Vapor-Liquid Equilibrium at Atmospheric Pressure

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

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AS A CONTINUATION of the study of the vapor-liquid equilibrium relationships at atmospheric pressure for systems which can be composed of ethyl alcohol, *n*-hexane, benzene, and methylcyclopentane, the ternary system ethyl alcohol–methylcyclopentane–*n*-hexane was investigated. Also, a number of points of equilibrium data for the quaternary system were determined. The latter data were limited to cases in which the concentration of *n*-hexane was approximately 75 mole % in the liquid phase. This is a continuation of the work of Sinor and Weber (*12*) and Belknap and Weber (*2*). Three of the possible four ternary systems which can be made with these four compounds and the quaternary systems over the range 15 to 75 mole % *n*-hexane in the liquid phase were studied. The six possible binary systems have been investigated by others (*5, 9, 10, 11, 13*).

The ternary system departed considerably from ideal liquid phase behavior, although no ternary azeotrope was found. The trend of quaternary data followed that of the previous investigations—i.e., as the concentration of *n*-hexane in the liquid increased, its relative volatility decreased. The quaternary system exhibited large deviations from ideal liquid phase behavior.

EXPERIMENTAL

Purity of Compounds. The *n*-hexane, benzene, and methylcyclopentane used in this study were pure grade materails of a minimum of 99 mole % purity (Phillips Petroleum Co.). The ethyl alcohol (U. S. Industrial Chemical Co.) and the hydrocarbons were not purified further. 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 Myers (*6*) and the experimental technique outlined by these authors was followed. Nitrogen was used to maintain the operating pressure in the still at 760 ± 0.4 mm. Hg. The pressure was controlled by a manostat and measured on an absolute mercury manometer.

Temperatures were measured by a copper-constantan thermocouple used with a Leeds and Northrup Type K potentiometer. The reported temperatures are 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.

Ternary and quaternary samples were analyzed by gas chromatography, using a Perkin-Elmer model 154-C Vapor Fractometer. Helium was the carrier gas. A 2-meter column packed with Perkin-Elmer material "F" was used for both ternary and quaternary analyses. The active agent on the column packing is tetraethylene glycol dimethyl ether.

The fractometer was operated at 50° C., 11.5 p.s.i.g. column pressure, and a detector voltage of 8 volts. The helium flow rate was 114 cc. per minute. At these operating conditions a ternary sample passed through the column in 25 minutes and a quaternary in 30 minutes. The peaks were completely separated on the chromatograms.

As in previous investigations (2, 12) calibration of the Vapor Fractometer was necessary, because the peak areas and mole fractions of the components are not directly proportional.

Considerable effort was made to determine the degree of accuracy obtained by the analytical technique. Several samples, ternary and quaternary, of known composition were made and run through the Fractometer. Calibration constants were then determined from each sample and mean value of the constants calculated. Using the mean value of the constants and the area data obtained from the chromatograms, the compositions were then recalculated and compared with the actual values. The average deviation obtained for all components was less than ±0.3 mole %; therefore, the error in the reported compositions is estimated conservatively to be something less than ±0.5 mole %.

VAPOR-LIQUID EQUILIBRIUM DATA

Ternary System. Liquid phase activity coefficients of ethyl alcohol-methylcyclopentane-n-hexane were calculated by two methods. One method assumed the only departures from ideal behavior were in the liquid phase and the activity coefficients simply reflect departures from Raoult's law, or

$$\gamma_i = \frac{y_i P}{x_i P_i^\circ} \tag{1}$$

The second method was more rigorous and takes into account the deviation from the Lewis and Randall rule in the vapor phase, the departure from the ideal gas law, as well as the effect of pressure on the liquid fugacity, or

$$\gamma_i = \frac{y_i}{x_i} \times \frac{\Phi_i}{\phi_i^\circ \, e[(V/RT)(P - P_i^\circ)]} \times \frac{P}{P_i^\circ} \tag{2}$$

Table I. Properties of Pure Compounds

Property	Ethyl Alcohol Exptl.	Ethyl Alcohol Lit.(*4*)	Benzene Exptl.	Benzene Lit.(*4*)	Methylcyclopentane Exptl.	Methylcyclopentane Lit.(*1*)	*n*-Hexane Exptl.	*n*-Hexane 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	6874

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Provided the quantities in the right member of Equation 2 can be evaluated correctly, the activity coefficients determined reflect only the departure from ideal liquid phase behavior. This may not be true of the activity coefficients calculated from Equation 1.

