Vapor-Liquid Equilibria for the Ternary System Methyl Acetate–Benzene–Cyclohexane

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SEPARATION of the benzene-cyclohexane mixtures resulting from hydrogenation of benzene into pure constituents is industrially important. This is effectively accomplished by azeotropic or extractive distillation of the mixtures with an entrainer. Several investigators have reported vapor-liquid equilibrium data for ternary systems including benzene and cyclohexane, which are needed to design suitable distillation equipment (*3, 4, 5, 7, 13, 24, 25*).

The objectives of this investigation are: to determine vapor-liquid equilibrium data on the methyl acetate–benzene–cyclohexane system and to correlate the experimental data by two methods; one is an analytical method expressing logarithm of activity coefficients, and the other is an algebraic one, for comparison.

EXPERIMENTAL

Purity of Compounds. First grade (Japanses Industrial Standards) methyl acetate was purified in accordance with the procedure by Hurd and Strong (*12*). Cyclohexane of guaranteed reagent grade was used without further purification. Special grade (Japanese Industrial Standards) benzene was purified by recrystallization repeated twice. The physical properties of the pure compounds are shown in Table I.

Analytical Method. The binary mixtures were analyzed by measuring refractive indices. The ternary mixtures were analyzed by combining refractive index and density measurements. Refractive index measurements were made using a Shimadzu Pulfrich refractometer. Prism temperature was controlled at 25 ± 0.1° C. by circulating water from a constant temperature bath. Monochromatic light was obtained from a sodium lamp. Modified Lipkin-type pycnometers were used for density determination. The values of refractive index and density were reproducible within ±0.0001. Figure 1 is a ternary calibration diagram constructed from analytical data listed in Table II.

Temperatures were measured by a copper-constantan thermocouple which was calibrated against a standard thermometer and was connected with a Yokogawa P-7 potentiometer. Observed temperatures were corrected to normal boiling points (*20*) and are believed to be accurate within ±0.05° C.

Vapor-liquid equilibrium data on the mixtures were obtained under atmospheric pressure using a Colburn vapor-recirculating still as described by Grisword and Buford (*8*). Atmospheric pressure recorded during experimental runs showed small deviations from 760 mm. of mercury (average deviation of ±3 mm. Hg.). Such deviations affect observed x-y data negligibly. No correction was made on them.

EXPERIMENTAL RESULTS

Binary Systems. The liquid phase activity coefficients were calculated using the following equation:

$$\gamma_i = \pi y_i / x_i p_i \qquad (1)$$

The vapor pressure data for methyl acetate were obtained from the compilation of Timmermans (*27*). The Antoine equations cited by Lange (*14*) were used to calculate the vapor pressures of benzene and cyclohexane. Binary equilibrium data are shown in Table III.

The area condition for isobaric binary systems has been shown by Herington (*11*) and Thijssen (*26*) to be

$$\int_0^1 \log \frac{\gamma_1}{\gamma_2}\, dx_1 = \frac{1}{2.3} \int_0^1 \frac{\Delta H_m}{RT^2} \left(\frac{dT}{dx_1}\right)_p dx_1 \qquad (2)$$

For close-boiling point and some azeotropic systems the right side of Equation 2 is nearly zero. The benzene-cyclohexane system is an example of this statement. In order to check thermodynamic consistency for a binary system showing an appreciable difference between both sides of Equation 2 the heat of mixing data at boiling points for the same system are necessary. Such data for the present systems were not available. So no further calculations using Equation 2 were made. Chao (*2*) modified the Redlich-Kister equations for isobaric conditions, accounting for the requirements of Equation 2. The equation used to correlate the experimental data on $\log \gamma_1/\gamma_2$ in terms of liquid compositions is

$$\log \frac{\gamma_1}{\gamma_2} = a + b(x_2 - x_1) + c(6x_1x_2 - 1) \qquad (3)$$

Constants of the equation are given in Table IV. The activity coefficients of the separate components are expressed by

$$\log \gamma_1 = x_1x_2[B + C(x_1 - x_2)] + x_2[a + b(x_2 - x_1) + c(6x_1x_2 - 1)] \qquad (4)$$

$$\log \gamma_2 = x_1x_2[B + C(x_1 - x_2)] - x_1[a + b(x_2 - x_1) + c(6x_1x_2 - 1)] \qquad (5)$$

B and C in Equations 4 and 5 are not independent of b and c respectively. They must fulfill the following relations to satisfy thermodynamic requirements (*19*).

$$B = b,\ C = c - a \qquad (6)$$

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Table I. Properties of Pure Compounds

	Methyl Acetate		Benzene		Cyclohexane	
Property	Exptl.	Lit.	Exptl.	Lit. (*28*)	Exptl.	Lit.
Density, 25° C.	0.9273	0.9273(*28*)	0.8739	0.8737	0.7738	0.7736(*3*)
Refractive index, 25° C.	1.3589		1.4979	1.4979	1.4236	1.4235(*28*)
	1.3615(20/D)	1.3614(*1*)				
Boiling point, ° C., at 760 mm. Hg.	56.8	56.8(*1*)	80.1	80.1	80.7	80.7(*28*)

