Isobaric Vapor-Liquid Equilibria in the Ternary Systems Methyl Acetate + Vinyl Acetate + Propyl Bromide and Methyl Acetate + Vinyl Acetate + Toluene

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Vapor-liquid equilibrium at 101.3 kPa has been determined for the title systems. The data were correlated by the Redlich-Kister and Wisniak-Tamir equations, and the appropriate parameters are reported. The activity coefficients of the ternary systems can be predicted from those of the pertinent binary systems. No ternary azeotrope is present.

The present work was undertaken to measure vapor-liquid equilibrium (VLE) data for the title systems for which no isobaric data are available. This is part of a program to determine UNIFAC parameters for organic bromides. Data for the binaries have already been reported (*1-5*).

Experimental Section

Purity of Materials. Methyl acetate (99.2+%) and propyl bromide (99.4+%) were purchased from Merck, vinyl acetate (99.0+%) from Fluka, and toluene (99.6+%) from Frutarom. The reagents were used without further purification after gas chromatography failed to show any significant impurities. Properties and purities (as determined by GLC) of the pure components appear in Table I.

Apparatus and Procedure. An all-glass modified Dvorak and Boublik recirculation still (*6*) was used in the VLE measurements. The experimental features have been described in a previous publication (*7*). All analyses were carried out by gas chromatography on a Packard-Becker Model 417 apparatus provided with a thermal conductivity detector and a Spectra Physics Model SP 4290 electronic integrator. The column was 3 m long and 0.2 cm in diameter, filled with 20% OV-17, and operated at 60 °C. The temperatures at the detector and injector were 120 and 200 °C, respectively. Very good separation was achieved under these conditions, and calibration analyses were carried out to convert the peak ratio to the weight composition of the sample. Concentration measurements were accurate to better than 0.008 mole fraction units. The accuracies in determination of pressure P and temperature t were at least ±0.5 mmHg and ±0.02 K, respectively.

Results

The temperature t, liquid-phase, x_i, and vapor-phase, y_i, mole fraction measurements at P = 101.3 kPa for the two systems are reported in Tables II and III, together with the activity coefficients γ_i which were calculated from the following equation (*8*):

$$\ln \gamma_i = \ln (Py_i/P_i^\circ x_i) + (B_{ii} - v_i^L)(P - P_i^\circ)/RT + (P/2RT)\sum_1^n\sum_1^n y_j y_k(2\delta_{ji} - \delta_{jk}) \quad (1)$$

where

$$\delta_{ji} = 2B_{ji} - B_{jj} - B_{ii} \quad (2)$$

Table I. GLC Purities, Refractive Indices n_D at Na D Line, and Normal Boiling Points T_i° of Pure Components

component i (purity/(mol %))	n_D(298.15 K)	T_i°/K
methyl acetate (99.5)	1.3588[a]	330.09[a]
	1.3589[b]	330.09[b]
vinyl acetate (99.6)	1.3932[a]	345.71[a]
	1.3934[c]	345.65[c]
toluene (99.5)	1.4926[a]	383.85[a]
	1.493 96[b]	383.78[b]
propyl bromide (99.4)	1.4320[a]	343.70[a]
	1.4317[b]	344.15[b]

[a] Measured. [b] Reference 14. [c] Reference 16.

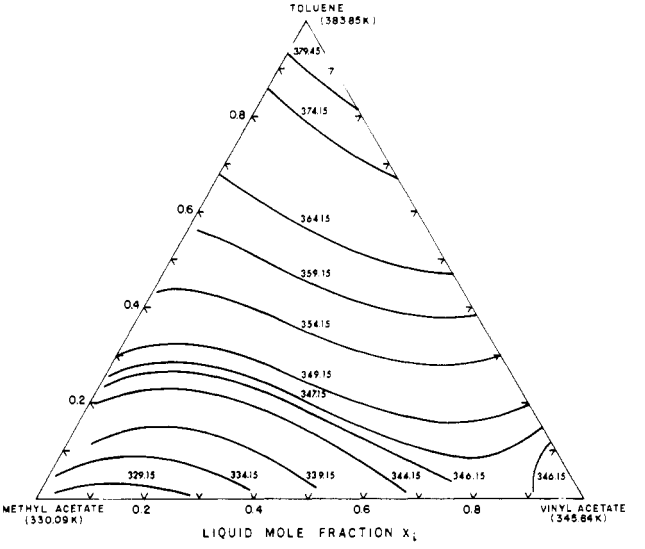

Figure 1. Isothermals for the ternary system methyl acetate + vinyl acetate + propyl bromide (101.3 kPa). Coefficients from eq 5.

