Vapor-Liquid Equilibria at Atmospheric Pressure

Systems Containing Ethyl Alcohol, *n*-Hexane, Benzene, and Methylcyclopentane

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VAPOR-LIQUID equilibrium data at a pressure of 760 mm. of mercury were determined for the systems ethyl alcohol-*n*-hexane, ethyl alcohol-methylcyclopentane, ethyl alcohol-benzene-methylcyclopentane and ethyl alcohol-*n*-hexane-benzene-methylcyclopentane. The quaternary system was investigated to a limited extent. Only a few mixtures which contained approximately 15 mole % of *n*-hexane were considered. With the data presented here and those presented by Myers (*8-10*), Wehe and Coates (*14*), and Ehrett and Weber (*3*), the vapor-liquid relationships at atmospheric pressure have been determined for the six binary systems which can be formed from ethyl alcohol, *n*-hexane, benzene, and methylcyclopentane.

The experimental results show that the systems ethyl alcohol-*n*-hexane and ethyl alcohol-methylcyclopentane deviate greatly from ideal liquid phase behavior and form minimum boiling azeotropes. The ternary system ethyl alcohol-benzene-methylcyclopentane also deviates greatly from ideal liquid phase behavior, but a ternary azeotrope was not found. The quaternary system also exhibited nonideal liquid phase behavior.

EXPERIMENTAL

Purity of Compounds. The *n*-hexane, benzene, and methylcyclopentane used in this study were pure grade materials of 99 mole % purity (Phillips Petroleum Co.). The ethyl alcohol (U.S. Industrial Chemicals Co.) and all chemicals used were not further purified. Physical constants for the materials are shown in Table I.

Procedure. Vapor-liquid equilibrium data were obtained using a Braun still as described by Hipkin and Meyers (*5*), and the experimental technique outlined by these authors was followed. Nitrogen was bled into the still to maintain the operating pressure of 760 ±0.5 mm. of mercury. The pressure was controlled by a manostat and measured on an absolute mercury manometer.

Temperatures were measured by copper-Constantan thermocouples used in conjunction with a Leeds and Northrup Type K potentiometer. Temperatures are believed to be accurate within ±0.1° C. *n*-Heptane was used as the jacket fluid. The pressure in the jacket was regulated so that the boiling temperature of the *n*-heptane was 0.1° C. or less, greater than the boiling temperature of the test sample.

The binary mixtures were analyzed by measuring their refractive indices. An Abbé refractometer was used for this purpose. Refractive indices can be read to four decimal places with this instrument. Because the difference between refractive indices of ethyl alcohol and *n*-hexane is 0.0132, the compositions for this system are accurate to ±0.7 mole %. For the ethyl alcohol-methylcyclopentane system the difference is 0.0479; consequently, the compositions for this system are accurate to ±0.2 mole %.

Ternary and quaternary samples were analyzed by vapor phase chromatography. A Perkin-Elmer Model 154-C Vapor Fractometer was used. Helium was the carrier gas. A 2-meter column packed with Perkin-Elmer packing material F (liquid phase is tetraethylene glycol dimethyl ether) was used to fractionate the samples. The fractometer was operated at 50° C., 11.5 p.s.i.g. column pressure, and a bridge voltage of 8 volts. Under these conditions and a helium flow rate of 125 cc. per minute, a ternary or quaternary sample could be analyzed in 30 minutes. Peak areas were measured with a planimeter and the final compositions are believed to be accurate within ±0.5 mole %.

As in previous investigations (*11, 13*), calibration of the Vapor Fractometer was necessary, because the peak areas and the mole fractions of the components are not directly proportional.