Table II. Data for Analysis of the System Methyl Acetate–Benzene–Cyclohexane

x_1[a]	x_2[b]	d_4^{25}	n_D^{25}	x_1	x_2	d_4^{25}	n_D^{25}	x_1	x_2	d_4^{25}	n_D^{25}
0.923	0.077	0.9218	1.3698	0.761	0	0.8706	1.3730	0.399	0	0.8123	1.3963
0.872	0.128	0.9181	1.3769	0.661	0.131	0.8704	1.3893	0.341	0.145	0.8200	1.4095
0.798	0.202	0.9131	1.3879	0.527	0.308	0.8708	1.4113	0.258	0.353	0.8315	1.4291
0.714	0.286	0.9081	1.3997	0.465	0.388	0.8708	1.4212	0.225	0.435	0.8365	1.4370
0.647	0.353	0.9041	1.4094	0.380	0.500	0.8711	1.4351	0.189	0.525	0.8420	1.4462
0.547	0.453	0.8986	1.4236	0.325	0.573	0.8714	1.4442	0.163	0.593	0.8461	1.4531
0.448	0.552	0.8920	1.4372	0.262	0.655	0.8718	1.4546	0.125	0.686	0.8522	1.4628
0.343	0.657	0.8881	1.4517	0.186	0.755	0.8721	1.4671	0.088	0.781	0.8583	1.4730
0.298	0.702	0.8861	1.4578	0.128	0.832	0.8727	1.4765	0.058	0.855	0.8635	1.4814
0.190	0.810	0.8814	1.4723								
				0.678	0	0.8546	1.3782	0.316	0	0.8021	1.4020
0	0.078	0.7791	1.4276	0.576	0.151	0.8569	1.3957	0.258	0.185	0.8132	1.4175
0	0.176	0.7860	1.4328	0.457	0.327	0.8602	1.4161	0.220	0.304	0.8208	1.4277
0	0.281	0.7941	1.4389	0.394	0.418	0.8618	1.4272	0.189	0.403	0.8274	1.4368
0	0.379	0.8025	1.4452	0.365	0.462	0.8626	1.4321	0.160	0.495	0.8338	1.4453
0	0.460	0.8100	1.4507	0.275	0.594	0.8652	1.4482	0.086	0.727	0.8512	1.4684
0	0.561	0.8202	1.4583	0.229	0.662	0.8667	1.4565	0.045	0.857	0.8617	1.4823
0	0.638	0.8281	1.4642	0.109	0.840	0.8703	1.4782				
0	0.714	0.8367	1.4707					0.268	0	0.7968	1.4051
0	0.795	0.8463	1.4779	0.624	0	0.8455	1.3816	0.221	0.175	0.8078	1.4187
0	0.867	0.8557	1.4847	0.535	0.143	0.8491	1.3975	0.186	0.305	0.8166	1.4298
				0.477	0.237	0.8516	1.4079	0.152	0.431	0.8260	1.4407
0.945	0	0.9129	1.3621	0.400	0.360	0.8549	1.4221	0.128	0.522	0.8326	1.4490
0.787	0.167	0.9041	1.3854	0.333	0.467	0.8580	1.4346	0.103	0.616	0.8402	1.4578
0.679	0.281	0.8990	1.4011	0.266	0.574	0.8608	1.4467	0.082	0.694	0.8464	1.4656
0.600	0.365	0.8954	1.4127	0.193	0.690	0.8641	1.4606	0.058	0.784	0.8541	1.4747
0.501	0.470	0.8911	1.4270	0.081	0.870	0.8696	1.4821	0.042	0.844	0.8593	1.4809
0.411	0.565	0.8874	1.4400								
0.342	0.637	0.8850	1.4498	0.550	0	0.8334	1.3865	0.154	0	0.7856	1.4132
0.248	0.737	0.8816	1.4631	0.461	0.162	0.8391	1.4034	0.128	0.171	0.7973	1.4246
0.179	0.811	0.8791	1.4728	0.404	0.265	0.8432	1.4144	0.097	0.371	0.8124	1.4394
				0.362	0.342	0.8461	1.4227	0.082	0.465	0.8201	1.4470
0.863	0	0.8928	1.3669	0.272	0.505	0.8527	1.4406	0.072	0.532	0.8260	1.4525
0.727	0.157	0.8887	1.3879	0.216	0.608	0.8570	1.4522	0.056	0.638	0.8358	1.4620
0.595	0.310	0.8853	1.4080	0.182	0.669	0.8593	1.4591	0.045	0.708	0.8424	1.4683
0.511	0.407	0.8830	1.4209	0.082	0.851	0.8672	1.4803	0.031	0.799	0.8517	1.4773
0.457	0.471	0.8816	1.4292					0.022	0.860	0.8580	1.4832
0.362	0.580	0.8799	1.4442	0.478	0	0.8230	1.3911				
0.300	0.652	0.8788	1.4531	0.402	0.158	0.8299	1.4066	0.076	0	0.7794	1.4185
0.208	0.758	0.8771	1.4670	0.349	0.269	0.8351	1.4179	0.063	0.180	0.7919	1.4293
0.136	0.843	0.8757	1.4779	0.300	0.374	0.8403	1.4286	0.049	0.365	0.8063	1.4416
				0.244	0.479	0.8454	1.4395	0.043	0.439	0.8129	1.4471
0.820	0	0.8831	1.3694	0.208	0.565	0.8498	1.4488	0.035	0.548	0.8228	1.4478
0.744	0.093	0.8818	1.3814	0.132	0.723	0.8584	1.4662	0.028	0.640	0.8321	1.4631
0.595	0.274	0.8793	1.4048	0.076	0.841	0.8649	1.4795	0.021	0.719	0.8403	1.4702
0.500	0.390	0.8780	1.4198					0.015	0.801	0.8494	1.4777
0.443	0.460	0.8772	1.4286					0.010	0.863	0.8568	1.4839
0.344	0.581	0.8763	1.4442								
0.274	0.660	0.8758	1.4551								
0.198	0.759	0.8748	1.4676								
0.152	0.815	0.8746	1.4743								

[a] Mole fraction of methyl acetate. [b] Mole fraction of benzene.

