Isobaric Vapor-Liquid Equilibria in the Ternary System Acetonitrile + Methyl Acetate + Propyl Bromide

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Vapor-liquid equilibrium at 101.3 kPa has been determined for the ternary system acetonitrile + methyl acetate + propyl bromide. The data were correlated by the Redlich-Kister and Wisniak-Tamir equations, and the appropriate parameters are reported. The activity coefficients of the ternary system 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 system 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 (*1-3*).

Experimental Section

Purity of Materials. Methyl acetate (99.2 + mol %) and propyl bromide (99.4 + mol %) were purchased from Merck, and acetonitrile (99.5 + mol %) was purchased from HPLC Bio-Lab. The reagents were used without further purification after gas chromatography failed to show any significant impurities. The 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 (*4*) was used in the VLE measurements. The experimental features have been described in a previous publication (*5*). 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 Poropak Q, and operated at 140 °C. The temperatures at the detector and injector were 240 and 220 °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 unit. The accuracies in determination of the pressure P and temperature t were at least ±0.1 kPa and 0.02 °C, respectively.

Results

The temperature T and liquid-phase x_i and vapor-phase y_i mole fraction measurements at P = 101.3 kPa are reported in Table II, together with the activity coefficients γ_i which were calculated from the following equation (*6*):

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

where

Table I. Mole Percent GLC Purities, Refractive Indexes n_D at the Na D Line, and Normal Boiling Points T of Pure Components

component (purity/(mol %))	n_D(298.15K)	T/K
acetonitrile (99.5)	1.3410[a]	354.65[a]
	1.3416[b]	354.75[b]
methyl acetate (99.2)	1.3588[a]	330.09[a]
	1.3589[b]	330.09[b]
propyl bromide (99.4)	1.4320[a]	343.70[a]
	1.4317[b]	344.15[b]

[a] Measured. [b] Reference 12.

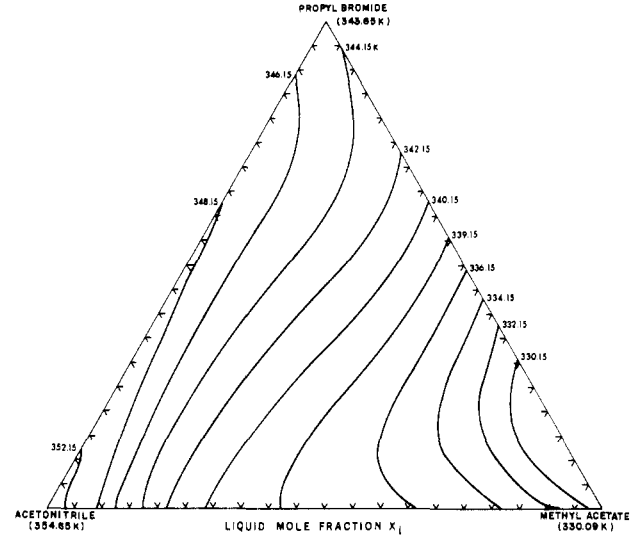

Figure 1. Isothermals for the ternary system acetonitrile + methyl acetate + propyl bromide (101.3 kPa). Coefficients from eq 5.

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

The pure component vapor pressures P_i° were calculated according to the Antoine 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 III. The molar virial coefficients B_{ii} and B_{ij} were estimated by the method of O'Connell and Prausnitz (*7*) using the molecular parameters suggested by the authors and assuming the association parameter η to be zero. The last two terms in eq 1 contributed less than 3% to the activity coefficient, and their influence was important only at very dilute concen-

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Table II. Experimental Vapor–Liquid Equilibrium Data for Acetonitrile (1) + Methyl Acetate (2) + Propyl Bromide (3) at 101.3 kPa