VAPOR-LIQUID EQUILIBRIUM DATA

Binary Systems Ethyl Alcohol-*n*-Hexane and Ethyl Alcohol-Methylcyclopentane. Liquid phase activity coefficients were calculated using the equation

Table I. Properties of Pure Compounds

	Ethyl Alcohol		Benzene		Methylcyclopentane		*n*-Hexane	
Property	Exptl.	Lit. (2)	Exptl.	Lit. (2)	Exptl.	Lit. (*1*)	Exptl.	Lit. (*1*)
Density, 25° C., g./ml.	0.7843	0.78404	0.8732	0.87368	0.7443	0.74394	0.6542	0.65481
Refractive index, 25° C.	1.3591	1.35914	1.4979	1.49790	1.4070	1.40700	1.3723	1.37226
Boiling point, °C. at 760 mm. Hg.	78.3	78.33	80.1	80.103	71.8	71.81	68.7	68.74

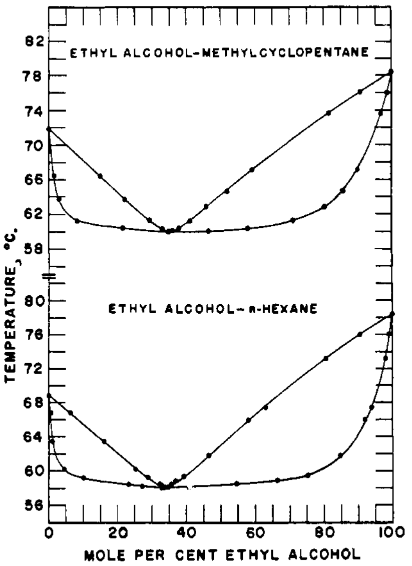

Figure 1. Temperature *vs.* composition diagrams

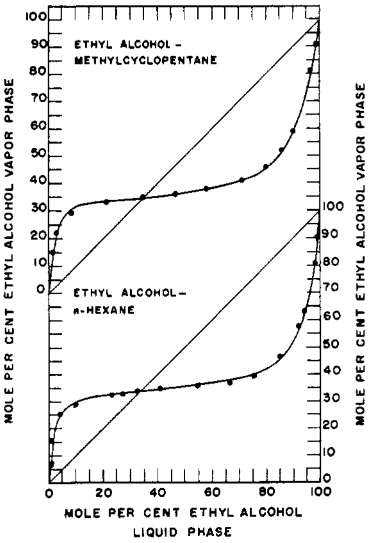

Figure 2. *x-y* Diagram

Data smoothed by Redlich and Kister equation

For ethyl alcohol–*n*-hexane system

$B = 0.91$, $C = 0.06$, $D = 0.17$, $E = 0.10$

For ethyl alcohol-methylcyclopentane

$B = 0.88$, $C = 0.013$, $D = 0.13$, $E = 0.15$

Table II. Experimental Data for Ethyl Alcohol–*n*-Hexane System at 760 Mm. of Mercury

Temp., ° C.	$x_{C_2H_5OH}$	$y_{C_2H_5OH}$	$\gamma_{C_2H_5OH}$	$\gamma_{nC_6H_{14}}$
76.0	0.990	0.905	1.00	7.60
73.2	0.980	0.807	1.01	8.18
67.4	0.940	0.635	1.06	6.34
65.9	0.920	0.580	1.05	5.75
61.8	0.848	0.468	1.10	4.38
59.4	0.755	0.395	1.16	3.34
58.7	0.667	0.370	1.27	2.62
58.35	0.548	0.360	1.53	1.98
58.1	0.412	0.350	2.00	1.56
58.0	0.330	0.340	2.47	1.40
58.25	0.275	0.330	2.81	1.30
58.45	0.235	0.325	3.21	1.23
59.15	0.102	0.290	6.39	1.08
60.2	0.045	0.255	12.14	1.03
63.5	0.010	0.160	29.63	1.00
66.7	0.006	0.065	17.52	1.00

$$\gamma = yP/xP_v \qquad (1)$$

The derivation of Equation 1 assumes that the vapor forms an ideal solution and the ratio of f_v^0 to f_L^0 equals the ratio of the total pressure, P, to the vapor pressure, P_v, of the component at the equilibrium temperature. The vapor pressure data for the pure components (*1, 2*) were used in the calculations.