The partial fugacities of components in mixtures and the fugacities of the pure components were calculated from Black's equation of state (3)

$$V = RT/P + b - a\xi/RT \tag{3}$$

and

$$V_m = RT/P + \Sigma b_i y_i - [\Sigma(a_i \xi_i^*)^{0.5} y_i]^2/RT$$
$$- [\Sigma(a_i \overline{\xi_i})^{0.5} y_i]^2/RT \tag{4}$$

The generalized constants given by Black were used in the calculations. The activity coefficients, calculated from Equations 1 and 2, are reported in Table II. Temperatures and liquid and vapor phase compositions are also given. The results show for any given case the two values of the activity coefficients are practically the same, the differences between the values in many cases being less than the experimental error.

Vapor phase activity coefficients,

$$\varphi_i = \frac{\overline{f_i}}{f_{L_i}^{\circ} y_i} \tag{5}$$

were also calculated, but were unity for all practical purposes and are not reported.

The experimental data are shown graphically. Figure 1 is

Table II. Vapor-Liquid Equilibrium Data of *n*-Hexane–Methylcyclopentane–Ethyl Atcohol at 760 mm. Hg

	Liquid Mole Fraction		Vapor Mole Fraction		Liquid Phase Activity Coeff.					
					Equation 1			Equation 2		
Temp., ° C.	Ethyl Alcohol	MCP	Ethyl Alcohol	MCP	*n*-Hexane	MCP	Ethyl Alcohol	*n*-Hexane	MCP	Ethyl Alcohol
62.5	0.050	0.839	0.269	0.633	1.07	1.01	10.48	1.09	1.01	10.43
60.5	0.156	0.727	0.334	0.571	1.06	1.13	4.52	1.08	1.12	4.47
60.2	0.292	0.606	0.354	0.547	1.29	1.31	2.59	1.31	1.30	2.56
60.1	0.416	0.485	0.364	0.519	1.56	1.56	1.88	1.58	1.55	1.86
60.2	0.522	0.382	0.383	0.483	1.84	1.83	1.57	1.86	1.83	1.55
60.3	0.626	0.280	0.382	0,440	2.50	2.27	1.30	2.53	2.27	1.28
61.1	0.731	0.184	0.415	0.371	3.20	2.84	1.17	3.23	2.85	1.15
62.2	0.798	0.105	0.452	0.258	3.70	3.34	1.11	3.73	3.37	1.09
60.5	0.752	0.089	0.407	0.184	3.35	2.97	1.14	3.35	3.00	1.13
60.0	0.616	0.191	0.397	0.287	2.17	2.19	1.39	2.18	2.20	1.37
59.8	0.537	0.275	0.383	0.355	1.87	1.89	1.55	1.88	1.90	1.53
59.7	0.409	0.400	0.356	0.425	1.54	1.57	1.90	1.56	1.57	1.88
60.3	0.151	0.634	0.320	0.496	1.12	1.13	4.52	1.14	1.13	4.48
62.3	0.045	0.736	0.259	0.557	1.03	1.02	11.30	1.05	1.02	11.24
62.3	0.040	0.631	0.243	0.490	1.00	1.05	11.76	1.01	1.05	11.70
59.8	0.215	0.475	0.333	0.382	1.23	1.18	3.36	1.24	1.18	3.33
59.4	0.288	0.398	0.342	0.360	1.28	1.35	2.63	1.29	1.35	2.60
59.4	0.419	0.293	0.362	0.309	1.55	1.57	1.91	1.56	1.57	1.89