T/K	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3	$-B_{12}$/ (cm^3 mol^{-1})	$-B_{13}$/ (cm^3 mol^{-1})	$-B_{23}$/ (cm^3 mol^{-1})	$-B_{11}$/ (cm^3 mol^{-1})	$-B_{22}$/ (cm^3 mol^{-1})	$-B_{33}$/ (cm^3 mol^{-1})
331.95	0.189	0.773	0.132	0.824	1.448	1.006	1.783	1029	1029	921	2384	1815	1984
332.58	0.169	0.613	0.118	0.680	1.410	1.030	1.373	1023	1024	916	2371	1805	1973
332.65	0.244	0.701	0.144	0.792	1.191	1.043	1.747	1023	1023	916	2369	1804	1972
332.65	0.248	0.657	0.153	0.738	1.241	1.039	1.712	1023	1023	916	2369	1804	1972
333.19	0.203	0.552	0.139	0.622	1.349	1.028	1.411	1018	1018	911	2359	1795	1964
333.32	0.212	0.621	0.165	0.666	1.525	0.9730	1.467	1017	1017	910	2356	1793	1961
333.35	0.193	0.557	0.160	0.598	1.621	0.9758	1.392	1016	1017	910	2355	1792	1961
333.42	0.219	0.498	0.150	0.578	1.336	1.054	1.376	1016	1016	910	2354	1791	1960
333.76	0.279	0.594	0.176	0.693	1.217	1.043	1.480	1013	1013	907	2347	1786	1955
334.42	0.212	0.361	0.188	0.403	1.664	0.9917	1.312	1007	1007	902	2334	1775	1944
334.44	0.297	0.466	0.199	0.549	1.256	1.037	1.474	1007	1007	900	2334	1775	1943
334.66	0.353	0.487	0.226	0.583	1.189	1.045	1.652	1005	1005	900	2329	1771	1940
334.69	0.327	0.531	0.207	0.630	1.178	1.032	1.592	1004	1004	900	2329	1771	1939
334.75	0.385	0.454	0.247	0.549	1.185	1.054	1.746	1004	1004	899	2328	1770	1939
335.11	0.368	0.474	0.239	0.567	1.187	1.030	1.674	1001	1001	896	2321	1764	1933
335.21	0.252	0.371	0.189	0.454	1.370	1.057	1.270	1000	1000	896	2319	1763	1931
335.66	0.262	0.330	0.202	0.406	1.386	1.051	1.267	996	996	892	2310	1756	1924
335.15	0.432	0.378	0.288	0.463	1.210	1.059	1.775	1000	1001	886	2320	1764	1932
335.86	0.422	0.506	0.264	0.633	1.114	1.050	1.922	994	994	891	2306	1752	1921
336.36	0.291	0.229	0.240	0.301	1.444	1.106	1.228	990	990	887	2296	1745	1913
336.40	0.254	0.188	0.228	0.247	1.573	1.110	1.203	989	990	886	2295	1744	1913
336.71	0.219	0.157	0.213	0.212	1.691	1.133	1.164	987	987	884	2289	1739	1908
336.74	0.431	0.259	0.304	0.336	1.211	1.076	1.484	986	987	884	2289	1739	1907
337.09	0.325	0.183	0.277	0.236	1.452	1.066	1.241	983	984	881	2282	1733	1902
337.18	0.279	0.151	0.254	0.195	1.552	1.069	1.205	982	983	881	2280	1732	1900
337.21	0.473	0.314	0.318	0.397	1.135	1.030	1.694	982	983	880	2280	1731	1900
337.32	0.234	0.118	0.230	0.173	1.673	1.211	1.141	981	982	880	2278	1730	1898
337.64	0.540	0.349	0.356	0.470	1.095	1.079	1.977	979	979	877	2272	1725	1893
337.65	0.195	0.094	0.208	0.145	1.802	1.266	1.113	978	979	877	2271	1725	1893
337.85	0.196	0.134	0.201	0.184	1.720	1.116	1.117	977	977	876	2268	1721	1890
337.90	0.167	0.084	0.182	0.110	1.834	1.071	1.145	976	977	875	2267	1721	1889
338.06	0.525	0.139	0.384	0.185	1.197	1.072	1.569	975	976	874	2264	1718	1887
338.12	0.547	0.399	0.357	0.545	1.069	1.075	1.271	974	975	874	2262	1717	1886
338.80	0.286	0.050	0.285	0.070	1.612	1.115	1.149	969	969	868	2250	1707	1875
338.82	0.576	0.169	0.426	0.220	1.176	1.022	1.667	968	969	868	2249	1707	1875
338.94	0.567	0.322	0.388	0.437	1.087	1.047	1.910	967	968	867	2247	1705	1873
339.00	0.622	0.237	0.422	0.336	1.072	1.098	2.065	967	968	867	2246	1704	1872
339.15	0.576	0.180	0.402	0.245	1.099	1.056	1.720	966	967	868	2243	1702	1870
339.40	0.528	0.066	0.404	0.090	1.199	1.063	1.458	964	964	864	2238	1698	1866
340.02	0.659	0.263	0.450	0.395	1.042	1.126	2.334	958	959	860	2227	1688	1857
340.46	0.629	0.081	0.453	0.108	1.085	1.005	1.723	955	956	856	2218	1682	1850
340.46	0.672	0.103	0.484	0.141	1.082	1.029	1.905	955	956	856	2218	1682	1850
341.11	0.686	0.225	0.468	0.349	1.004	1.128	2.332	949	951	852	2206	1672	1840
342.40	0.736	0.156	0.535	0.244	1.022	1.103	2.230	939	940	842	2183	1653	1821
343.28	0.792	0.041	0.575	0.061	0.9929	1.036	2.298	932	933	836	2167	1640	1808
343.65	0.784	0.094	0.604	0.144	1.038	1.050	2.170	929	930	834	2160	1634	1803
343.94	0.737	0.220	0.539	0.359	0.9803	1.094	2.491	926	928	832	2155	1630	1798
345.30	0.809	0.155	0.624	0.288	0.9867	1.205	2.475	916	917	822	2130	1610	1778
345.74	0.857	0.047	0.659	0.080	0.9693	1.104	2.690	912	914	819	2123	1604	1772
346.05	0.817	0.143	0.637	0.253	0.9738	1.125	2.270	910	912	817	2117	1599	1768
348.91	0.881	0.095	0.738	0.189	0.9555	1.175	2.788	888	890	798	2067	1559	1727
349.92	0.909	0.074	0.813	0.159	0.9880	1.240	1.477	881	883	791	2050	1545	1713
350.79	0.934	0.053	0.853	0.114	0.9822	1.217	2.224	874	877	786	2035	1532	1701