The pure component vapor pressures P_i° were calculated according to Antoine's equation:

$$\log (P_i^\circ/\text{kPa}) = A_i - B_i/(T/\text{K} - C_i) \quad (3)$$

where the constants A_i, B_i, and C_i are reported in Table IV. The molar virial coefficients B_{11}, B_{12}, and B_{22} were estimated by the method of Tsonopoulos (*9*) using the molecular parameters suggested by the same researcher. The last two terms in eq 1 contributed between 1% and 3% to the activity coefficient, and their influence was important only at very dilute concentrations.

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Table II. Experimental Vapor–Liquid Equilibrium Data for Methyl Acetate (1) + Vinyl Acetate (2) + Propyl Bromide (4) at 101.3 kPa

t/K	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_4	t/K	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_4
330.59	0.873	0.081	0.908	0.046	1.023	0.9329	1.534	336.66	0.362	0.501	0.463	0.389	1.033	1.036	1.362
331.10	0.900	0.063	0.927	0.036	0.9959	0.9221	1.509	336.86	0.270	0.285	0.360	0.231	1.070	1.075	1.151
331.25	0.863	0.085	0.885	0.061	0.9866	1.152	1.559	336.86	0.393	0.431	0.490	0.323	1.001	0.9934	1.331
331.54	0.729	0.182	0.795	0.114	1.039	0.9954	1.520	337.01	0.290	0.445	0.381	0.339	1.049	1.005	1.317
331.84	0.664	0.039	0.713	0.031	1.013	1.250	1.269	337.30	0.273	0.211	0.376	0.165	1.090	1.022	1.098
332.15	0.671	0.228	0.743	0.148	1.034	1.010	1.573	337.38	0.255	0.182	0.360	0.148	1.115	1.060	1.076
332.21	0.620	0.068	0.690	0.043	1.038	0.9818	1.244	337.55	0.254	0.254	0.356	0.200	1.101	1.020	1.106
332.59	0.706	0.178	0.791	0.103	1.032	0.8867	1.313	337.58	0.207	0.240	0.293	0.206	1.110	1.111	1.109
332.65	0.555	0.162	0.639	0.110	1.058	1.038	1.271	337.65	0.223	0.367	0.308	0.306	1.081	1.077	1.150
333.08	0.537	0.174	0.633	0.112	1.068	0.9699	1.247	337.70	0.218	0.136	0.315	0.118	1.130	1.119	1.070
333.08	0.604	0.160	0.663	0.119	0.9946	1.121	1.306	337.78	0.210	0.353	0.287	0.295	1.066	1.074	1.163
333.08	0.659	0.256	0.740	0.172	1.017	1.012	1.464	337.96	0.187	0.320	0.264	0.275	1.095	1.098	1.131
333.12	0.532	0.081	0.619	0.055	1.053	1.022	1.189	338.26	0.168	0.293	0.246	0.256	1.125	1.106	1.107
333.29	0.613	0.263	0.721	0.155	1.058	0.8816	1.404	338.40	0.320	0.622	0.420	0.510	1.003	1.033	1.440
333.36	0.649	0.243	0.702	0.182	0.9711	1.118	1.505	338.45	0.321	0.541	0.410	0.438	0.9750	1.018	1.312
