.782	1.005
	339.95	0.1064	0.3498	1.779	1.004
	337.58	0.1481	0.4312	1.695	1.023
	335.79	0.1863	0.4944	1.633	1.031
	334.73	0.2130	0.5291	1.581	1.042
	334.08	0.2290	0.5498	1.560	1.047
	333.54	0.2410	0.5635	1.545	1.057
	332.87	0.2620	0.5870	1.513	1.061
	332.09	0.2842	0.6088	1.483	1.074
	331.77	0.2977	0.6194	1.456	1.081
	331.16	0.3171	0.6372	1.434	1.090
	330.72	0.3329	0.6485	1.411	1.104
	329.77	0.3678	0.6753	1.372	1.126
	329.16	0.3967	0.6924	1.331	1.150
	328.44	0.4267	0.7102	1.300	1.180
	327.90	0.4561	0.7271	1.268	1.202
	327.30	0.4903	0.7477	1.237	1.221
	326.89	0.5124	0.7558	1.214	1.261
	326.34	0.5436	0.7708	1.189	1.298
	325.78	0.5833	0.7886	1.155	1.348
	325.28	0.6174	0.8037	1.132	1.398
	324.93	0.6483	0.8168	1.108	1.444
	324.45	0.6846	0.8323	1.087	1.510
	324.07	0.7154	0.8460	1.072	1.567
	323.85	0.7328	0.8540	1.064	1.600
	323.45	0.7665	0.8692	1.050	1.674
	323.03	0.8028	0.8854	1.036	1.774
	322.69	0.8363	0.9015	1.025	1.870
	322.40	0.8643	0.9159	1.018	1.955
	322.14	0.8966	0.9333	1.009	2.063
	321.79	0.9302	0.9531	1.006	2.190
	321.56	0.9590	0.9712	1.002	2.318
	321.40	0.9808	0.9860	1.000	2.428
	321.21	1.0000	1.0000	1.000	–
101.32	355.26	0.0000	0.0000	–	1.000
	353.07	0.0265	0.0937	1.729	1.007
	351.98	0.0432	0.1476	1.723	1.005
	351.27	0.0542	0.1811	1.719	1.004
	350.18	0.0717	0.2303	1.705	1.004
	349.33	0.0855	0.2675	1.702	1.003
	348.32	0.1038	0.3107	1.677	1.003
	347.52	0.1176	0.3407	1.661	1.006
	345.84	0.1503	0.4041	1.620	1.011
	344.82	0.1739	0.4426	1.581	1.014
	344.16	0.1904	0.4683	1.558	1.014
	343.41	0.2083	0.4899	1.524	1.027
	342.86	0.2248	0.5109	1.498	1.029
	341.87	0.2498	0.5401	1.468	1.042
	341.77	0.2529	0.5450	1.468	1.039
	341.19	0.2733	0.5648	1.433	1.047
	340.09	0.3056	0.5953	1.398	1.068
	339.17	0.3414	0.6256	1.353	1.083
	338.50	0.3656	0.6433	1.326	1.103
	337.87	0.3913	0.6586	1.294	1.130
	337.13	0.4168	0.6770	1.278	1.153
	336.64	0.4605	0.7060	1.226	1.159
	336.03	0.4836	0.7170	1.208	1.197
	335.56	0.5074	0.7290	1.189	1.226
	335.16	0.5318	0.7441	1.173	1.240
	334.65	0.5623	0.7602	1.152	1.271
	334.27	0.5892	0.7731	1.132	1.304
	333.85	0.6178	0.7874	1.114	1.338
	333.43	0.6505	0.8031	1.094	1.380
	333.03	0.6797	0.8173	1.080	1.423
	332.57	0.7124	0.8329	1.066	1.480
	332.26	0.7427	0.8480	1.051	1.526
	331.86	0.7759	0.8640	1.039	1.596
	331.47	0.8112	0.8808	1.026	1.690
	331.18	0.8406	0.8942	1.015	1.800
	330.91	0.8673	0.9095	1.009	1.873
	330.67	0.8926	0.9253	1.006	1.931
	330.40	0.9205	0.9426	1.002	2.029
	330.19	0.9455	0.9597	1.001	2.098
	329.99	0.9703	0.9776	1.000	2.160
	329.87	0.9893	0.9911	0.998	2.396
	329.79	0.9923	0.9925	0.999	2.816
	329.76	1.0000	1.0000	1.000	–
127.99	361.10	0.0000	0.0000	–	1.000
	358.15	0.0515	0.1596	1.646	0.987
	357.18	0.0647	0.1937	1.633	0.996
	355.83	0.0856	0.2455	1.624	1.003
	355.09	0.0999	0.2779	1.607	1.003
	354.31	0.1138	0.3071	1.594	1.007
	353.38	0.1340	0.3446	1.559	1.010
	352.89	0.1457	0.3642	1.536	1.012
	351.85	0.1695	0.4029	1.505	1.018
	351.00	0.1886	0.4337	1.491	1.021
	350.25	0.2082	0.4604	1.465	1.027
	349.66	0.2251	0.4837	1.448	1.028
	348.96	0.2467	0.5083	1.417	1.035
	348.11	0.2686	0.5317	1.395	1.050
	347.67	0.2823	0.5454	1.380	1.057
	346.63	0.3207	0.5833	1.339	1.068
	346.36	0.3310	0.5933	1.330	1.070
	345.72	0.3531	0.6113	1.309	1.085
	345.13	0.3795	0.6322	1.282	1.096
	344.46	0.4092	0.6531	1.253	1.116
	343.98	0.4378	0.6732	1.229	1.132
	343.19	0.4664	0.6906	1.208	1.161
	342.61	0.5005	0.7104	1.179	1.190
	342.07	0.5304	0.7280	1.159	1.215
	341.73	0.5532	0.7397	1.140	1.240
	341.23	0.5862	0.7572	1.119	1.275
	340.80	0.6149	0.7735	1.104	1.301
	340.42	0.6397	0.7860	1.091	1.335
	339.97	0.6729	0.8030	1.074	1.380
	339.54	0.7067	0.8201	1.059	1.431
	339.16	0.7388	0.8365	1.045	1.485
	338.78	0.7687	0.8528	1.036	1.534
	338.46	0.8017	0.8700	1.024	1.602
	338.05	0.8337	0.8889	1.019	1.661
	337.76	0.8650	0.9063	1.010	1.748
	337.48	0.8940	0.9251	1.007	1.801
	337.25	0.9214	0.9426	1.003	1.880
	337.02	0.9466	0.9592	1.000	1.986
	336.82	0.9714	0.9774	1.000	2.072
	336.67	0.9915	0.9926	0.999	2.298
	336.60	1.0000	1.0000	1.000	–
	x_1 Methyl propanoate + x_2 Propan-2-ol				
74.66	347.65	0.0000	0.0000	–	1.000
	347.09	0.0198	0.0408	1.826	1.000
	346.10	0.0570	0.1120	1.798	1.002
	345.47	0.0836	0.1572	1.757	1.004
	344.86	0.1103	0.1973	1.705	1.010
	344.37	0.1364	0.2329	1.654	1.015
	343.86	0.1673	0.2725	1.605	1.020
	343.46	0.1947	0.3027	1.552	1.028
	343.03	0.2214	0.3311	1.514	1.038
	342.68	0.2523	0.3621	1.471	1.046
	342.48	0.2850	0.3914	1.407	1.044
	342.33	0.3146	0.4159	1.371	1.060
	342.06	0.3466	0.4414	1.332	1.076
	341.79	0.3808	0.4673	1.296	1.095
	341.33	0.4132	0.4906	1.273	1.127
	341.13	0.4439	0.5123	1.246	1.148
	340.95	0.4666	0.5313	1.237	1.159
	340.98	0.4748	0.5331	1.218	1.171
	340.83	0.4920	0.5489	1.217	1.177
	340.74	0.5175	0.5653	1.195	1.199
	340.68	0.5407	0.5810	1.178	1.217
	340.61	0.5646	0.5963	1.161	1.241