Table III. Binary Vapor-Liquid Equilibrium Data

Methyl Acetate-Cyclohexane

t, °C.	x_1[a]	y_1	γ_1	γ_2
74.3	0.033	0.182	3.130	1.031
68.4	0.085	0.350	2.804	1.046
64.9	0.142	0.443	2.383	1.073
59.7	0.283	0.575	1.843	1.170
59.0	0.313	0.594	1.761	1.195
57.9	0.373	0.625	1.614	1.288
56.8	0.478	0.664	1.389	1.406
56.7	0.507	0.673	1.333	1.454
56.0	0.616	0.714	1.194	1.674
55.8	0.688	0.744	1.120	1.857
55.7	0.722	0.759	1.093	1.969
55.5	0.781	0.789	1.054	2.204
55.55	0.835	0.820	1.027	2.491
55.8	0.940	0.914	1.007	3.244

[a] Mole fraction of methyl acetate.

Benzene-Cyclohexane

t, °C.	x_1[a]	y_1	γ_1	γ_2
79.5	0.101	0.131	1.321	1.003
78.9	0.171	0.211	1.278	1.005
78.4	0.256	0.293	1.206	1.020
77.8	0.343	0.376	1.177	1.038
77.5	0.428	0.445	1.127	1.071
77.4	0.525	0.529	1.088	1.098
77.4	0.571	0.564	1.074	1.122
77.6	0.665	0.645	1.048	1.164
77.9	0.759	0.728	1.027	1.230
78.2	0.810	0.777	1.017	1.268
78.6	0.863	0.834	1.012	1.297
79.3	0.945	0.926	1.004	1.405

[a] Mole fraction of benzene.

Table IV. Constants Used in Expressing Log γ_i/γ_j

System	a_{ij}	b_{ij}	c_{ij}
Methyl Acetate-Benzene	−0.0308	0.1245	−0.0183
Benzene-Cyclohexane	0	0.1447	0.0121
Cyclohexane-Methyl Acetate	0.0257	0.5274	0.0016

Experimental and calculated activity coefficients are plotted in Figure 2. It is practical to compare calculated vapor conpositions and boiling points with the experimental data to estimate the accuracy of numerical correlations (Figures 3 and 4). The calculated vapor compositions closely agree with the observed values, but the calculated temperatures are higher than the experimental results. The

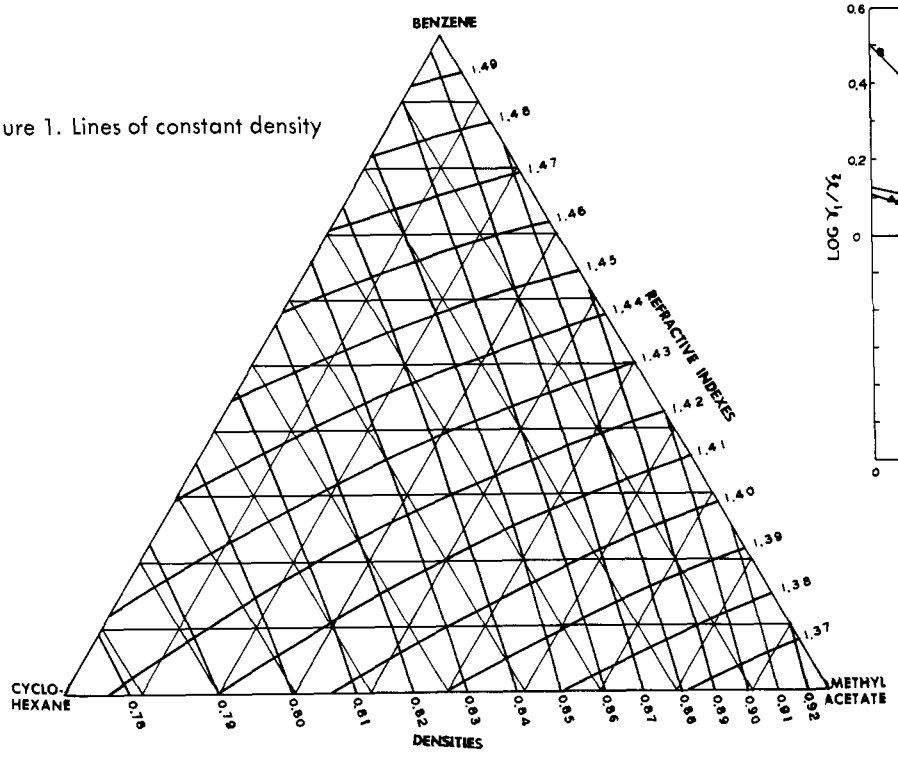

Figure 1. Lines of constant density

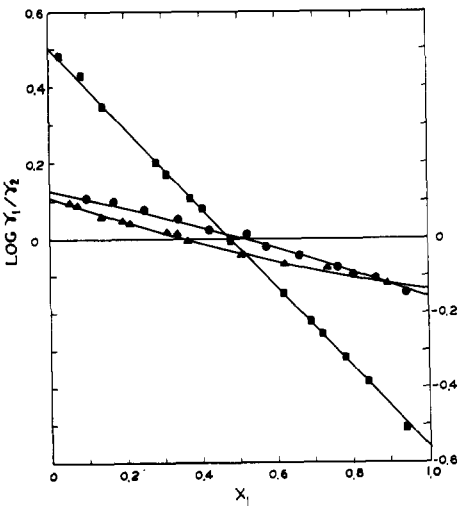

Figure 2. Log γ_1/γ_2 vs. composition diagram

- ■ Methyl acetate-cyclohexane
- ● Benzene-cyclohexane
- ▲ Methyl acetate-benzene
- —— Calculated