333.82	0.522	0.266	0.617	0.183	1.046	1.011	1.302	338.54	0.148	0.012	0.248	0.012	1.276	1.254	1.046
334.05	0.374	0.036	0.494	0.024	1.160	0.9718	1.119	338.68	0.178	0.075	0.277	0.070	1.180	1.165	1.034
334.20	0.654	0.318	0.766	0.203	1.023	0.9256	1.510	338.70	0.364	0.583	0.470	0.462	0.9779	0.9882	1.517
334.45	0.418	0.280	0.508	0.207	1.053	1.063	1.276	338.92	0.146	0.146	0.239	0.130	1.232	1.103	1.046
334.46	0.546	0.254	0.637	0.172	1.011	0.9733	1.291	339.11	0.323	0.597	0.427	0.483	0.9885	0.9953	1.313
334.54	0.506	0.263	0.591	0.186	1.009	1.014	1.302	339.32	0.157	0.322	0.228	0.283	1.079	1.074	1.088
334.64	0.483	0.329	0.574	0.231	1.022	1.002	1.393	339.32	0.264	0.595	0.356	0.479	1.002	0.9836	1.357
334.64	0.578	0.399	0.686	0.287	1.021	1.026	1.576	339.36	0.208	0.509	0.283	0.420	1.010	1.007	1.215
334.72	0.517	0.386	0.617	0.279	1.025	1.030	1.438	339.45	0.129	0.128	0.214	0.121	1.228	1.150	1.033
334.85	0.504	0.252	0.592	0.177	1.005	0.9962	1.264	339.52	0.143	0.328	0.207	0.291	1.069	1.077	1.093
334.91	0.419	0.147	0.523	0.104	1.066	1.002	1.145	339.86	0.112	0.114	0.185	0.115	1.207	1.211	1.031
335.05	0.430	0.206	0.530	0.148	1.048	1.012	1.773	339.95	0.110	0.249	0.169	0.234	1.120	1.125	1.059
335.41	0.579	0.387	0.692	0.270	1.004	0.9709	1.466	340.12	0.235	0.725	0.323	0.626	0.9961	1.028	1.442
335.55	0.353	0.258	0.448	0.199	1.062	1.069	1.185	340.38	0.219	0.662	0.296	0.570	0.9717	1.016	1.264
335.72	0.343	0.117	0.449	0.092	1.090	1.083	1.103	340.61	0.106	0.042	0.183	0.045	1.233	1.256	1.009
335.72	0.389	0.212	0.485	0.160	1.038	1.040	1.155	341.32	0.182	0.786	0.258	0.700	0.9901	1.020	1.431
335.78	0.444	0.329	0.535	0.243	1.001	1.015	1.268	341.46	0.046	0.413	0.072	0.389	1.089	1.074	1.081
335.80	0.385	0.333	0.479	0.249	1.033	1.027	1.249	341.51	0.057	0.524	0.088	0.478	1.072	1.038	1.122
335.85	0.338	0.120	0.441	0.099	1.081	1.131	1.097	341.54	0.130	0.679	0.155	0.519	0.8273	0.8688	1.848
335.92	0.407	0.438	0.505	0.332	1.026	1.037	1.357	341.70	0.052	0.185	0.088	0.191	1.169	1.168	1.018
336.17	0.435	0.484	0.543	0.366	1.024	1.026	1.438	341.70	0.070	0.636	0.103	0.570	1.016	1.014	1.198
336.22	0.367	0.281	0.475	0.205	1.060	0.9880	1.162	342.15	0.141	0.773	0.202	0.691	0.9756	0.9963	1.323
336.52	0.320	0.366	0.411	0.285	1.042	1.044	1.225	343.04	0.108	0.816	0.159	0.757	0.9759	1.005	1.144

Table III. Experimental Vapor–Liquid Equilibrium Data for Methyl Acetate (1) + Vinyl Acetate (2) + Toluene (3) at 101.3 kPa