P/kPa	T/K	x_1	y_1	γ_1	γ_2
	340.54	0.5934	0.6150	1.142	1.271
	340.51	0.6218	0.6332	1.123	1.303
	340.49	0.6511	0.6530	1.107	1.338
	340.52	0.6756	0.6672	1.088	1.378
	340.55	0.7007	0.6858	1.078	1.408
	340.59	0.7332	0.7112	1.067	1.450
	340.69	0.7651	0.7369	1.055	1.494
	340.80	0.7963	0.7627	1.046	1.546
	340.95	0.8259	0.7894	1.038	1.595
	341.12	0.8507	0.8130	1.032	1.640
	341.25	0.8712	0.8352	1.031	1.666
	341.34	0.8935	0.8575	1.029	1.736
	341.56	0.9167	0.8854	1.028	1.768
	341.79	0.9394	0.9132	1.026	1.823
	341.97	0.9585	0.9375	1.026	1.902
	342.26	0.9773	0.9646	1.026	1.946
	342.47	0.9920	0.9862	1.026	2.133
	342.63	1.0000	1.0000	1.000	–
101.32	355.26	0.0000	0.0000	–	1.000
	354.52	0.0237	0.0439	1.737	1.001
	354.27	0.0342	0.0627	1.732	1.002
	354.04	0.0453	0.0814	1.710	1.002
	353.76	0.0590	0.1029	1.674	1.004
	353.48	0.0716	0.1232	1.666	1.005
	353.15	0.0886	0.1498	1.654	1.005
	352.76	0.1111	0.1802	1.606	1.009
	352.38	0.1321	0.2083	1.580	1.013
	352.02	0.1534	0.2369	1.565	1.015
	351.65	0.1795	0.2654	1.516	1.023
	351.27	0.2084	0.2973	1.481	1.029
	350.93	0.2368	0.3255	1.442	1.038
	350.63	0.2643	0.3528	1.414	1.046
	350.33	0.2964	0.3825	1.380	1.056
	350.13	0.3223	0.4031	1.346	1.068
	349.88	0.3536	0.4297	1.318	1.080
	349.68	0.3856	0.4537	1.285	1.097
	349.50	0.4173	0.4777	1.257	1.114
	349.34	0.4488	0.5006	1.231	1.133
	349.21	0.4800	0.5232	1.208	1.152
	349.11	0.5090	0.5441	1.189	1.171
	349.11	0.5104	0.5446	1.186	1.173
	349.02	0.5360	0.5623	1.170	1.194
	348.97	0.5615	0.5804	1.155	1.214
	348.93	0.5897	0.6003	1.139	1.238
	348.90	0.6142	0.6171	1.125	1.262
	348.88	0.6373	0.6340	1.115	1.284
	348.89	0.6595	0.6493	1.103	1.310
	348.95	0.6866	0.6677	1.087	1.345
	348.99	0.7078	0.6842	1.079	1.369