The experimental data for the two binary systems are reported in Tables II and III and shown in the form of a temperature *vs.* composition diagram and an *x-y* diagram (Figures 1 and 2, respectively). Liquid phase activity coefficients are shown in Figures 3 and 4 as logarithm (γ_1/γ_2) *vs.* composition and logarithm γ *vs.* composition, respectively.

The experimental data were smoothed using the four-constant form of the equation by Redlich and Kister (*12*). These authors and Herrington (*4*) show that the relationship

$$\int_0^1 \log\left(\frac{\gamma_1}{\gamma_2}\right) dx_1 = 0 \qquad (2)$$

must be satisfied in order for the experimental data to be

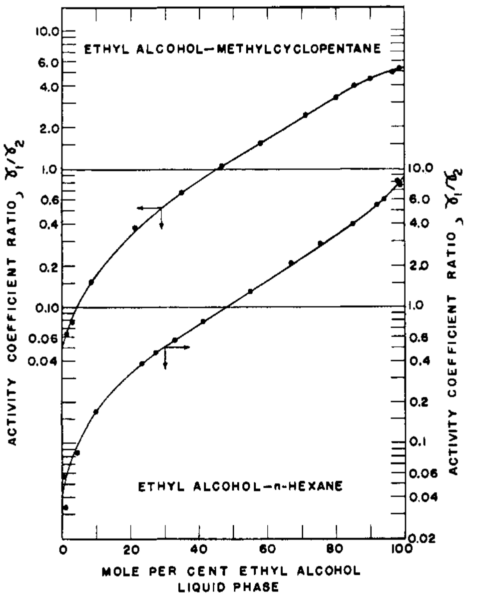

Figure 3. Logarithm of ratios of activity coefficients *vs.* composition

Table III. Experimental Data for Ethyl Alcohol–Methylcyclopentane System at 760 Mm. of Mercury

Temp., ° C.	$x_{C_2H_5OH}$	$y_{C_2H_5OH}$	$\gamma_{C_2H_5OH}$	$\gamma_{C_6H_{12}}$
76.1	0.985	0.908	1.01	5.32
73.65	0.965	0.815	1.02	5.00
67.0	0.898	0.593	1.05	4.64
64.6	0.857	0.519	1.07	4.22
62.8	0.800	0.460	1.10	3.59
61.2	0.713	0.413	1.19	2.87
60.3	0.580	0.382	1.40	2.13
60.1	0.467	0.361	1.66	1.74
60.05	0.348	0.350	2.17	1.45
60.3	0.216	0.332	3.28	1.23
61.25	0.085	0.295	7.10	1.08
63.7	0.030	0.222	13.52	1.04
66.3	0.015	0.150	16.41	1.03

Table IV. Vapor-Liquid Equilibrium Data for Ethyl Alcohol–Benzene-Methylcyclopentane System at 760 Mm. of Mercury