t/K	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3	t/K	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3
332.59	0.843	0.100	0.913	0.069	0.9955	1.065	1.712	345.35	0.350	0.244	0.604	0.247	1.058	1.020	1.233
332.85	0.803	0.164	0.885	0.106	1.004	0.9885	1.464	345.61	0.109	0.789	0.171	0.786	0.9544	0.9948	1.403
333.39	0.767	0.196	0.860	0.128	1.004	0.9801	1.704	345.62	0.088	0.828	0.137	0.827	0.9468	0.9970	1.426
333.99	0.774	0.189	0.855	0.133	0.9694	1.034	1.665	345.66	0.224	0.542	0.360	0.548	0.9760	1.008	1.306
334.26	0.749	0.161	0.842	0.131	0.9778	1.185	1.524	345.68	0.255	0.451	0.429	0.468	1.021	1.034	1.163
334.68	0.694	0.255	0.805	0.178	0.9951	1.002	1.666	345.78	0.406	0.074	0.724	0.088	1.079	1.182	1.196
335.53	0.635	0.302	0.781	0.200	1.026	0.9230	1.459	345.88	0.185	0.618	0.297	0.626	0.9685	1.003	1.288
336.59	0.700	0.041	0.893	0.031	1.028	1.017	1.363	345.94	0.301	0.348	0.488	0.375	0.9761	1.065	1.284
337.52	0.666	0.047	0.862	0.053	1.013	1.469	1.328	346.10	0.299	0.341	0.490	0.360	0.9819	1.038	1.363
337.78	0.589	0.121	0.810	0.100	1.067	1.067	1.378	346.51	0.055	0.856	0.099	0.864	1.066	0.9795	1.340
338.34	0.529	0.300	0.717	0.228	1.033	0.9629	1.398	346.86	0.233	0.442	0.406	0.474	1.021	1.030	1.175
338.48	0.482	0.428	0.633	0.335	0.9964	0.9869	1.537	347.25	0.292	0.269	0.540	0.298	1.070	1.051	1.159
338.961	0.598	0.063	0.848	0.048	1.060	0.9457	1.303	348.35	0.331	0.147	0.639	0.174	1.081	1.085	1.082
339.18	0.470	0.392	0.630	0.327	0.9946	1.027	1.312	348.94	0.323	0.072	0.683	0.083	1.164	1.037	1.145
339.72	0.410	0.490	0.547	0.417	0.9733	1.029	1.486	349.20	0.254	0.265	0.487	0.320	1.048	1.078	1.177
339.98	0.566	0.063	0.829	0.054	1.060	1.028	1.289	349.38	0.198	0.396	0.375	0.466	1.029	1.044	1.141
340.26	0.508	0.233	0.706	0.212	0.9966	1.081	1.281	349.84	0.247	0.246	0.510	0.288	1.107	1.024	1.143
340.52	0.402	0.457	0.561	0.390	0.9927	1.005	1.392	350.16	0.107	0.559	0.204	0.657	1.013	1.018	1.180
340.84	0.492	0.194	0.750	0.153	1.073	0.9195	1.223	350.70	0.154	0.402	0.317	0.507	1.076	1.074	1.103
341.12	0.397	0.453	0.551	0.397	0.9689	1.012	1.358	351.00	0.153	0.387	0.320	0.494	1.084	1.078	1.114
341.72	0.478	0.193	0.694	0.198	0.9947	1.162	1.258	351.48	0.183	0.304	0.394	0.402	1.101	1.100	1.078
341.81	0.474	0.104	0.778	0.099	1.121	1.075	1.114	351.55	0.163	0.344	0.329	0.441	1.030	1.064	1.261
342.15	0.388	0.366	0.555	0.324	0.9671	0.9885	1.855	352.30	0.211	0.214	0.471	0.294	1.114	1.115	1.077
342.60	0.490	0.071	0.789	0.070	1.073	1.085	1.192	352.76	0.161	0.284	0.369	0.397	1.129	1.119	1.094
343.20	0.469	0.065	0.788	0.065	1.010	1.080	1.146	352.85	0.183	0.244	0.416	0.342	1.117	1.119	1.092
343.35	0.196	0.728	0.291	0.678	0.9675	1.000	1.473	355.56	0.224	0.054	0.595	0.081	1.208	1.104	1.059
343.52	0.433	0.125	0.714	0.149	1.069	1.273	1.113	357.00	0.059	0.359	0.149	0.571	1.104	1.122	1.082
343.52	0.318	0.443	0.497	0.420	1.013	1.013	1.246	360.36	0.089	0.204	0.265	0.372	1.187	1.167	1.035
344.70	0.393	0.162	0.692	0.160	1.101	1.016	1.144	360.66	0.122	0.130	0.368	0.250	1.192	1.220	1.020
344.80	0.148	0.728	0.230	0.722	0.9688	1.016	1.326	362.35	0.141	0.036	0.471	0.085	1.261	1.428	1.020
345.01	0.272	0.468	0.428	0.465	0.9745	1.012	1.399	364.11	0.086	0.092	0.311	0.200	1.303	1.252	1.064
345.12	0.313	0.350	0.521	0.363	1.027	1.052	1.166	366.60	0.052	0.137	0.177	0.302	1.149	1.185	1.063
345.22	0.412	0.077	0.743	0.083	1.110	1.091	1.150	367.16	0.042	0.137	0.157	0.318	1.244	1.228	1.040
345.24	0.377	0.135	0.714	0.122	1.165	0.9163	1.134	368.44	0.058	0.074	0.230	0.183	1.277	1.264	1.057
345.29	0.397	0.081	0.723	0.093	1.118	1.159	1.187	369.15	0.034	0.119	0.135	0.290	1.256	1.222	1.038