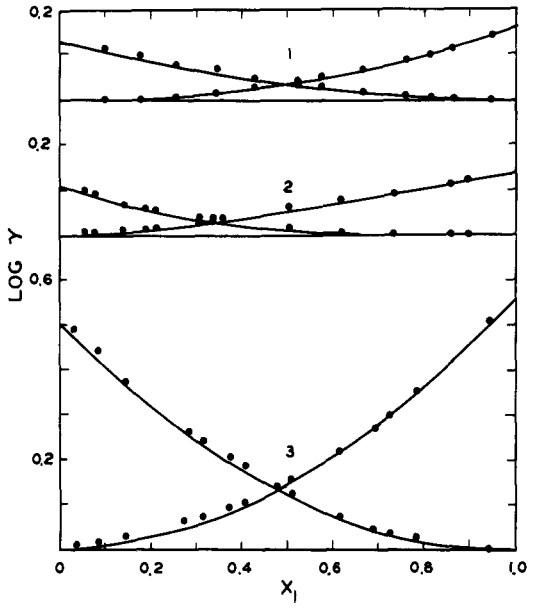

Figure 3. Log γ vs. composition diagram

- 1 Benzene-cyclohexane
- 2 Methyl acetate-benzene
- 3 Methyl acetate-cyclohexane
- ● Experimental
- —— Calculated

vapor-liquid equilibrium data for the benzene-cyclohexane system have been reported by several investigators (*3, 6, 20, 22, 23, 24*). The author's results agreee well with those of Donald and Ridgway (*6*) and of Sieg (*23*). The data on the methyl acetate–benzene system were given by the author (*17*). The data on the methyl acetate–cyclohexane system are not reported in the literature. This system shows azeotropic behavior.

Ternary system. The ternary vapor-liquid equilibrium data are listed with the calculated results in Table V. The logarithm of activity coefficients of the ternary system are expressed by an extension of the binary equations (*17*).

$$\log \gamma_1 = (G^E_{123}/2.3RT) + a_{12}x_2 - a_{31}x_3 + [x_2(x_2 + x_3) - x_1x_2]$$
$$[b_{12} + c_{12}(x_1 - x_2) + \ldots] - 2x_2x_3[b_{23} + c_{23}(x_2 - x_3) + \ldots]$$
$$+ [(x_3 - x_1)(x_2 + x_3) + x_1x_2][b_{31} + c_{31}(x_3 - x_1) + \ldots]$$
$$+ [x_1x_2(x_2 + x_3) + x_1x_2^2](c_{12} + \ldots) + [x_2x_3(x_2 + x_3) - 2x_2^2x_3]$$
$$(c_{23} \ldots) + [-2x_3x_1(x_2 + x_3) + x_1x_2x_3](c_{31} + \ldots)$$
$$+ [(x_2 + x_3)(x_2x_3 - x_1x_2) - x_2(x_1x_3 - x_1x_2)][b + c_1(x_2 - x_3)$$
$$+ c_2(x_3 - x_1) + c_3(x_1 - x_2) + \ldots] + x_1x_2x_3[(x_2 + x_3)$$
$$(c_1 - 2c_2 + c_3) - x_2(2c_1 - c_2 - c_3) + \ldots] \quad (7)$$

Cyclic advancement of the subscripts gives log γ_2 and log γ_3. G^E values are expressed by

$$G^E_{123} = G^E_{12} + G^E_{23} + G^E_{31} + 2.3RTx_1x_2x_3$$
$$[B + C_1(x_2 - x_3) + C_2(x_3 - x_1) + C_3(x_1 - x_2) + \ldots] \quad (8)$$

$$G^E_{12} = 2.3RTx_1x_2[B_{12} + C_{12}(x_1 - x_2) + \ldots] \quad (9)$$

In the numerical determination of ternary constants from the data, b was assumed to be equal to B, and the other ternary constants were set to zero, for the sake of simplicity. The value of b = 0.102 was determined in the concentration range where the ternary constant b has a significant contribution to log γ and was retained to give the precise fit of the experimental and the calculated data as shown in Figure V. The deviation of the calculated vapor compositions from the experimental results is 0.007 for methyl acetate, 0.007 for benzene, and 0.005 for cyclohexane, respectively. The calculated temperatures average 0.5° C. higher than the observed data. Repeated trail calculations indicated that the benzene-cyclohexane azeotrope diminishes completely at the liquid concentration of methyl acetate of 0.293 mole fraction. There is no ternary azeotrope.