59.3	0.544	0.189	0.369	0.247	1.95	1.95	1.51	1.96	1.96	1.49
59.6	0.623	0.100	0.368	0.144	2.37	2.13	1.30	2.36	2.16	1.28
59.0	0.520	0.097	0.356	0.118	1.89	1.84	1.54	1.88	1.86	1.52
59.2	0.405	0.200	0.349	0.198	1.57	1.48	1.92	1.57	1.49	1.89
59.3	0.276	0.309	0.343	0.268	1.27	1.30	2.76	1.28	1.30	2.73
59.9	0.165	0.478	0.319	0.367	1.17	1.13	4.18	1.18	1.13	4.13
60.3	0.098	0.480	0.300	0.346	1.10	1.04	6.49	1.11	1.04	6.43
59.6	0.137	0.379	0.311	0.281	1.14	1.10	4.97	1.14	1.10	4.92
59.3	0.159	0.325	0.306	0.259	1.14	1.19	4.28	1.14	1.20	4.24
58.9	0.300	0.208	0.339	0.176	1.36	1.28	2.56	1.36	1.29	2.52
58.9	0.427	0.103	0.347	0.107	1.60	1.58	1.84	1.59	1.60	1.82
58.7	0.276	0.110	0.326	0.097	1.30	1.35	2.70	1.30	1.36	2.67
59.3	0.165	0.222	0.315	0.172	1.14	1.16	4.26	1.13	1.17	4.21
60.9	0.049	0.327	0.266	0.245	1.01	1.06	11.18	1.01	1.06	11.10
59.8	0.097	0.175	0.300	0.128	1.05	1.07	6.74	1.05	1.08	6.68
59.1	0.170	0.118	0.322	0.085	1.14	1.08	4.25	1.13	1.09	4.20
61.0	0.044	0.114	0.244	0.086	1.02	1.06	11.54	1.02	1.08	11.47
64.0	0.012	0.057	0.155	0.046	1.00	1.03	22.91	1.00	1.04	22.95
64.0	0.016	0.163	0.156	0.131	1.01	1.03	17.42	1.01	1.04	17.45
64.5	0.015	0.271	0.156	0.221	1.00	1.03	18.80	1.00	1.04	18.84
64.6	0.019	0.529	0.176	0.417	1.03	0.99	16.37	1.03	0.99	16.38
65.4	0.015	0.815	0.165	0.682	1.01	1.02	18.58	1.02	1.02	18.62
61.8	0.058	0.769	0.277	0.571	1.10	1.02	9.51	1.12	1.02	9.45
59.9	0.431	0.468	0.364	0.505	1.73	1.58	1.83	1.75	1.58	1.81
60.3	0.305	0.645	0.358	0.591	1.38	1.32	2.49	1.40	1.32	2.46
60.7	0.635	0.319	0.410	0.507	2.38	2.27	1.35	2.42	2.26	1.33
63.3	0.826	0.132	0.496	0.369	3.88	3.65	1.12	3.94	3.67	1.10
67.1	0.919	0.039	0.578	0.187	5.94	5.51	0.99	6.03	5.59	0.98
62.1	0.825	0.045	0.451	0.125	4.04	3.76	1.07	4.06	3.81	1.06
59.0	0.552	0.027	0.366	0.065	1.85	3.65	1.50	1.85	3.70	1.48
58.9	0.164	0.063	0.303	0.046	1.16	1.10	4.18	1.15	1.12	4.14
60.3	0.323	0.600	0.352	0.565	1.43	1.36	2.31	1.45	1.35	2.29
60.1	0.322	0.557	0.358	0.510	1.45	1.33	2.39	1.47	1.33	2.36
59.9	0.336	0.500	0.345	0.480	1.42	1.41	2.22	1.44	1.40	2.20
59.8	0.266	0.518	0.337	0.451	1.31	1.28	2.75	1.33	1.28	2.72
59.4	0.357	0.360	0.351	0.346	1.45	1.43	2.18	1.46	1.43	2.15
60.2	0.328	0.588	0.349	0.565	1.36	1.39	2.27	1.38	1.39	2.25
59.4	0.373	0.295	0.352	0.286	1.48	1.45	2.09	1.48	1.45	2.06
59.3	0.215	0.311	0.334	0.257	1.17	1.24	3.45	1.17	1.24	3.41

Table III. Vapor-Liquid Equilibrium Data of *n*-Hexane–Methylcyclopentane–Ethyl Alcohol–Benzene at 760 Mm. Hg