Table IV. Antoine Coefficients, Equation 3

compound	A_i	B_i	C_i
methyl acetate[a]	6.186 21	1156.43	53.46
propyl bromide[a]	6.035 55	1194.889	47.64
vinyl acetate[b]	6.117 17	1191.99	56.14
toluene[a]	6.079 54	1344.80	53.668

[a] Reference 14. [b] Reference 15.

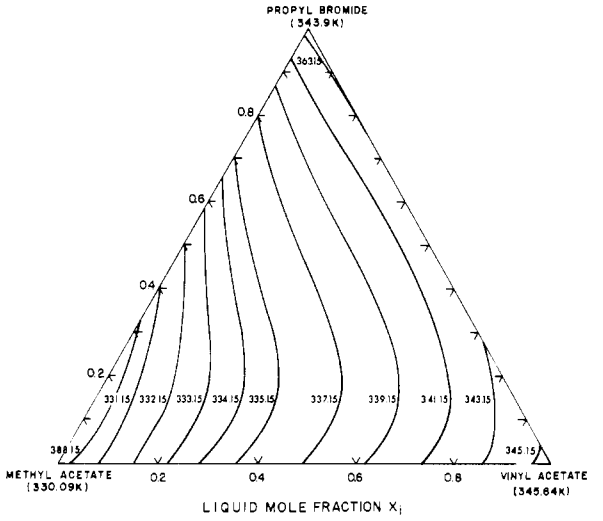

Figure 2. Isothermals for the ternary system methyl acetate + vinyl acetate + toluene (101.3 kPa). Coefficients from eq 5.

The ternary data reported in Table III were found to be thermodynamically consistent as tested by the McDermot-Ellis method (*10*) modified by Wisniak and Tamir (*11*).

The activity coefficients for the ternary system were correlated by the following Redlich-Kister expansion (*12*):

$$\ln \gamma_1/\gamma_2 = b_{12}(x_2 - x_1) - c_{12}[(x_1 - x_2)^2 - 2x_1x_2] + d_{12}(x_2 - x_1)[(x_1 - x_2)^2 - 4x_1x_2] + x_3[b_{13} + c_{13}(2x_1 - x_3) + d_{13}(x_1 - x_3)(3x_1 - x_3) - b_{23} - c_{23}(2x_2 - x_3) - d_{23}(x_2 - x_3)(3x_2 - x_3) + C_1(x_2 - x_1)] \quad (4)$$

where b_{ij}, c_{ij}, and d_{ij} are constants for the pertinent binary and C_1 is a ternary constant. The equations for two other pair of activity coefficients were obtained by cyclic rotation of the indices. The binary data used for calculating the binary constants have been reported elsewhere (*1-5*).

The ternary Redlich-Kister coefficient was obtained by a Simplex optimization technique. The differences between the values of the root mean square deviation for the activity coefficient for the two cases—with and without the ternary constant C_1 (Table V)—are statistically not significant, suggesting that ternary data can be predicted directly from the binary systems.