Table III. Antoine Coefficients, Equation 3

compound	A_i	B_i	C_i
acetonitrile[a]	6.198 43	1279.20	49.15
methyl acetate[b]	6.186 21	1156.43	53.46
propyl bromide[b]	6.035 55	1194.889	47.64

[a] Reference 13. [b] Reference 12.

trations. The calculated activity coefficients are reported in Table II and are estimated accurate to within ±3%.

The ternary data reported in Table II were found to be thermodynamically consistent as tested by the McDermot–Ellis method (*10*) modified by Wisniak and Tamir (*8*). The values of D_{max} were at least 0.044 while the values of D for any given point never exceeded 0.039. The test requires that $D < D_{max}$ for every point. The activity coefficients for the ternary system were correlated by the following Redlich–Kister expansion (*9*):

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

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 pairs of activity coefficients were obtained by cyclic rotation of the indices. The binary data used for calculating the binary constants have been reported elsewhere (*1–3*).

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 IV)—are statistically not significant,

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

	b_{12}	c_{12}	d_{12}	b_{13}	c_{13}	d_{13}	b_{23}	c_{23}	d_{23}	C_1	rmsd γ_1/γ_2	rmsd γ_1/γ_3
acetonitrile (1) + methyl acetate (2) + propyl bromide (3)	0.1395	−0.1253	0.0980	0.4512	0	0	0.0836	−0.1428	0.2507	0	0.011	0.020
										0.011	0.011	0.017

Table V. Coefficients in the 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
acetonitrile (1) + methyl acetate (2)	−17.837	−5.7460	6.4429	–	0.03
acetonitrile (1) + propyl bromide (3)	−35.530	−11.723	−19.298	–	0.04
methyl acetate (2) + propyl bromide (3)	−19.418	5.3963	0	–	0.03
system		A	B	C	rmsd
acetonitrile (1) + methyl acetate (2) + propyl bromide (3)		5.4876	−82.087	–	0.12

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 (*10*):

$$T/\mathrm{K} = \sum_{i=1}^{n} x_i(T_i^\circ/\mathrm{K}) + \sum_{i,j=1}^{n}\{x_i x_j \sum_{k=0}^{l} C_k(x_i - x_j)^k\} + x_1x_2x_3\{A + B(x_1 - x_2) + C(x_1 - x_3) + D(x_2 - x_3)\} \quad (5)$$

In these equations n is the number of components (n = 2 or 3), T_i° is the boiling point of the pure component i (K or °C), and l is the number of terms in the series expansion of $x_i - x_j$. C_k are the binary constants whereas 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 (Figure 1). The various constants of eq 5 are reported in Table V, 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, $\{\sum(T_{\mathrm{exptl}} - T_{\mathrm{calcd}})^2\}^{0.5}/N$
rmsd(γ_i)	root mean square deviation, $\{\sum(\gamma_{i,\mathrm{exptl}} - \gamma_{i,\mathrm{calcd}})^2\}^{0.5}/N$
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

exptl	experimental value
calcd	calculated value

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