		Liquid Mole Fractions			Vapor, Mole Fractions			Activity Coefficients		
Run	Temp., ° C.	MCP	Ethyl alcohol	Benzene	MCP	Ethyl alcohol	Benzene	MCP	Ethyl alcohol	Benzene
1	63.0	0.845	0.047	0.107	0.657	0.258	0.084	1.03	10.39	1.37
2	60.7	0.670	0.232	0.099	0.585	0.340	0.075	1.25	3.07	1.43
3	60.5	0.499	0.422	0.079	0.565	0.363	0.072	1.63	1.82	1.74
4	60.7	0.422	0.495	0.083	0.551	0.371	0.078	1.86	1.57	1.78
5	60.9	0.359	0.569	0.071	0.538	0.386	0.076	2.12	1.41	2.01
6	61.5	0.272	0.650	0.079	0.501	0.407	0.092	2.56	1.27	2.14
7	63.0	0.173	0.763	0.067	0.443	0.457	0.099	3.39	1.14	2.58
8	60.5	0.540	0.352	0.109	0.554	0.356	0.090	1.47	2.14	1.57
9	67.1	0.842	0.062	0.096	0.250	0.564	0.186	4.67	1.06	2.94
10	62.1	0.443	0.179	0.380	0.412	0.337	0.250	1.28	3.71	1.19
11	65.7	0.075	0.746	0.178	0.232	0.497	0.271	3.75	1.12	2.43
12	62.0	0.321	0.324	0.355	0.374	0.347	0.279	1.59	2.12	1.42
13	64.7	0.098	0.669	0.232	0.243	0.454	0.302	3.10	1.19	2.14
14	62.7	0.258	0.292	0.440	0.327	0.338	0.335	1.63	2.22	1.34
15	63.1	0.167	0.613	0.219	0.340	0.413	0.247	2.68	1.27	1.96
16	64.2	0.195	0.227	0.578	0.245	0.335	0.420	1.60	2.65	1.22
17	62.5	0.309	0.497	0.192	0.449	0.371	0.179	1.95	1.44	1.66
18	71.0	0.077	0.051	0.872	0.109	0.217	0.674	1.45	5.73	1.03
19	61.3	0.486	0.281	0.234	0.483	0.344	0.173	1.39	2.50	1.37
20	67.4	0.127	0.120	0.754	0.159	0.304	0.538	1.44	3.96	1.07
21	65.5	0.121	0.262	0.617	0.168	0.363	0.468	1.69	2.35	1.22
22	66.1	0.185	0.127	0.687	0.219	0.302	0.479	1.42	3.94	1.10
23	65.4	0.098	0.366	0.536	0.160	0.395	0.445	2.00	1.78	1.34
24	65.5	0.243	0.101	0.655	0.271	0.279	0.450	1.36	4.69	1.10
25	65.1	0.092	0.490	0.418	0.176	0.416	0.408	2.36	1.47	1.59
26	64.0	0.370	0.124	0.505	0.365	0.290	0.345	1.26	4.24	1.15
27	64.6	0.103	0.570	0.328	0.216	0.426	0.359	2.63	1.32	1.81
28	63.6	0.495	0.091	0.414	0.443	0.278	0.279	1.16	5.63	1.15
29	62.8	0.592	0.094	0.314	0.498	0.284	0.218	1.12	5.77	1.22
30	63.6	0.327	0.175	0.498	0.343	0.317	0.339	1.36	3.34	1.16
31	61.8	0.689	0.106	0.205	0.563	0.292	0.145	1.15	5.50	1.29
32	61.3	0.584	0.224	0.192	0.532	0.330	0.138	1.28	3.01	1.33
33	61.8	0.486	0.218	0.296	0.459	0.328	0.213	1.33	3.00	1.31
34	61.9	0.388	0.323	0.289	0.427	0.347	0.227	1.51	2.14	1.43
35	64.4	0.182	0.324	0.494	0.247	0.396	0.384	1.72	2.03	1.29
36	61.3	0.394	0.399	0.206	0.465	0.361	0.174	1.65	1.85	1.57
37	62.1	0.325	0.389	0.286	0.404	0.360	0.236	1.69	1.82	1.49
38	63.4	0.217	0.402	0.381	0.304	0.373	0.324	1.83	1.73	1.46
39	63.1	0.208	0.477	0.316	0.321	0.387	0.292	2.04	1.53	1.61
40	64.5	0.236	0.199	0.565	0.278	0.327	0.395	1.48	2.91	1.16
41	63.4	0.157	0.690	0.153	0.358	0.442	0.200	2.98	1.19	2.25
42	61.0	0.722	0.174	0.104	0.595	0.328	0.077	1.16	3.90	1.39
43	67.7	0.068	0.878	0.053	0.296	0.594	0.110	4.95	1.04	3.09
44	61.3	0.847	0.096	0.057	0.646	0.308	0.046	1.07	6.55	1.50
45	61.6	0.312	0.504	0.185	0.446	0.380	0.174	1.98	1.52	1.72
46	62.7	0.182	0.690	0.128	0.403	0.432	0.165	2.96	1.20	2.28
47	60.2	0.568	0.395	0.037	0.597	0.396	0.033	1.52	2.00	1.72
48	67.0	0.353	0.052	0.595	0.357	0.225	0.419	1.18	6.89	1.07