P/kPa	T/K	x_1	y_1	γ_1	γ_2
	349.26	0.7224	0.6936	1.063	1.383
	349.30	0.7360	0.7046	1.059	1.400
	349.42	0.7779	0.7418	1.051	1.447
	349.47	0.7828	0.7459	1.048	1.454
	349.61	0.8050	0.7662	1.042	1.481
	349.96	0.8703	0.8306	1.034	1.591
	350.12	0.8975	0.8605	1.033	1.647
	350.49	0.9325	0.9046	1.034	1.685
	350.81	0.9588	0.9394	1.033	1.731
	351.08	0.9782	0.9666	1.033	1.784
	351.67	1.0000	1.0000	1.000	–
127.99	361.10	0.0000	0.0000	–	1.000
	359.98	0.0561	0.0900	1.602	1.004
	359.53	0.0811	0.1272	1.587	1.005
	359.06	0.1105	0.1661	1.542	1.010
	358.60	0.1401	0.2055	1.525	1.012
	358.17	0.1721	0.2419	1.480	1.019
	357.80	0.2033	0.2766	1.448	1.025
	357.44	0.2376	0.3100	1.403	1.035
	357.08	0.2753	0.3449	1.362	1.048
	356.78	0.3131	0.3779	1.324	1.062
	356.51	0.3525	0.4111	1.290	1.077
	356.31	0.3903	0.4410	1.257	1.094
	356.24	0.4142	0.4594	1.236	1.104
	356.19	0.4352	0.4756	1.220	1.113
	356.15	0.4418	0.4757	1.203	1.128
	356.09	0.4748	0.4997	1.178	1.146
	356.03	0.5034	0.5204	1.160	1.165
	356.00	0.5291	0.5387	1.143	1.183
	355.99	0.5491	0.5530	1.131	1.198
	355.98	0.5687	0.5667	1.119	1.214
	355.99	0.5852	0.5787	1.111	1.227
	356.00	0.6038	0.5924	1.101	1.242
	356.01	0.6204	0.6047	1.094	1.257
	356.04	0.6429	0.6213	1.084	1.279
	356.08	0.6618	0.6355	1.075	1.298
	356.14	0.6838	0.6525	1.067	1.320
	356.27	0.7183	0.6810	1.056	1.354
	356.42	0.7563	0.7140	1.047	1.395
	356.65	0.7960	0.7503	1.038	1.443
	356.77	0.8299	0.7826	1.034	1.500
	356.93	0.8605	0.8148	1.034	1.549
	357.14	0.8925	0.8502	1.034	1.613
	357.52	0.9230	0.8887	1.033	1.649
	357.83	0.9474	0.9207	1.033	1.701
	358.12	0.9663	0.9474	1.033	1.742
	358.40	0.9835	0.9727	1.034	1.827
	358.87	1.0000	1.0000	1.000	–