Temp., ° C.	59.2	59.8	62.1	65.2	65.8	62.2	60.1	61.6	66.3	65.3
				Liquid Mole Fractions						
n-Hexane	0.733	0.743	0.725	0.705	0.720	0.732	0.742	0.704	0.716	0.717
MCP	0.052	0.105	0.177	0.234	0.153	0.111	0.057	0.056	0.106	0.058
Ethyl Alcohol	0.157	0.107	0.039	0.015	0.010	0.035	0.090	0.084	0.015	0.016
Benzene	0.059	0.045	0.060	0.046	0.118	0.123	0.111	0.156	0.163	0.210
				Vapor Mole Fractions						
n-Hexane	0.606	0.590	0.601	0.635	0.657	0.597	0.596	0.616	0.672	0.655
MCP	0.041	0.081	0.131	0.200	0.134	0.086	0.042	0.043	0.092	0.047
Ethyl Alcohol	0.303	0.294	0.223	0.129	0.108	0.221	0.277	0.225	0.095	0.126
Benzene	0.050	0.035	0.045	0.037	0.102	0.096	0.085	0.116	0.141	0.172
				Liquid Phase Activity Coefficients Equation 1						
n-Hexane	1.13	1.06	1.03	1.01	1.00	1.01	1.06	1.10	1.01	1.02
MCP	1.18	1.14	1.01	1.05	1.06	1.05	1.09	1.08	1.03	1.00
Ethyl Alcohol	4.32	5.97	11.36	14.46	18.39	12.47	6.59	5.36	10.34	13.73
Benzene	1.69	1.53	1.34	1.29	1.37	1.41	1.47	1.36	1.35	1.33
				Liquid Phase Activity Coefficients Equation 2						
n-Hexane	1.12	1.06	1.03	1.01	1.00	1.01	1.06	1.10	1.02	1.02
MCP	1.20	1.15	1.02	1.06	1.07	1.06	1.10	1.09	1.05	1.02
Ethyl Alcohol	4.27	5.90	11.29	14.49	18.45	12.40	6.51	5.33	10.39	13.76
Benzene	1.70	1.55	1.35	1.30	1.38	1.42	1.48	1.37	1.36	1.33

a bubble point diagram and Figures 2–4 show, respectively, γ for *n*-hexane, methylcyclopentane, and ethyl alcohol, as functions of composition.

As in previous investigations, the data were checked for internal consistency by the method proposed by Krishnamurty and Rao (*7, 8*). The equations employed were

$$Q = \frac{\Delta G^E}{2.3\,RT} = x_1 \log \gamma_1 + x_2 \log \gamma_2 + x_3 \log \gamma_3 \tag{6}$$

If Equation 2 is differentiated, x_3 being a constant value, the Gibbs-Duhem equation substituted, and use made of the relationship $dx_1 = -dx_2$, the result is

$$\frac{dQ}{dx_1} = \log(\gamma_1/\gamma_2) \tag{7}$$

integrating

$$\int_{Q'}^{''Q} dQ = \int_{x_1 \geqq 0 = x_1'}^{x' \leqq (1 - x_3) = x_1''} \log(\gamma_1/\gamma_2)\,dx_1 \tag{8}$$

Constant compositions of 10, 20, and 40 mole % *n*-hexane were examined. The deviations of the term of the right and left members of Equation 8 were 1.4, 0.63, and 5.3, %, respectively. Constant compositions of 10, 30 and 50 mole % methylcyclopentane were also examined. The deviations were 0.68, 5.4, and 3.6%, respectively.

The values of the two members of Equation 8 were small and the following relationship was used to determine the per cent deviation

$$D = \frac{A - B}{\Sigma'}\,(100) \tag{9}$$

The $Q'' - Q'$ term was calculated for constant mole percentages of ethyl alcohol of 15, 40, and 60. These differences were 0.00268, 0.00815, and 0.00512, respectively. Since the activity coefficients are accurate to ±0.005, the differences in their values were frequently as large, or