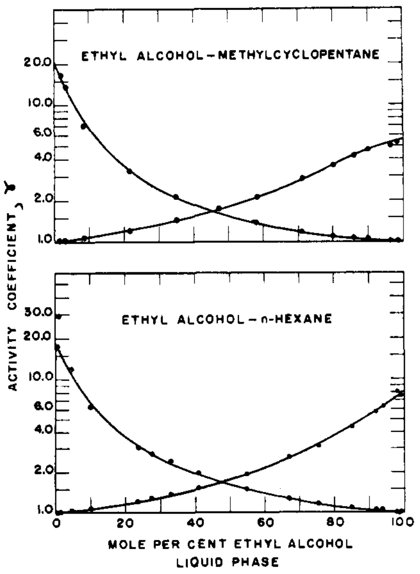

Figure 4. Logarithm of activity coefficients *vs.* composition

internally consistent. Equation 2 means if log (γ_1/γ_2) is plotted *vs.* x_1, the total area under the curve is equal to zero. Or, the area above the abscissa axis is equal to the area below that axis. This is the so-called area condition and is strictly valid for isobaric and isothermal conditions only, because the Gibbs-Duhem equation was used in the development of the equation. However, Equation 2 may also be applied when the range of boiling temperatures is not large. The curves drawn in Figure 3 meet the area condition.

In Figure 2 the x-y curves are those obtained through the application of the equations of Redlich and Kister (*12*). The four constants of the equation proposed by these authors are also reported. In both cases the azeotrope compositions predicted by the equations were in close agreement with the compositions estimated from the experimental work. The data appear to be internally consistent.

Ternary System Ethyl Alcohol–Benzene-Methylcyclopentane. The liquid phase activity coefficients for the system ethyl alcohol-benzene-methylcyclopentane were calculated by Equation 1. These results and the experimental data are shown in Table IV. Figure 5 is a bubble point diagram and Figures 6,7, and 8 show the values of the activity coefficients for ethyl alcohol, benzene, and methylcyclopentane, respectively.

The ternary data were checked for internal thermodynamic consistency by the method of Krishnamurty and Rao (*6, 7*). The authors define a Q term as

$$Q = \frac{\Delta G^E}{2.3\,RT} = x_1 \log \gamma_1 + x_2 \log \gamma_2 + x_3 \log \gamma_3 \qquad (3)$$

If Equation 3 is differentiated, x_3 being constant, the Gibbs-Duhem equation substituted, and use made of the relationship $dx_1 = -dx_2$, the result is

$$\frac{dQ}{dx_1} = \log\left(\frac{\gamma_1}{\gamma_2}\right) \qquad (4)$$

Integrating

$$\int_{Q'}^{Q''} dQ = \int_{x_1 \geq 0 = x_1'}^{x_1 \leq (1 - x_3) = x_1''} \log\left(\frac{\gamma_1}{\gamma_2}\right) dx_1 \qquad (5)$$

The right member of Equation 5 is evaluated graphically, while the left member is evaluated analytically. Rigorously, Equation 5 applies to isothermal and isobaric conditions only.

To check the internal consistency of the experimental data, Equation 5 was applied to conditions where the mole fraction of benzene was held constant at 0.20, 0.40, and 0.60, the mole fraction of ethyl alcohol at 0.50, and the mole fraction of methylcyclopentane at 0.50. The internal consistency checks in which the mole fraction of benzene was held constant were preferable because of the sharp intersection between the composition and activity coefficient parameters. Distinct intersections were not possible in the case of the other two compounds. In the five cases listed the differences between the two members of Equation 5 were 1.4, 4.1, 3.5, 4.6, and 7.5%, respectively. The ternary data appear to be internally consistent.