1. Experimental Section

1.1 Components

All the components used in the experiments were from Fluka AG and were degassed by ultrasound and stored in darkness on a molecular sieve(ref. 69828 from Fluka) for several days prior to use. The physical properties of the methyl esters at 298.15K did not display any significant differences with respect to those presented in earlier papers[16, 22]. The values for the propan-2-ol at 298.15K were: $\rho/(\mathrm{kg \cdot m^{-3}}) = 781.08$, $781.26^{[20]}$; $n_D = 1.3753$, $1.3752^{[20]}$. The normal boiling point was: 355.26K, 355.392K[20].

1.2 Equipment and Procedure

The experimental equilibrium still used to achieve the vapor-liquid equilibria was the same as that described previously by Ortega et al.[14]. Pressure was regulated using a Fisher VKH100 controller equipped with electronic valves, and total pressure was measured using an MKS Instruments system with reading intervals of ± 0.001 kPa. The accuracy of the readings was better than ± 0.02 kPa. Temperature measurements were taken using a Comark-6800 digital thermometer with platinum probes and reading intervals of ±0.01K. Calibration of this equipment recorded measurement errors of 0.01% in the readings.

Analysis of the concentrations of the liquid and vapor phases was carried out using an Anton Paar 60/602 vibrating-tube densimeter calibrated with water and n-nonane as described by Ortega et al.[13] employing standard curves for density on concentration obrtained beforehand for the binary mixtures (x_1 methyl ethanoate or x_1 methyl propanoate + x_2 propan-2-ol) at 298.15 ±0.01K. The equations used to estimate the concentrations were:

$$\rho/(\mathrm{kg \cdot m^{-3}}) = 780.95 + 127.35\,x_1 + 18.52\,x_1^2 \qquad (1)$$
$$(ME + PR - 2)$$

$$\rho / (\text{kg} \cdot \text{m}^{-3}) = 781.01 + 141.25\, x_1 - 13.62\, x_1^2$$
$$(MA + PR - 2) \qquad (2)$$

which yielded correlation coefficients very close to unity.

In addition, the uniform distribution of V^E values for each of the mixtures was also verified, and our results were compared with those for the system (x_1 methyl ethanoate $+x_2$ propan-2-ol) reported by Acevedo et al.[1]. The mean error was 43%, with errors greater than 100% for certain points, and we were unable to account for the large differences between the data reported by those authors and our own data. The concentration values for the liquid phase obtained using Eqs. (1) and (2) were accurate to ±0.001; those for the vapor phase were accurate to ±0.002, on account of the high volatility of the methyl ethanoate in the least favorable cases.

2. Results

Table 1 presents the VLE data p, T, x_1, and y_1 collected from direct measurements of the mixtures $\{x_1 C_u H_{2u+1} COOCH_3\ (u = 1,2) + x_2 CH_3 CHOHCH_3\}$ at pressures of 74.66 ± 0.02kPa. (560 ± 0.15 Torr), 101.32 ± 0.02kPa. (760 ± 0.15 Torr), and 127.99 ± 0.02kPa. (960 ± 0.15 Torr). Our VLE data at 101.32 kPa agree well with those published by Nagata et al.[12] for the system $\{x_1 CH_3 COOCH_3 + x_2 CH_3 CHOHCH_3\}$, with a mean error for the vapor phase mole fraction, y_1, lower than 1.7%. The activity coefficients, γ_1, were calculated by means of:

$$\gamma_i = (\phi_i y_i p / (x_i \phi_i^{\circ} p_i^{\circ})\ \exp[\,(p_i^{\circ} - p)\, v_i^{L} / RT\,] \qquad (3)$$

where:

$$\phi_i = \exp\left[\,(p/RT)\,(2\sum_j y_j B_{ij} - \sum_i \sum_j y_i y_j B_{ij})\,\right] \qquad (4)$$

The values of ϕ_i° were calculated using Eq. 4 and taking into account only pure component i. A modified version of Rackett's equation (See Spencer and Danner[21]), was used to determine the molar volumes, v_i^{L}, for the pure components and variations in the molar volumes with temperature.