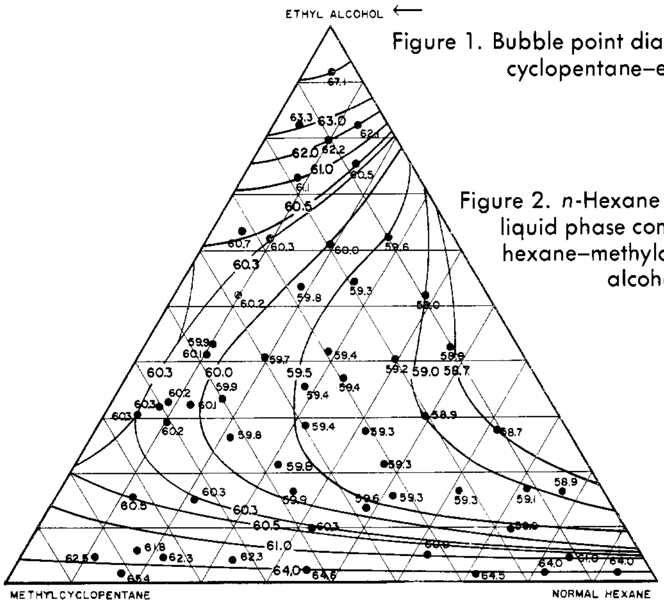

Figure 1. Bubble point diagram of the *n-hexane–methylcyclopentane–ethyl alcohol* system

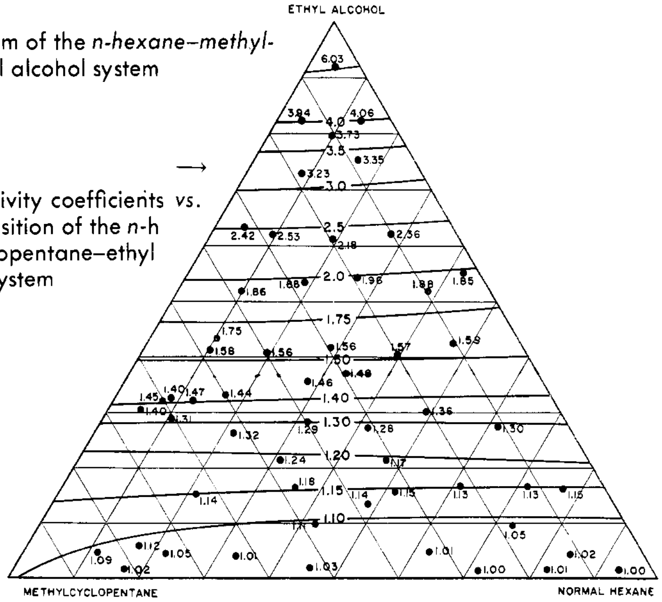

Figure 2. *n*-Hexane activity coefficients *vs.* liquid phase composition of the *n*-hexane–methylcyclopentane–ethyl alcohol system

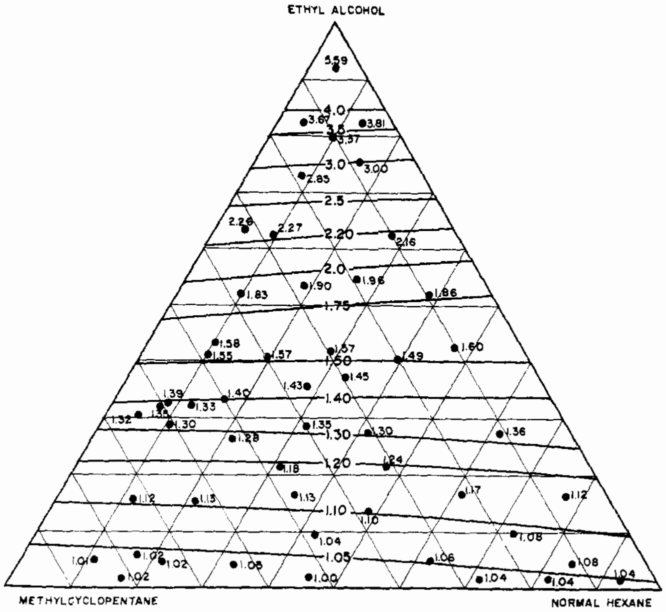

Figure 3. Methylcyclopentane activity coefficients *vs.* liquid phase composition in the *n*-hexane–methylcyclopentane–ethyl alcohol system