Quaternary System Ethyl Alcohol–*n*-Hexane–Benzene-Methylcyclopentane. A thorough investigation of the quaternary system ethyl alcohol–*n*-hexane–benzene-methylcyclopentane was not attempted, but only a limited amount of

Table V. Vapor-Liquid Equilibrium Data for
Ethyl Alcohol–Benzene-Methylcyclopentane–*n*-Hexane System at 760 Mm. of Mercury

	Temperature, ° C.									
Compound	61.3	61.9	62.3	60.3	65.4	61.2	61.7	63.2	60.9	60.8
					Liquid, Mole Fractions					
n-Hexane	0.150	0.140	0.152	0.147	0.146	0.126	0.162	0.148	0.139	0.156
MCP	0.284	0.155	0.352	0.341	0.110	0.085	0.656	0.184	0.166	0.510
Ethyl alcohol	0.286	0.358	0.128	0.359	0.085	0.677	0.068	0.153	0.514	0.154
Benzene	0.298	0.346	0.369	0.152	0.659	0.112	0.114	0.516	0.180	0.180
					Vapor, Mole Fractions					
n-Hexane	0.169	0.199	0.153	0.175	0.177	0.294	0.140	0.169	0.228	0.145
MCP	0.279	0.183	0.304	0.354	0.117	0.172	0.503	0.183	0.231	0.417
Ethyl alcohol	0.329	0.343	0.291	0.346	0.261	0.402	0.274	0.298	0.370	0.310
Benzene	0.223	0.275	0.252	0.125	0.445	0.132	0.083	0.350	0.171	0.128
					Activity Coefficients					
n-Hexane	1.43	1.77	1.24	1.56	1.35	2.97	1.08	1.36	2.11	1.20
MCP	1.37	1.62	1.17	1.50	1.30	2.84	1.06	1.31	1.97	1.16
Ethyl alcohol	2.50	1.90	4.44	2.06	5.07	1.22	8.08	3.66	1.50	4.20
Benzene	1.39	1.44	1.22	1.58	1.09	2.19	1.33	1.18	1.79	1.34