Thermodynamic calculations using VLE data ware to a considerable extent subject to the relations employed for the vapor pressures. The Antoine equation is the best-known relation used for this purpose; however, although the literature sets out values for the components considered in this experiment, the same equilibrium still was utilized to make experimental measurements of T and p_i° over a range of pressures and temperatures close to those in the present experiment, and these values were correlated by a non-linear regression procedure, yielding the values for the constants A, B, and C given in **Table 2**, which also contains the standard deviations, $s(p_i^{\circ})$, for the experimental data.

The second virial coefficients for both the pure components and the mixtures were calculated using Tsonopoulos's[24] empirical equations, in view of the good

Table 2. Values of the constants A, B, and C for Antoine equation $\log p_i^{\circ} = A - B/(T - C)$ and standard deviations, $s(p_i^{\circ})$

Components	Reference	A	B	C	$s(p_i^{\circ})$/kPa
Methyl ethate	this work	6.4934	1329.46	33.52	0.04
	(20)	6.24410	1183.70	50.736	–
Methyl propanoate	this work	6.6042	1478.55	30.07	0.05
	(20)	6.06734	1170.236	64.40	–
Propan-2-ol	this work	7.1115	1505.94	60.15	0.05
	(20)	6.8662	1360.131	75.558	–

results obtained in previous studies[15, 16, 17, 18, 19, 22].

3. Reduction of Experimental Data

To carry out an effective reduction of the data, the experimental values for the parameters p, T, x_1, and y_1 were first correlated by means of the polynomial equation

$$Q = x_1 x_2 \sum_{i=0}^{m} A_i\,[x_i / (x_i + k x_2)]^i \qquad (5)$$

Thus, the correlations for the compositions were calculated by setting Q equal to y_1-x_1. An equation similar to that for binary mixtures by Tamir[23] was used to correlate the temperatures and the equation for the liquid phase was

$$T = \sum_i x_i T_i^{\circ} + Q \qquad (6)$$

where Q was as in Eq. (5), x_1 was the mole fraction, and T_i° was the boiling point of pure component i at the working pressure. Application of Eq. (5) to the data was performed using a method of least squares for a fixed value of k; the degree of the polynomial was optimized according to a statistical criterion (F-test). The calculation procedure was iterated for different values of k until the minimum standard deviation, $s(Q)$, for the data was found.

The first reduction of the set of data was visual and consisted in discarding all those points that presented some relevant discrepancy in the representation of the experimental points obtained directly, due to systematic experimental errors, i.e.: (y_1-x_1) on x_1, T on x_1 and T on y_1. After this initial selection, the thermodynamic consistency of the data was verified using two versions of the point-to-point test of Van Ness et al.[26]. One of the versions, presented by Fredenslund et al.[4], calculated the virial coefficients according to the method of Hayden and O'Connell[7]. In addition, so as to be able to present the results in coherent fashion, the subroutine used to calculate the virial coefficients was replaced by another that employed Tsonopoulos's[24] empirical expressions, thereby yielding a second version of the consistency test. Both versions pointed up those experimental points that gave rise to an inconsistency in the mixtures with a difference in mole fraction of the vapor phase y_1 higher

Table 3. Coefficients obtained for Eqs. (5) and (6), and standard deviation, $s(Q)$, in the cases studied

p/kPa	correlation	function employed	k	A_o	A_1	A_2	A_3	s
							Coefficients	
	x_1 Methyl ethanoate + x_2 propan-2-ol							
74.66	y vs x_1	(5)	0.636	3.466	−6.904	6.264	−2.563	0.001
	T vs x_1	(6) (5)	0.79	−60.29	72.95	−31.47	−	0.04
	g^E/RT vs x_1	(5)	0.240	0.631	0.268	−	−	0.002
101.32	y vs x_1	(5)	0.926	2.869	−6.658	7.267	−3.328	0.002
	T vs x_1	(6) (5)	0.34	−56.94	39.79	−	−	0.06
	g^E/RT vs x_1	(5)	0.112	1.130	−2.352	3.249	−1.240	0.003
127.99	y vs x_1	(5)	0.634	2.537	−4.286	3.308	−1.352	0.001
	T vs x_1	(6) (5)	0.13	−25.76	−60.66	69.63	−	0.04
	g^E/RT vs x_1	(6) (5)	0.326	0.504	0.224	−	−	0.001
	x_1 Methyl propanoate + x_2 propan-2-ol							
74.66			0.816	1.225	−2.939	3.037	−1.908	0.001
			0.46	−28.29	31.69	−22.06	−	0.08
			0.174	0.396	1.841	−3.632	2.225	0.004
101.32			0.86	0.943	−2.077	1.778	−1.222	0.001
			0.93	−24.12	24.32	−21.21	−	0.06
			2.056	0.615	0.145	−	−	0.002
127.99			1.892	0.722	−2.575	2.483	−1.305	0.001
			2.67	−18.86	18.54	−24.06	−	0.02
			1.404	0.525	0.624	−1.724	1.525	0.003

than 0.01. Table 1 shows all experimental VLE data obtained for the mixtures studied.