The boiling points of the systems were correlated by the equation proposed by Wisniak and Tamir (*13*):

$$T/\mathrm{K} = \sum_{i=1}^{n} x_i\,(T_i^\circ/\mathrm{K}) + \sum_{i,j=1}^{n}\{x_ix_j\sum_{k=0}^{l} C_k(x_i - x_j)^{k'}\} + x_1x_2x_3\{A + B(x_1 - x_2) + C(x_1 - x_3) + D(x_2 - x_3)\} \quad (5)$$

In these equations n is the number of components ($n = 2$ or 3), T_i° is the boiling point of the pure component i, and l is the number of terms in the series expansion of $x_i - x_j$. C_k are the binary constants and A, B, C, and D are ternary constants. An equation of the same structure can be used for the direct correlation of ternary data, without use of binary data. Both forms will require about the same number of constants for similar accuracy, but the direct correlation allows an easier calculation of boiling isotherms (Figures 1 and 2). The various constants of eq 5 are reported in Table VI, which also contains information indicating the degree of goodness of the correlation.

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Glossary

A_i,B_i,C_i	Antoine constants, eq 3
B_{ii},B_{ij}	second molar virial coefficients, eqs 1 and 2
b_{ii},c_{ij},d_{ii}	Redlich-Kister constants, eq 4
N	number of measurements
P	total pressure
P_i°	vapor pressure of pure component i
R	gas constant
rmsd(T)	root mean square deviation, $\{\Sigma(T_{expt} - T_{calc})^2\}^{0.5}/N$

Table V. Redlich-Kister Coefficients, Ternary Data, and Root Mean Square Deviations in Activity Coefficients, rmsd

system	b_{ij}	c_{ij}	d_{ij}	b_{ik}	c_{ik}	d_{ik}	b_{jk}	c_{jk}	d_{jk}	C_1	rmsd
methyl acetate (1) + vinyl acetate (2) + toluene (3)	−0.0193	−0.0011	0.0212	0.1735	0.0311	0.0256	0.0818	−0.0403	−0.0491	0	0.122
										0.107 14	0.126
methyl acetate (1) + vinyl acetate (2) + propyl bromide (4)	−0.0193	−0.0011	0.0212	0.1285	−0.1560	−0.2086	0.1500	−0.0025	0.0330	0	0.139
										0.015 43	0.138

Table VI. Coefficients in Correlation of Boiling Points, Equation 5 ($D = 0$), and Root Mean Square Deviations in Temperature, rmsd(T/K)

system	C_0	C_1	C_2	C_3	rmsd(T/K)
methyl acetate (1) + propyl bromide (4)[a]	−19.361	5.3265	−1.1257		0.15
methyl acetate (1) + toluene (3)[a]	−52.545	27.524	−39.156	45.146	0.33
vinyl acetate (2) + propyl bromide (4)[b]	−9.0581	−1.9391			0.12
vinyl acetate (2) + toluene (3)[c]	−29.993	17.168	−15.498		0.21
methyl acetate (1) + vinyl acetate (2)[d]	−2.5616	0.31773	1.5682		0.09
vinyl acetate (2) + propyl bromide (4)[b]	−9.0319	−1.8841			0.12

system	A	B	C	rmsd(T/K)
methyl acetate (1) + propyl bromide (2) + propyl bromide (4)	−0.996 67	−0.689 66		0.52
methyl acetate (1) + vinyl acetate (2) + toluene (3)	12.992	−131.84	89.618	0.94

[a] Reference 2. [b] Reference 1. [c] Reference 3. [d] Reference 4.

rmsd(γ_i)	root mean square deviation, $\{\sum(\gamma_{i,\,expt} - \gamma_{i,\,calc})^2\}^{0.5}/N$
t,T	boiling temperature of a mixture
T_i°	boiling temperature of pure component i
v_i^L	molar volume of liquid component i
x_i,y_i	mole fraction of component i in the liquid and vapor phases
γ_i	activity coefficient of component i
δ_{ij}	molar virial coefficient parameter, eq 2

Subscripts

expt	experimental value
calc	calculated value

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