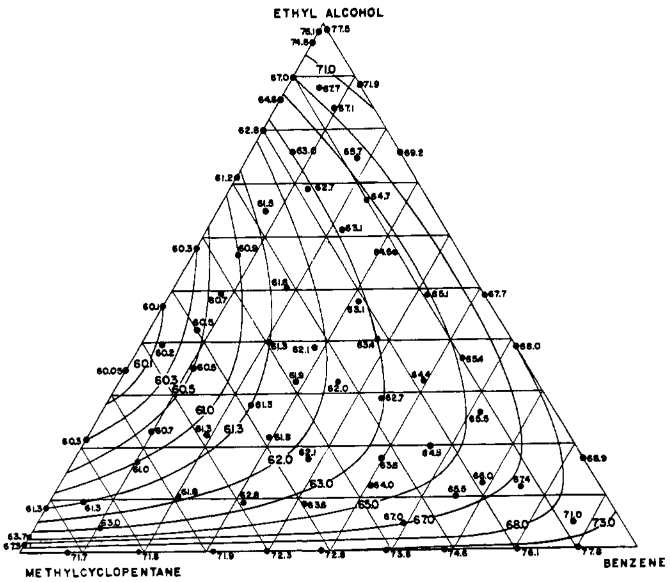

Figure 5.
Bubble point diagram

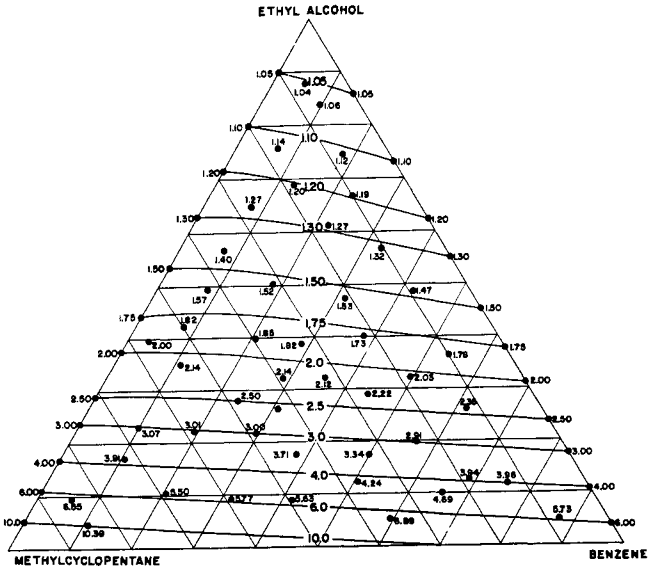

Figure 6. Ethyl alcohol activity coefficients vs. liquid phase composition

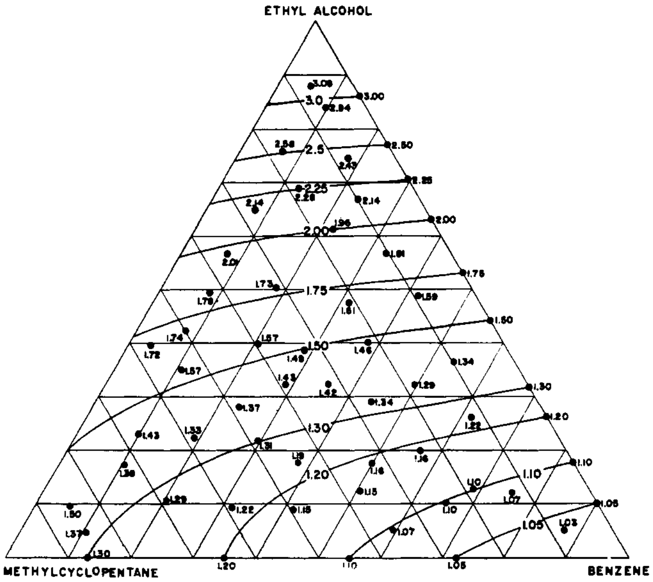

Figure 7. Benzene activity coefficients vs. liquid phase composition

data in which the mole fraction of the *n*-hexane in the liquid phase was approximately 0.15 was obtained. The experimental data and the calculated values of the activity coefficients are shown in Table V. The values of the activity coefficients were determined by Equation 1.

An attempt was made to represent the vapor-liquid equilibrium data graphically and the result is included as Figure 9. Vapor-liquid tie lines for a quaternary system can be represented by a tetrahedron. Figure 9 represents a plane through such a tetrahedron at a constant mole fraction of 0.15 of *n*-hexane. The point representing pure *n*-hexane is above the plane of Figure 9, and the plane of the ternary system in which *n*-hexane is absent is below the plane of Figure 9. The numbers beside each point on the diagram indicate how far directly above or below the plane of the paper the points would be in the actual tetrahedron.

No conclusions can be drawn from these limited data other than that the tie lines are approximately in the same direction and same length as the tie lines in the *n*-hexane-free ternary system.