Table V. Ternary Vapor-Liquid Equilibrium Data for the Methyl Acetate-Benzene-Cyclohexane

Liquid Compn.			Vapor Compn.									Temp., ° C.			Obsd. Activity Coeff.			Calcd. Activity Coeff.[a]		
			Obsd.			Calcd.[a]			Calcd.[b]				Calcd.							
x_1[c]	x_2[d]	x_3[e]	y_1	y_2	y_3	y_1	y_2	y_3	y_1	y_2	y_3	Obsd.	[a]	[f]	γ_1	γ_2	γ_3	γ_1	γ_2	γ_3
0.067	0.874	0.059	0.154	0.773	0.073	0.159	0.768	0.073	0.151	0.771	0.078	75.0	75.9	75.1	1.277	1.038	1.385	1.279	1.002	1.436
0.237	0.685	0.078	0.413	0.503	0.084	0.415	0.497	0.088	0.393	0.510	0.097	68.9	69.3	68.5	1.168	1.063	1.560	1.162	1.022	1.602
0.213	0.732	0.055	0.394	0.542	0.064	0.386	0.550	0.064	0.367	0.569	0.064	69.5	70.4	69.8	1.216	1.037	1.653	1.159	1.021	1.607
0.167	0.790	0.043	0.318	0.614	0.068	0.326	0.622	0.052	0.305	0.638	0.057	71.3	72.2	71.3	1.185	1.028	2.121	1.184	1.013	1.565
0.328	0.594	0.078	0.518	0.392	0.090	0.508	0.405	0.087	0.481	0.423	0.096	65.8	66.7	66.4	1.171	1.047	1.852	1.116	1.046	1.738
0.427	0.488	0.085	0.601	0.302	0.097	0.595	0.311	0.094	0.563	0.333	0.104	63.2	64.0	64.0	1.136	1.072	1.996	1.095	1.076	1.882
0.518	0.416	0.066	0.667	0.258	0.075	0.661	0.262	0.077	0.630	0.293	0.077	62.2	62.5	63.0	1.075	1.114	2.059	1.055	1.119	2.084
0.596	0.322	0.082	0.708	0.178	0.114	0.709	0.196	0.095	0.684	0.213	0.103	60.8	60.9	61.3	1.040	1.044	2.645	1.038	1.143	2.198
0.708	0.222	0.070	0.776	0.128			0.133	0.087	0.761	0.147	0.092	59.1	59.1	59.8	1.015	1.153	2.765	1.019	1.199	2.484
0.807	0.151	0.042	0.848	0.092	0.060	0.851	0.092	0.057	0.838	0.102	0.060	58.3	58.2	58.8	0.994	1.255	2.962	1.007	1.258	2.826
0.793	0.136	0.071	0.829	0.079	0.092	0.828	0.080	0.092	0.816	0.090	0.094	57.7	57.7	58.6	1.014	1.223	2.743	1.013	1.233	2.662
0.081	0.790	0.129	0.179	0.676	0.145	0.190	0.666	0.144	0.188	0.659	0.153	74.3	74.3	73.6	1.253	1.027	1.369	1.330	1.012	1.368
0.125	0.715	0.160	0.267	0.567	0.166	0.265	0.564	0.171	0.263	0.568	0.169	71.6	72.4	71.0	1.317	1.039	1.378	1.274	1.008	1.387
0.212	0.646	0.142	0.381	0.475	0.144	0.390	0.462	0.148	0.375	0.468	0.157	69.0	69.1	68.7	1.199	1.045	1.458	1.226	1.017	1.499
0.314	0.546	0.140	0.497	0.360	0.143	0.498	0.360	0.142	0.474	0.373	0.153	65.5	66.1	66.0	1.186	1.057	1.655	1.165	1.037	1.615
0.407	0.480	0.113	0.573	0.309	0.118	0.586	0.312	0.102	0.548	0.322	0.130	64.0	64.8	64.1	1.107	1.086	1.778	1.102	1.065	1.494
0.479	0.379	0.142	0.632	0.226	0.142	0.626	0.228	0.146	0.600	0.245	0.155	61.5	62.0	62.5	1.128	1.096	1.856	1.098	1.085	1.876
0.668	0.206	0.126	0.749	0.114	0.137	0.751	0.120	0.129	0.724	0.132	0.144	58.3	59.1	59.6	1.114	1.130	2.255	1.041	1.161	2.072
0.734	0.129	0.137	0.772	0.072	0.156	0.775	0.073	0.152	0.762	0.082	0.156	57.5	57.8	58.2	1.027	1.185	2.427	1.020	1.184	2.340
0.077	0.710	0.213	0.183	0.597	0.220	0.183	0.594	0.223	0.193	0.578	0.229	73.4	74.0	73.1	1.386	1.039	1.295	1.360	1.012	1.287
0.137	0.645	0.218	0.288	0.494	0.218	0.271	0.507	0.222	0.292	0.485	0.223	70.7	72.1	70.2	1.333	0.987	1.367	1.203	1.014	1.331
0.214	0.557	0.229	0.384	0.394	0.222	0.401	0.385	0.214	0.390	0.389	0.221	67.9	68.0	67.5	1.242	1.047	1.450	1.296	1.020	1.392
0.296	0.474	0.230	0.479	0.310	0.211	0.487	0.305	0.208	0.469	0.314	0.217	65.1	65.4	65.4	1.228	1.062	1.506	1.235	1.035	1.474
0.413	0.390	0.197	0.586	0.231	0.183	0.579	0.236	0.186	0.556	0.250	0.194	62.2	62.8	63.1	1.184	1.064	1.683	1.147	1.063	1.672
0.500	0.279	0.221	0.628	0.177	0.195	0.638	0.160	0.202	0.616	0.175	0.209	60.5	60.6	61.3	1.110	1.211	1.696	1.124	1.085	1.754
0.598	0.207	0.195	0.702	0.118	0.180	0.697	0.115	0.188	0.676	0.129	0.195	58.3	59.0	59.9	1.116	1.174	1.914	1.082	1.118	1.948
0.715	0.092	0.193	0.761	0.050	0.189	0.760	0.049	0.191	0.746	0.057	0.197	56.8	57.0	57.5	1.064	1.184	2.139	1.055	1.161	2.156
0.086	0.620	0.294	0.210	0.505	0.285	0.216	0.502	0.282	0.216	0.498	0.286	72.3	72.7	72.1	1.474	1.043	1.260	1.500	1.025	1.230
0.151	0.555	0.294	0.316	0.416	0.268	0.330	0.405	0.265	0.319	0.402	0.279	69.3	69.5	68.6	1.385	1.058	1.303	1.435	1.022	1.280
0.192	0.506	0.302	0.380	0.355	0.265	0.385	0.351	0.264	0.377	0.354	0.269	67.4	67.9	67.6	1.392	1.056	1.331	1.386	1.026	1.303
0.338	0.396	0.266	0.525	0.244	0.231	0.528	0.242	0.230	0.508	0.255	0.237	63.5	63.8	63.9	1.242	1.057	1.507	1.236	1.041	1.479
0.397	0.322	0.281	0.579	0.186	0.235	0.574	0.190	0.236	0.554	0.203	0.243	61.4	62.1	62.4	1.251	1.068	1.558	1.211	1.053	1.528
0.511	0.197	0.292	0.651	0.109	0.240	0.650	0.108	0.242	0.629	0.122	0.249	59.0	59.5	59.9	1.184	1.111	1.661	1.162	1.081	1.653
0.635	0.094	0.271	0.720	0.046	0.234	0.716	0.049	0.235	0.701	0.058	0.241	56.8	57.4	57.8	1.134	1.066	1.886	1.106	1.119	1.859
0.061	0.580	0.359	0.150	0.500	0.350	0.170	0.492	0.338	0.177	0.480	0.343	73.7	73.6	72.9	1.421	1.055	1.212	1.620	1.040	1.172
0.040	0.586	0.374	0.111	0.510	0.379	0.120	0.520	0.360	0.127	0.507	0.366	74.7	74.8	74.3	1.554	1.031	1.220	1.676	1.047	1.153
0.130	0.495	0.375	0.300	0.375	0.325	0.310	0.370	0.320	0.307	0.369	0.324	69.4	69.7	69.3	1.522	1.065	1.235	1.565	1.038	1.205
0.232	0.367	0.401	0.441	0.244	0.315	0.449	0.239	0.312	0.449	0.256	0.295	65.2	65.6	65.6	1.438	1.076	1.285	1.448	1.042	1.256
0.298	0.325	0.377	0.511	0.198	0.291	0.509	0.199	0.292	0.493	0.212	0.295	62.9	63.7	63.6	1.398	1.068	1.365	1.360	1.044	1.331
0.398	0.220	0.382	0.585	0.127	0.288	0.590	0.122	0.288	0.570	0.139	0.291	60.6	61.1	61.1	1.295	1.098	1.443	1.282	1.038	1.416

