Vapor-Liquid Equilibrium at Atmospheric Pressure

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

ROWAN C. BELKNAP and JAMES H. WEBER
Department of Chemical Engineering, University of Nebraska, Lincoln 8, Neb.

VAPOR-LIQUID equilibrium relationships at atmospheric pressure for the ternary system *n*-hexane–benzene–methylcyclopentane and the quaternary system ethyl alcohol–*n*-hexane–benzene–methylcyclopentane were determined. The latter system was investigated at *n*-hexane concentrations of approximately 35 and 50 mole % in the liquid phase. This is a continuation of the work of Sinor and Weber (*10*) and means that two of the possible four ternary systems which can be made with the four compounds have been investigated and additional quaternary data are available. The six binary systems have been investigated by Myers (*7–9*), Wehe and Coates (*11*), and Ehrett and Weber (*3*).

The experimental results show that the ternary hydrocarbon system deviated to some extent from ideal liquid phase behavior, the maximum value of the activity coefficients being approximately 1.40. No ternary azeotrope was found. Concerning the quaternary system, qualitatively, as the concentration of *n*-hexane was increased in the liquid phase, the relative volatility of *n*-hexane tended to change from a value greater than 1 to a value less than 1. The quaternary system also exhibited large deviations from ideal liquid phase behavior.

EXPERIMENTAL

Purity of Compounds. The *n*-hexane, benzene, and methylcyclopentane were pure grade materials of 99 mole % (minimum) purity (Phillips Petroleum Co.). The ethyl alcohol (U. S. Industrial Chemicals Co.) and the hydrocarbons were not purified further. When these materials were run, singly, through the Vapor Fractometer no small peaks appeared, indicating the purity of the compounds was in all probability considerably higher than the minimum claimed value. 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 (*4*), 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 Hg. The pressure was controlled by a manostat and measured on an absolute mercury manometer.

Temperatures were measured by copper-constantan thermocouples used 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.

Ternary and quaternary samples were analyzed by gas chromatography, using a Perkin-Elmer Model 154-C Vapor Fractometer. Helium was the carrier gas. To separate the components of the ternary mixture, a 2-meter column packed with Perkin-Elmer Type A column material was used. This packing is finely powdered diatomaceous earth with diisodecyl phthalate as the adsorbed liquid. Perkin-Elmer Type F packing was used to separate the components of the quaternary mixture. This packing is diatomaceous earth with tetraethylene glycol dimethyl ether as the adsorbed liquid phase.

To analyze the ternary mixtures, the Fractometer was operated at 50° C. with a column pressure of 15 p.s.i.g. and a detector voltage of 8 volts. The helium flow rate was 164 cc. per minute measured at 22° C. Twenty-four minutes were required to run one sample. The peak areas were well spaced and completely separated.

To analyze the quaternary mixtures, the Fractometer was operated as given above, except the column pressure was 11.5 p.s.i.g. and the helium flow rate was 116 cc. per minute and the time required for the analysis of one sample was 30 minutes. The peaks were well spaced and completely separated. In both cases, the peak areas were measured with a planimeter and the final compositions are believed to be accurate within ± 0.5 mole %.

VAPOR-LIQUID EQUILIBRIUM DATA

Ternary System *n*-Hexane–Benzene–Methylcyclopentane. Liquid phase activity coefficients were calculated using the equation

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

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 and the liquid phase activity coefficients are included in Table II. Figure 1 is a bubble point diagram for the system and Figures 2 to 4 show, as a function of composition, the liquid phase activity coefficients for benzene, *n*-hexane, and methylcyclopentane, respectively.

As in previous works the data were checked for internal

Table I. Properties of Pure Compounds

Property	Ethyl Alcohol Exptl.	Ethyl Alcohol Lit. (*2*)	Benzene Exptl.	Benzene Lit. (*2*)	Methylcyclopentane Exptl.	Methylcyclopentane Lit. (*1*)	*n*-Hexane Exptl.	*n*-Hexane Lit. (*1*)
Density, 25° C., gram/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

Table II. Vapor-Liquid Equilibrium Data of Benzene–*n*-Hexane–Methylcyclopentane System at 760 Mm. Hg