We think it interesting to draw attention to the influence of the parameter k_{ij} used in the mixing rule for the modified version of the test of Van Ness et al.[26]. Although Tsonopoulos[24] and other workers reported this parameter to be characteristic and constant for each mixture, in actuality quite the converse is true, because the influence of this parameter on the calculations of the virial coefficients B_{ij} was very pronounced in certain cases. Not unexpectedly, the influence of this parameter has an effect on the γ_i values and also of course on the thermodynamic consistency test. Except for the mixture of methyl ethanoate and propan-2-ol at 74.66 kPa, for which the optimum value of k_{ij} was higher than 0.2, the optimum calculations for the remaining mixtures took values of $k_{ij} \simeq 0.01$ (see Tsonopoulos[24, 25]).

Table 3 contains the values of the coefficients of Eq. (5) and the corresponding standard deviations, $s(Q)$, for correlations of the functions (y_1-x_1), T, and g^E/RT on the composition, x_1, of the liquid phase. Using the data in Table 3 the corresponding magnitudes can be estimated as well as the activity coefficients, γ_i, by setting Q equal to g^E/RT in Eq. (5). In this case, the expressions for those coefficients, written for an indeterminate number of parameters, took the forms:

$$ln\ \gamma_1 = x_2^2 \left[\sum_1^n A_{j-i} z^{j-i} + x_1 k \left(\frac{z}{x_1}\right)^2 \sum_1^{n-1} j\ A_j z^{j-1} \right] \quad (7)$$

Table 4. Azeotropes obtained by using of Eqs. 6 and 10-13 for the system: (x_1 methyl propanoate + x_2 propan-2-ol) at various pressures

p/kPa	$x_1 = y_1$	T/K	literature values	
74.66	0.666	340.47		
101.32	0.624	348.88	0.527	349.5 K (ref. 8)
			0.637	350.15 K (ref. 8)
127.99	0.554	355.98		

$$ln\ \gamma_2 = x_1^2 \left[\sum_1^n A_{j-i} z^{j-i} + x_2 k \left(\frac{z}{x_1}\right)^2 \sum_1^{n-1} j\ A_j z^{j-i} \right] \quad (8)$$

where

$$z = x_1 / (x_1 + k x_2) \quad (9)$$

4. Azeotropes

Of all the mixtures considered here, only the system composed of methyl propanoate and propan-2-ol presented a minimum azeotrope; the system composed of methyl ethanoate and propan-1-ol also failed to present an azeotrope. The correlations for y_1 on x_1 and T on x_1, the coefficients for which appear in Table 3, were used to determine the exact location of the singular points, and the following conditions were established for the azeotropic point in binary mixtures at constant pressure:

$$y_1 = x_1 \quad \left(\frac{\partial T}{\partial x_1}\right)_P = 0 \quad \left(\frac{\partial T}{\partial y_1}\right)_P = 0 \quad (10)$$

These conditions in turn gave rise to the following equations:

from Eq. (5) and as: $\quad Q = y_1 - x_1 \quad 0 = \sum_{i=0}^{2} A_i z^i \quad (11)$

from Eq. (6):

$$0 = T_1° - T_2° + (1 - 2x_1)\alpha + x_1 x_2 \beta k z^2/x_1^2 \quad (12)$$

where $\quad x_2 = 1 - x_1 \quad a = \sum_{i=0}^{2} A_i z^i \quad \beta = (d\alpha/dz) \quad (13)$

The coefficients A_i in α correlated the temperature values and thus were different from the coefficients thus designated in Eq. (10) (see Table 3). In addition to the preceding equations, Eq. (6) was also needed, in order to calculate the temperature of the azeotropes, and these values are set out in **Table 4**. One of the two azeotropes described by Horsley[8] at 101.32 kPa yielded a composition value that rather closely mirrored our results, though with a temperature difference greater than 1 K, whereas for the other of these azeotropic values the converse held true, i.e., the temperature closely matched our results but the composition value differed. It is interesting to note the quasi-linear variation in composition of the azeotrope with pressure, although the narrow range of pressures used in this study meant that reliable extrapolations could not be made.