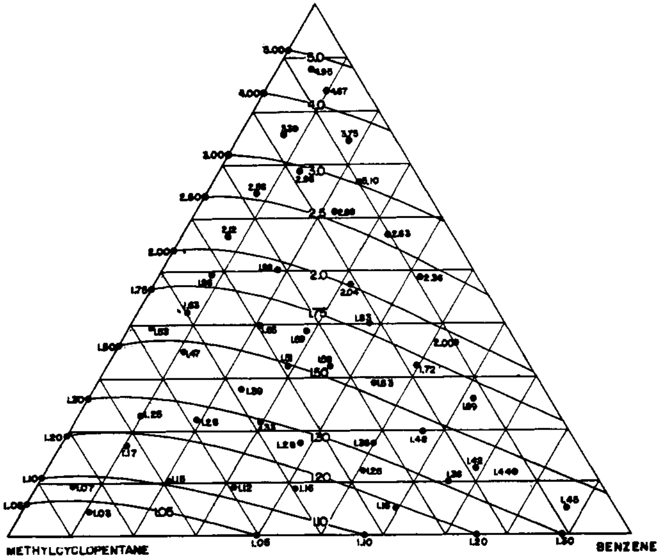

Figure 8. Methylcyclopentane activity coefficients vs. liquid phase composition

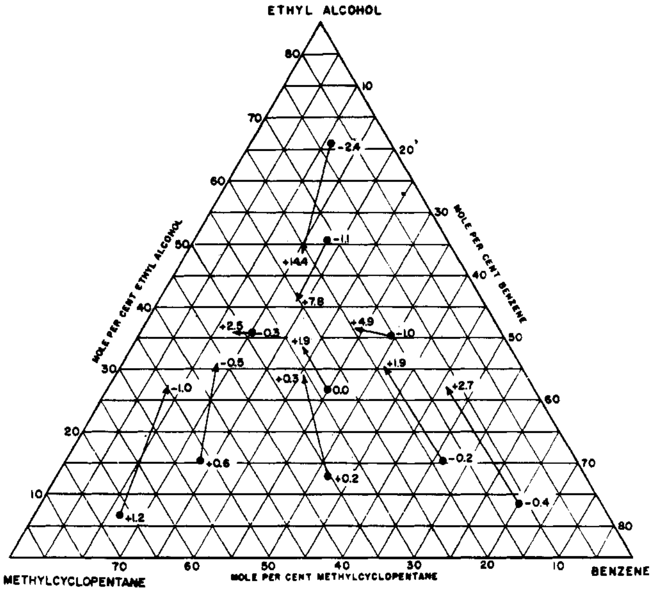

Figure 9. Vapor-liquid equilibrium tie lines for quaternary system

+ Mole per cent above plane of paper
− Mole per cent below plane of paper
● Liquid composition
⟶ Vapor composition

NOMENCLATURE

$B, C, D, E,$ = constants of Redlich and Kister equation
ΔG^E = excess molal free energy at mixing
P = total pressure, mm. of mercury
P_v = vapor pressure, mm. of mercury
Q = defined by Equation 3
f^0 = fugacity of pure component in standard state at temperature and pressure of system
x = mole fraction in liquid phase
y = mole fraction in vapor phase
γ = liquid phase activity coefficient

Subscripts

l = liquid phase
v = vapor phase
1, 2, 3 = components in mixture

LITERATURE CITED

(1) Am. Petrol. Inst. Research Project 44, Carnegie Inst. Technol., Pittsburgh, Pa., 1953.
(2) Dreisbach, R. R., "Physical Properties of Chemical Substances," Dow Chemical Co., Midland, Mich., 1952.
(3) Ehrett, W. E., Weber, J. H., J. CHEM. ENG. DATA **4**, 142 (1959).
(4) Herrington, E. F. G., *Nature* **160**, 610 (1947).
(5) Hipkin, H., Myers, H. S., *Ind. Eng. Chem.* **46**, 2524 (1954).
(6) Krishnamurty, V. V. G., Rao, C. V., *J. Sci. Ind. Research (India)* **14B**, 188 (1955).
(7) *Ibid.*, **15B**, 55 (1956).
(8) Myers, H. S., *Ind. Eng. Chem.* **47**, 2215 (1955).
(9) *Ibid.*, **48**, 1105 (1956).
(10) Myers, H.S., *Petrol. Refiner* **36**, No. 3, 175 (1957).
(11) Nielsen, R.L., Weber, J.H., J. CHEM. ENG. DATA **4**, 145 (1959).
(12) Redlich, O., Kister, A.T., *Ind. Eng. Chem.* **40**, 345 (1948).
(13) Wagner, I.F., Weber, J.H., IND. ENG. CHEM., CHEM. ENG. DATA SER. **3**, 220 (1958).
(14) Wehe, A.H., Coates, J., *A.I.Ch.E. Journal* **1**, 241 (1955).

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