	Liquid, Mole Fraction			Vapor, Mole Fraction			Liquid Phase, Activity Coeff.		
Temp., ° C.	Benzene	MCP	*n*-Hexane	Benzene	MCP	*n*-Hexane	Benzene	MCP	*n*-Hexane
70.8	0.414	0.241	0.346	0.366	0.244	0.390	1.20	1.04	1.06
70.7	0.346	0.376	0.278	0.312	0.375	0.313	1.22	1.03	1.06
70.8	0.257	0.536	0.207	0.240	0.527	0.233	1.26	1.01	1.06
71.0	0.190	0.650	0.160	0.181	0.648	0.171	1.27	1.02	1.00
71.8	0.433	0.457	0.110	0.382	0.488	0.130	1.15	1.07	1.08
73.0	0.593	0.330	0.077	0.514	0.382	0.104	1.08	1.12	1.18
74.5	0.729	0.220	0.051	0.643	0.280	0.077	1.05	1.18	1.28
75.2	0.776	0.184	0.041	0.696	0.239	0.065	1.03	1.20	1.32
76.0	0.826	0.143	0.031	0.745	0.200	0.055	1.03	1.23	1.40
72.7	0.576	0.319	0.105	0.499	0.366	0.136	1.09	1.11	1.14
72.3	0.498	0.412	0.090	0.445	0.442	0.113	1.14	1.06	1.13
71.9	0.416	0.510	0.074	0.366	0.544	0.090	1.15	1.06	1.10
71.7	0.337	0.604	0.059	0.309	0.619	0.072	1.20	1.03	1.11
71.3	0.242	0.660	0.098	0.228	0.661	0.111	1.24	1.02	1.06
72.0	0.482	0.395	0.123	0.419	0.431	0.150	1.12	1.08	1.10
71.2	0.454	0.282	0.264	0.396	0.295	0.309	1.16	1.06	1.09
70.4	0.369	0.229	0.402	0.333	0.231	0.436	1.23	1.05	1.03
69.9	0.305	0.188	0.507	0.272	0.183	0.545	1.23	1.03	1.04
69.5	0.246	0.150	0.604	0.222	0.147	0.632	1.26	1.05	1.02
69.3	0.184	0.117	0.699	0.171	0.110	0.719	1.31	1.02	1.01
69.0	0.132	0.085	0.783	0.130	0.079	0.790	1.41	1.01	1.00
68.9	0.087	0.058	0.855	0.088	0.045	0.867	1.45	1.02	1.01
70.0	0.252	0.310	0.439	0.231	0.302	0.467	1.27	1.03	1.02
72.5	0.627	0.156	0.217	0.535	0.179	0.286	1.09	1.13	1.18
74.3	0.754	0.103	0.144	0.666	0.127	0.206	1.06	1.15	1.21
75.8	0.842	0.067	0.091	0.754	0.093	0.153	1.02	1.24	1.36
77.2	0.902	0.042	0.056	0.829	0.065	0.105	1.01	1.32	1.46
71.6	0.388	0.505	0.108	0.350	0.523	0.127	1.18	1.05	1.08
70.5	0.305	0.405	0.290	0.276	0.401	0.323	1.23	1.03	1.06
69.7	0.217	0.292	0.492	0.207	0.283	0.509	1.33	1.03	1.00
69.4	0.129	0.251	0.620	0.128	0.237	0.636	1.40	1.02	1.01
69.2	0.088	0.174	0.739	0.089	0.163	0.748	1.43	1.02	1.00
69.1	0.062	0.124	0.814	0.062	0.115	0.823	1.43	1.01	1.00
68.8	0.028	0.055	0.917	0.028	0.051	0.921	1.46	1.02	1.00
69.7	0.102	0.392	0.506	0.100	0.372	0.527	1.37	1.01	1.01
70.2	0.138	0.471	0.392	0.135	0.455	0.410	1.35	1.01	1.01
70.4	0.109	0.583	0.308	0.106	0.563	0.331	1.33	1.01	1.02
70.6	0.227	0.510	0.263	0.211	0.497	0.292	1.26	1.01	1.05
70.8	0.168	0.631	0.201	0.164	0.621	0.215	1.31	1.02	1.01
71.1	0.112	0.757	0.132	0.113	0.739	0.148	1.35	1.00	1.05
71.3	0.068	0.849	0.083	0.070	0.841	0.089	1.37	1.01	1.00
71.4	0.042	0.906	0.052	0.043	0.899	0.058	1.36	1.00	1.01
71.2	0.519	0.149	0.332	0.443	0.159	0.399	1.15	1.08	1.11
72.5	0.673	0.103	0.224	0.566	0.123	0.311	1.07	1.25	1.24
76.2	0.855	0.047	0.099	0.765	0.066	0.170	1.01	1.24	1.37
71.2	0.529	0.125	0.346	0.446	0.132	0.422	1.14	1.07	1.13
70.2	0.417	0.101	0.483	0.364	0.101	0.535	1.18	1.06	1.06
69.7	0.340	0.080	0.580	0.305	0.077	0.618	1.25	1.03	1.04
69.2	0.240	0.056	0.704	0.220	0.055	0.725	1.30	1.06	1.02
72.1	0.643	0.058	0.299	0.542	0.065	0.393	1.09	1.11	1.19
71.3	0.402	0.413	0.185	0.357	0.424	0.218	1.17	1.04	1.09
72.8	0.609	0.251	0.140	0.528	0.288	0.184	1.10	1.11	1.16
71.5	0.213	0.731	0.056	0.202	0.734	0.064	1.25	1.01	1.05
70.9	0.073	0.731	0.196	0.074	0.715	0.211	1.35	1.01	1.01