0.510	0.120	0.370	0.661	0.064	0.275	0.663	0.062	0.275	0.640	0.075	0.285	57.8	58.2	58.8	1.252	1.120	1.567	1.240	1.081	1.547
0.053	0.472	0.475	0.162	0.412	0.426	0.165	0.413	0.422	0.178	0.420	0.402	72.5	73.6	72.6	1.834	1.111	1.172	1.806	1.073	1.110
0.125	0.402	0.473	0.310	0.307	0.383	0.317	0.303	0.380	0.316	0.305	0.375	68.7	69.3	68.7	1.673	1.099	1.180	1.676	1.063	1.146
0.057	0.489	0.454	0.158	0.430	0.412	0.172	0.422	0.406	0.179	0.414	0.407	72.5	73.4	72.7	1.663	1.119	1.158	1.763	1.067	1.121
0.127	0.400	0.473	0.313	0.306	0.381	0.321	0.300	0.379	0.303	0.310	0.387	68.7	69.2	68.9	1.663	1.101	1.173	1.674	1.062	1.147
0.073	0.439	0.488	0.210	0.370	0.420	0.216	0.367	0.417	0.220	0.362	0.418	71.2	72.2	71.2	1.971	1.234	1.275	1.789	1.073	1.115
0.196	0.299	0.505	0.420	0.210	0.370	0.429	0.202	0.369	0.419	0.212	0.369	65.8	66.0	65.5	1.589	1.114	1.176	1.616	1.065	1.167
0.280	0.204	0.516	0.518	0.127	0.355	0.523	0.124	0.353	0.507	0.138	0.355	62.0	62.9	62.6	1.555	1.125	1.255	1.524	1.067	1.213
0.451	0.082	0.467	0.636	0.044	0.320	0.638	0.043	0.319	0.623	0.053	0.324	58.3	58.5	58.6	1.341	1.105	1.421	1.333	1.084	1.403
0.125	0.277	0.598	0.334	0.215	0.451	0.344	0.211	0.445	0.336	0.212	0.452	68.0	68.5	67.4	1.844	1.145	1.125	1.868	1.102	1.091
0.052	0.374	0.574	0.161	0.341	0.498	0.183	0.332	0.485	0.180	0.330	0.490	73.3	73.3	72.6	1.813	1.130	1.092	2.055	1.099	1.063
0.132	0.323	0.545	0.336	0.243	0.421	0.345	0.241	0.414	0.340	0.248	0.412	68.2	68.7	67.3	1.745	1.102	1.144	1.762	1.077	1.106
0.250	0.201	0.549	0.499	0.128	0.373	0.501	0.126	0.373	0.487	0.139	0.374	62.7	63.5	63.1	1.639	1.124	1.210	1.603	1.077	1.177
0.300	0.113	0.589	0.569	0.076	0.355	0.577	0.069	0.354	0.542	0.078	0.380	60.9	62.6	61.0	1.654	1.262	1.146	1.584	1.085	1.074
0.043	0.297	0.660	0.147	0.286	0.567	0.161	0.280	0.559	0.164	0.278	0.558	74.0	73.9	73.1	1.959	1.124	1.057	2.163	1.146	1.047
0.115	0.193	0.692	0.335	0.160	0.505	0.351	0.155	0.494	0.345	0.158	0.497	67.9	69.1	67.6	2.016	1.215	1.092	2.034	1.140	1.029
0.215	0.120	0.665	0.484	0.080	0.436	0.493	0.078	0.429	0.480	0.090	0.430	62.8	63.8	63.1	1.954	1.173	1.164	1.813	1.113	1.104
0.065	0.221	0.714	0.218	0.210	0.572	0.231	0.195	0.574	0.235	0.203	0.562	71.1	71.4	71.1	2.099	1.224	1.048	2.205	1.164	1.074
0.109	0.108	0.783	0.354	0.088	0.558	0.361	0.086	0.553	0.351	0.097	0.552	68.6	68.6	67.4	2.199	1.177	1.042	2.244	1.150	1.034
0.920	0.036	0.044	0.912	0.020	0.068	0.918	0.020	0.062	0.904	0.033	0.063	56.6	56.7	57.6	0.998	1.219	3.399	1.003	1.232	3.087