Table 5. Average per cent error, $\bar{e}$, obtained in prediction of γ_i in the isobaric VLE using different models considering the interactions indicated below. Values in parentheses indicate the vapor-phase mole fraction, y_1, of the azeotropic points with the various models

| p/kPa | ASOG | UNIFAC-1 | | | UNIFAC-2 |
	OH/COO[9]	COH/COO[2]	CCOH/COOC[4]	OH/COOC[6]	OH/COOC[10]
Methyl ethanoate + propan-2-ol					
74.66	2.4	6.5	3.8	3.5	2.3
101.32	3.8	4.2	2.3	4.6	1.8
127.99	4.9	2.6	1.9	5.7	1.2
Methyl propanoate + propan-2-ol					
74.66	3.1	4.0	2.8	5.4	1.8
	(0.607)	(0.570)	(0.637)	(0.664)	(0.635)
101.66	4.7	2.5	2.7	6.6	2.1
	(0.575)	(0.535)	(0.596)	(0.631)	(0.589)
127.99	4.4	1.9	3.6	7.4	1.8
	(0.555)	(0.511)	(0.586)	(0.626)	(0.568)

% average error, $\bar{e} = \Sigma \mid (\gamma_{i,\,exp} - \gamma_{i,\,cal})/\gamma_{i,\,exp} \mid \cdot 100/N$

5. Prediction of Isobaric VLE Values Using Different Group Contribution Models

Isobaric VLE values were predicted for the systems considered using the ASOG model[9] and the versions of the UNIFAC model published by Fredenslund et al.[2] (UNIFAC-1) and more recently by Larsen et al.[10] (UNIFAC-2), even though this latter version is not commonly employed by researchers when studying isobaric equilibria and in fact yielded rather poor results in an earlier study[18]. In all cases the predictions were evaluated by comparing with the activity coefficients, γ_i, (estimated and experimental from Table 1) as the concentration values of the vapor phase, y_i, obtained implicitly by applying Eqs. (3) and (4). **Table 5** gives quantitatively the mean percentage errors in estimates of the activity coefficients for the systems considered under the different working conditions employed.

Application of the different models took into account the different cases contemplated in the current literature, particularly for the UNIFAC-1 model, in which different alkanol/ester interaction pairs can be considered. **Figures 1** and **2** present a qualitative plot of the differences among the estimates of ester concentration in the vapor phase. It is interesting to observe that the greater differences in the estimation of y_1 for the system methyl ethanoate + propan-2-ol appear at high concentrations of alkanol, perhaps due to association effects; contrarily, for the system methyl propanote + propan-2-ol, where the estimated values were always lower than the experimentals, excluding the inexplicable case of the OH/COOC group (UNIFAC-1) at 101.32 kPa, where the differences were higher and positive at concentrations closer to unity. Even though an alkanol isomer that usually gives rise to large differences in the predictions was considered here, the overall assessment
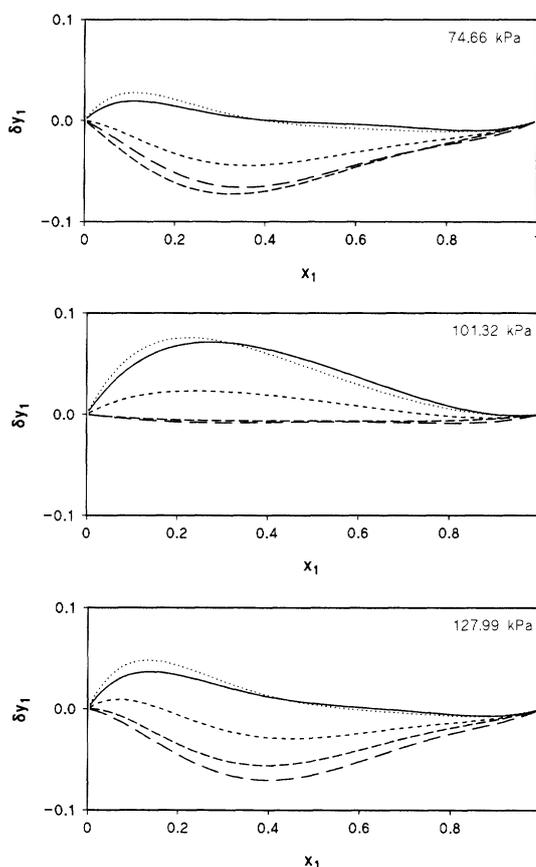

Fig. 1 Deviations at various pressures, $\delta y_1 = (y_{1,\,the} - y_{1,\,cal})$, for the system ($x_1$ methyl ethanoate + x_2 propan-2-ol) between the curves corresponding to experimental data and those obtained by use of respective models. UNIFAC-1: ———, OH/COOC; – – – –, CCOH/COOC; — — —, COH/COO. ASOG: • • • • • UNIFAC-2: —— ——.

was extremely positive; and in any case, the interaction pair OH/COOC in the UNIFAC-1 model cannot be regarded as yielding the worst estimates produced for the values. Overall mean errors were less than 7% in all cases, which is a rather eloquent statement of the usefulness of the models applied.