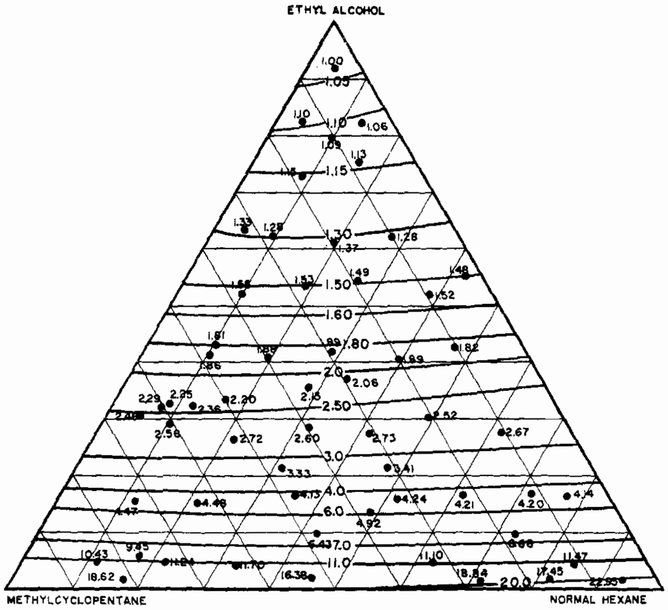

Figure 4. Ethyl alcohol activity coefficients *vs.* liquid phase composition of the *n*-hexane–methylcyclopentane–ethyl alcohol system

larger, than the quantity $Q'' - Q'$; hence, these particular checks were meaningless.

The data are believed to be internally consistent.

Quaternary System. This system is ethyl alcohol-*n*-hexane-benzene-methylcyclopentane. In previous work (*2*, *12*) a number of vapor-liquid equilibrium data were determined for cases in which the liquid phase mole fraction of *n*-hexane was approximately 15, 35 and 50%. In this work data were obtained for cases in which the liquid phase mole fraction of *n*-hexane was approximately 0.75. The experimental data and activity coefficients, calculated by Equations 1 and 2, are reported in Table III. Liquid phase activity coefficients calculated by Equation 2 differed only slightly from those calculated by Equation 1. The tie line data are shown in Figure 5. The trend of the relative volatility of *n*-hexane shown in previous works continued and was more pronounced in the present results—i.e., the relative volatility of *n*-hexane decreased as the composition of the *n*-hexane in the liquid phase increased. In this case, the concentration of *n*-hexane in the liquid phase was approximately 75% and in the vapor phase, approximately 60%.

NOMENCLATURE

A = value of left member of Equation 8
B = value of right member of Equation 8
D = deviation in per cent – Equation 9
ΔG^E = excess molal free energy of mixing
P = total pressure
P° = vapor pressure
Q = defined by Equation 6
R = gas law constant
T = absolute temperature
a = van der Waals attraction coefficient
b = van der Waals covolume
f° = fugacity of a pure component in standard state at temperature and pressure of system
$\bar{f}$ = partial fugacity of a component
x = mole fraction in liquid phase
y = mole fraction in vapor phase
Σ' = total area enclosed by abscissa axis and the log γ_1/γ_2 plot
ϕ = fugacity coefficient for a pure component
Φ = fugacity coefficient for a component in a mixture
γ = liquid phase activity coefficient
φ = vapor phase activity coefficient
ξ = Black's attraction coefficient

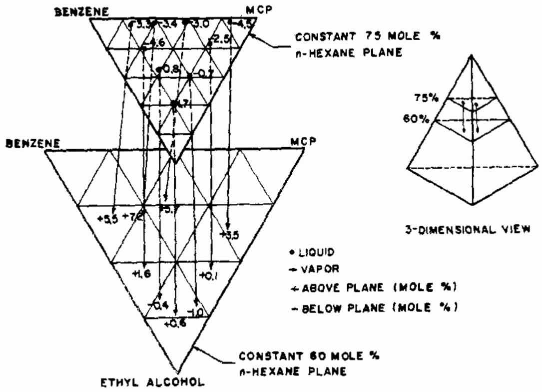

Figure 5. *n*-Hexane–methylcyclopentane–ethyl alcohol–benzene system

Subscripts

L = liquid phase
i = component "i" in a mixture
m = mixture
v = vapor
1,2,3 = components in a ternary mixture

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