[a] Modified Redlich-Kister equation (*16*).
[b] Method of Lu, Li, and Ting (*15*).
[c] Mole fraction of methyl acetate.
[d] Mole fraction of benzene.
[e] Mole fraction of cyclohexane.
[f] Method of Nagata (*18*).

Algebraic Method. The algebraic equations enable us to carry out rapid calculation of vapor-liquid equilibrium data. The ordinary three-constant Prahl equation involves more additional terms which improves the fit of the experimental x-y data (*9, 10, 15, 21*).

The following equation was used to correlated the binary x-y data.

$$\frac{y_i}{y_j} = \frac{x_i}{x_j}\left(\frac{x_i + x_j a_{ij} + x_i x_j d_{ij}}{x_i b_{ij} + x_j c_{ij}}\right) \tag{10}$$

This equation has another advantage: the ternary (or multicomponent) vapor-liquid equilibrium are predicable from component binary data as suggested by Lu, Li, and Ting (*15*) if b values satisfy the condition of Equation 11 approximately.

$$b_{12} \cdot b_{23} \cdot b_{31} = 1 \tag{11}$$

A three-index equation based on Equation 10 is expressed by

$$y_1 : y_2 : y_3 =$$

$$\left(\frac{b_{31}}{b_{12}}\right)^{1/3} x_1\left(x_1 + x_2 a_{12} + x_3 \frac{c_{31}}{b_{31}} + x_1 x_2 d_{12} + x_2 x_3 \alpha_1\right)$$

$$: \left(\frac{b_{12}}{b_{23}}\right)^{1/3} x_2\left(x_2 + x_3 a_{23} + x_1 \frac{c_{12}}{b_{12}} + x_2 x_3 d_{23} + x_3 x_1 \alpha_2\right)$$

$$: \left(\frac{b_{23}}{b_{31}}\right)^{1/3} x_3\left(x_3 + x_1 a_{31} + x_2 \frac{c_{23}}{b_{23}} + x_3 x_1 d_{31} + x_1 x_2 \alpha_3\right) \tag{12}$$

where α's are ternary constants to be determined from the experimental data.

Boiling temperatures of the binary and ternary systems were calculated in accordance with the method proposed by the author (*16, 18*). For the present ternary mixtures

$$T_m = \sum T_i y_{ii} + \sum\sum_{i \neq j} T_{ij}(y_{ij} + y_{ji}) + T_{123}(y_{123} + y_{231} + y_{312}) \tag{13}$$

where y_{123} is defined by

$$y_{123} = y_1 \frac{x_2 x_3 \alpha_1}{x_1 + x_2 a_{12} + x_3 c_{31}/b_{31} + x_1 x_2 d_{12} + x_2 x_3 \alpha_1} \tag{14}$$

Similarly for y_{231} and y_{312}. Constants of Equations 12 and

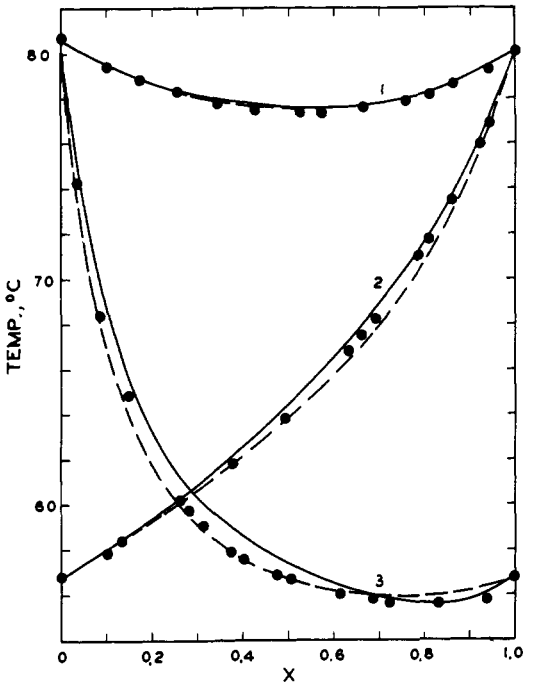

Figure 5. Boiling points vs. composition diagram

1 Benzene-cyclohexane
2 Benzene-methyl acetate
3 Methyl acetate-cyclohexane
● Experimental
—— Calculated (Modified Redlich-Kister)
---- Calculated (Nagata method)

13 are listed in Table VI. The average deviations of the calculated from the experimental results are as follows:

Vapor Composition	
Methyl acetate	0.015 mole fraction
Benzene	0.012 mole fraction
Cyclohexane	0.007 mole fraction
Boiling Temperature	0.5° C.