On the other hand, the differences among the estimates of the azeotropic point for the system (x_1 methyl propanoate + x_2 propan-2-ol) were greater. As pointed out above, it is difficult in cases such as these, in which significant errors do not exist, to select one or another of the models as the most appropriate, since for this system one of the best estimations of the singular point was achieved using the interaction pair OH/COOC in the UNIFAC-1 model, which yielded an overall mean error for the three working pressures of less than 5%.

In conclusion, excellent results were obtained using the ASOG group-contribution model to produce reasonable predictions of the isobaric vapor-liquid equilibrium values for systems consisting of a (methyl ester + propan-2-ol). Generally speaking, and even considering here the results we have presented for non-isomers in other papers, the utilization of these models was
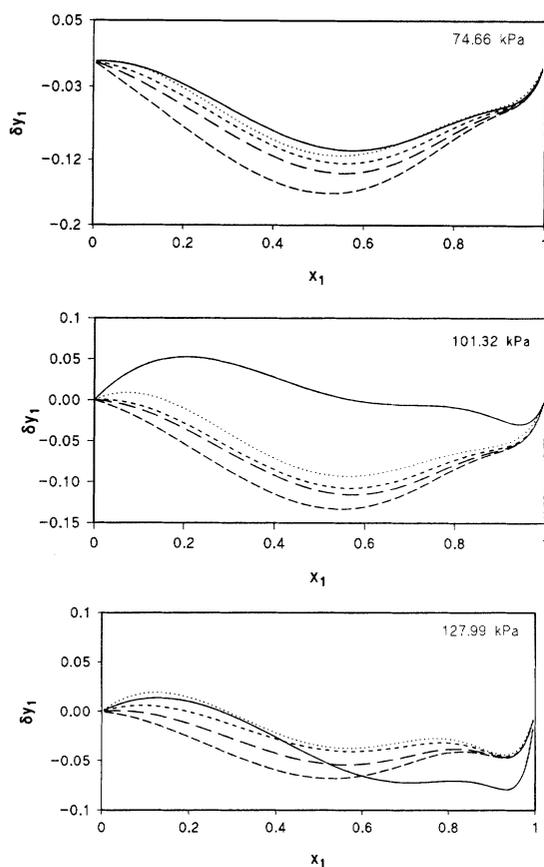
Fig. 2 Deviations at different pressures, $\delta y_1 = (y_{1,\text{the}} - y_{1,\text{cal}})$, for the system ($x_1$ methyl propanoate + x_2 propan-2-ol) between the curves corresponding to experimental data and those obtained by using of respective models. UNIFAC-1: ———, OH/COOC; – – – –, CCOH/COOC; — — —, COH/COO. ASOG: • • • • • UNIFAC-2: —— ——.

highly acceptable, yielding errors of between 5 and 10% in the prediction of γ_i. Nevertheless, we intend to extend future investigations to include other components in the (alkyl ester + alkanol) series as well as wider pressure ranges.

Acknowledgment

Nomenclature

A, B, C	=	Antoine equation constants	[–]
A_i	=	coefficients in Eq. (5)	[–]
B_{ij}	=	cross-virial coefficient	[m³. kmol⁻¹]
e	=	average percent error	[–]
k	=	parameter in Eq. (5)	[–]
N	=	number of experimental points	[–]
p	=	total pressure	[kPa]
P_i^o	=	vapor pressure of pure component i	[kPa]
R	=	universal gas constant	[J.K.⁻¹·kmol⁻¹]
s	=	standard deviation	[–]
T	=	temperature	[K]
T_i^o	=	boiling temperature of pure component i	[K]
v_i^L	=	molar volume of pure component i	[m³. kmol⁻¹]
x	=	liquid-phase molar fraction	[–]
y	=	vapor-phase molar fraction	[–]
z	=	function defined by Eq. (9)	[–]
ρ	=	density	[kg. m⁻³]
γ_i	=	activity coefficient of component i	[–]
ϕ_i	=	fugacity coefficient of component i	[–]

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