Table VI. Constants of Ternary Algebraic Equations

a_{12}	b_{12}	c_{12}	d_{12}	α_1	T_{12}	$b_{12} \cdot b_{23} \cdot b_{31}$
0.760	0.277	0.629	0	0.724	338.7	0.876
a_{23}	b_{23}	c_{23}	d_{23}	α_2	T_{23}	T_{123}
1.473	1.015	1.406	0	2.311	348.8	360.0
a_{31}	b_{31}	c_{31}	d_{31}	α_3	T_{13}	
5.009	3.115	6.698	−2.385	0	327.7	

CONCLUSIONS

The methyl acetate is suitable as an entrainer for azeotropic distillation of the benzene-cyclohexane mixtures. Both the analytical and algebraic methods give the boiling temperatures of the same accuracy. The former provides us with more precise vapor compositions than the latter does, although the method is slow.

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NOMENCLATURE

a_{12}, b_{12}, c_{12}; a_{21}, b_{23}, c_{23}; a_{31}, b_{31}, c_{31} = binary constants of modified Redlich-Kister equations

b, c_1, c_2, c_3; B, C_1, C_2, C_3 = ternary constants of modified Redlich-Kister equations

$a_{23}, b_{12}, c_{12}, d_{12}$; $a_{23}, b_{23}, c_{23}, d_{23}$; $a_{31}, b_{31}, c_{31}, d_{31}$ = binary constants of algebraic equations

d_4^{25} = density at 25° C. with respect to water at 4° C.

G^E = excess free energy

ΔH_m = heat of mixing

n_D^{25} = refractive index for sodium D line at 25° C.

p_i = vapor pressure of component i

R = gas constant

T = boiling temperature, ° K.

$T_{12}, T_{23}, T_{13}, T_{123}$ = constants

x = mole fraction in liquid phase

y = mole fraction in vapor phase

$y_{11}, y_{22}, y_{33}, y_{123}$; $y_{12}, y_{21}, y_{13}, y_{231}$; $y_{23}, y_{32}, y_{31}, y_{312}$ = variables

$\alpha_1, \alpha_2, \alpha_3$ = ternary constants of algebraic equations

γ = liquid phase activity coefficient

π = total pressure

Subscripts

1, 2, 3, i, j = components

m = mixture

LITERATURE CITED

(1) Bushmakin, I.N., Kish, I.N., *Zhur. Priklad. Khim.* **30**, 200 (1957).
(2) Chao, K.C., *Ind. Eng. Chem.* **51**, 93 (1959).
(3) Chao, K.C., Hougen, O.A., *Chem. Eng. Sci.* **7**, 246 (1958).
(4) Dakshinamurty, P., Jayarama Rao, G., Acharya, M.V.R., Venkata Rao, C., *Ibid.*, **5**, 188 (1956).
(5) Dakshinamurty, P., Venkata Rao. C., *J. Appl. Chem. (London)* **7**, 655 (1957).
(6) Donald, M.B., Ridgway, K., *Ibid.*, **8**, 403 (1958).
(7) *Ibid.*, p. 408.
(8) Griswold, J., Buford, C.B., *Ind. Eng. Chem.* **41**, 2347 (1949).
(9) Hála, E., *Collection Czech. Chem. Commun.* **24**, 2453 (1959).
(10) Hála, E., private communication, 1961.
(11) Herington, E.F.G., *J. Inst. Petrol.* **37**, 457 (1951).
(12) Hurd, C.D., Strong, J.S., *Anal. Chem.* **23**, 542 (1951).
(13) Kurmanadha Rao, K.V., Krishnamurty, V.V.G., Venkata Rao, C., *Rec. Trav. Chim.* **76**, 769 (1957).
(14) Lange, N.A., ed., "Handbook of Chemistry," 9th ed., p. 1424, Handbook, Sandusky, Ohio, 1956.
(15) Lu, B.C.-Y., Li, J.C.M., Ting, T.-W., *Ind. Eng. Chem.* **51**, 219 (1959).
(16) Nagata, Isamu, J. CHEM. ENG. DATA **6**, 586 (1961).
(17) *Ibid.*, **7**, No. 3 (1962).
(18) *Ibid.*, **7**, No. 4 (1962).
(19) Naphtali, L.M., Chao, K.C., *Ind. Eng. Chem.* **51**, 1318 (1959).
(20) Perry, J.H., ed., "Chemical Engineers' Handbook," 3rd ed., p. 293, McGraw-Hill, New York, 1950.
(21) Prahl, W.H., *Ind. Eng. Chem.* **43**, 1767 (1951).
(22) Richards, A.S., Hargreaves, E., *Ibid.*, **36**, 805 (1944).
(23) Sieg, L., *Chem.-Ing.-Tech.* **22**, 322 (1950).
(24) Thornton, J.D., Garner, F.H., *J. Appl. Chem. (London)* **1**, suppl. No. 1, s 61 (1950).
(25) *Ibid.*, p. s 68.
(26) Thijssen, M.A., *Chem. Eng. Sci.* **4**, 75 (1955).
(27) Timmermans, J., "Physico-Chemical Constants of Pure Organic Compounds," Elsevier, New York, 1950.
(28) Weissberger, A., Proskauer, E.S., Riddick, J.A., Toops, E., Jr., "Organic Solvents," 2nd ed., Interscience, New York, 1955.

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