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

(Mole fraction of *n*-hexane in liquid phase is approximately 0.35)

Property	Temp.,° C.	59.4	9.6	60.2	60.1	60.5	61.3	62.6	62.6	62.9	64.5
Liquid, mole fractions	*n*-Hexane	0.330	0.354	0.347	0.359	0.361	0.348	0.371	0.362	0.358	0.320
	MCP	0.076	0.208	0.101	0.360	0.218	0.100	0.502	0.360	0.212	0.085
	Ethyl alcohol	0.515	0.365	0.336	0.165	0.189	0.185	0.034	0.052	0.063	0.057
	Benzene	0.079	0.105	0.216	0.116	0.232	0.367	0.094	0.226	0.366	0.539
Vapor, mole fractions	*n*-Hexane	0.469	0.376	0.402	0.322	0.342	0.358	0.317	0.320	0.331	0.358
	MCP	0.097	0.201	0.100	0.282	0.191	0.090	0.395	0.287	0.183	0.074
	Ethyl alcohol	0.361	0.339	0.330	0.311	0.306	0.304	0.216	0.230	0.237	0.216
	Benzene	0.073	0.084	0.168	0.084	0.161	0.249	0.071	0.163	0.250	0.352
Activity coefficients	*n*-Hexane	1.92	1.43	1.52	1.18	1.23	1.31	1.20	1.08	1.11	1.28
	MCP	1.91	1.43	1.45	1.14	1.26	1.26	1.05	1.07	1.14	1.10
	Ethyl alcohol	1.49	2.06	2.10	4.05	3.41	3.32	12.06	8.40	7.04	6.64
	Benzene	1.84	1.57	1.49	1.40	1.33	1.26	1.35	1.28	1.19	1.09

consistency by the method of Krishnamurty and Rao (5, 6). The basic equations employed in this check were:

$$Q = \Delta G^E/2.3RT = x_1 \log \gamma_1 + x_2 \log \gamma_2 + x_3 \log \gamma_3 \qquad (2)$$

If Equation 2 is differentiated, x_3 being constant, the Gibbs-Duhem equation substituted, and the relationship $dx_1 = -dx_2$ used, the result is

$$dQ/dx_1 = \log(\gamma_1/\gamma_2) \qquad (3)$$

Integrating

$$\int_{Q'}^{Q''} dQ = \int_{x_1 \geq 0 = x_1'}^{x_1' \leq (1-x_3) = x_1''} \log(\gamma_1/\gamma_2)dx_1 \qquad (4)$$

However, the consistency checks were not meaningful because of the small values of the activity coefficients, and the minimum absolute deviation in their values is ± 0.005. Based on a deviation of this magnitude, the value of the left-hand member of Equation 4 could vary by a factor of 2.

Quaternary System Ethyl Alcohol-*n*-Hexane-Benzene-Methylcyclopentane. In previous work (*10*), a number of vapor-liquid equilibrium data were determined for systems in which the liquid phase mole fraction of *n*-hexane was approximately 15%. For this investigation, the experimental data liquid phase activity coefficients, calculated by Equation 1, are reported in Tables III and IV, respectively. The tie line data are also shown in Figures 5 and 6. Consistency checks were not attempted on these data.

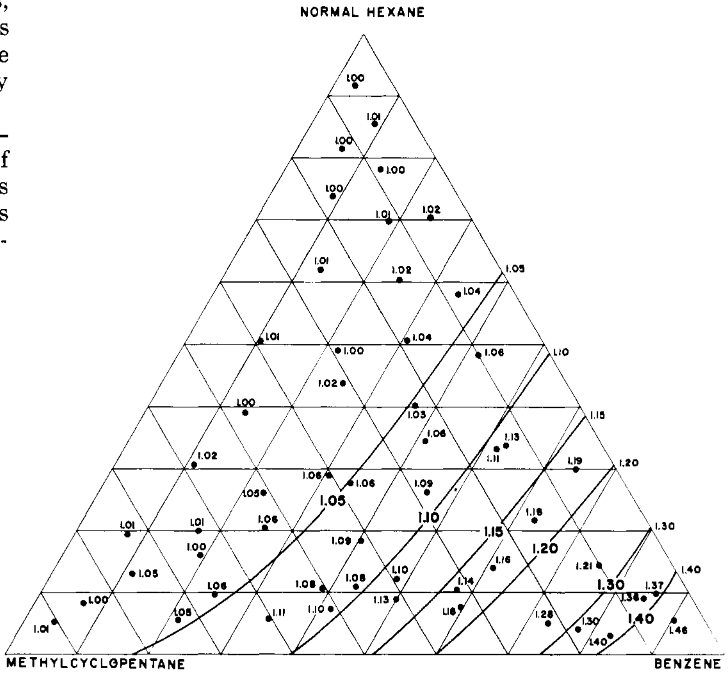


Figure 3. *n*-Hexane activity coefficients vs. liquid phase composition of benzene-*n*-hexane-methylcyclopentane system

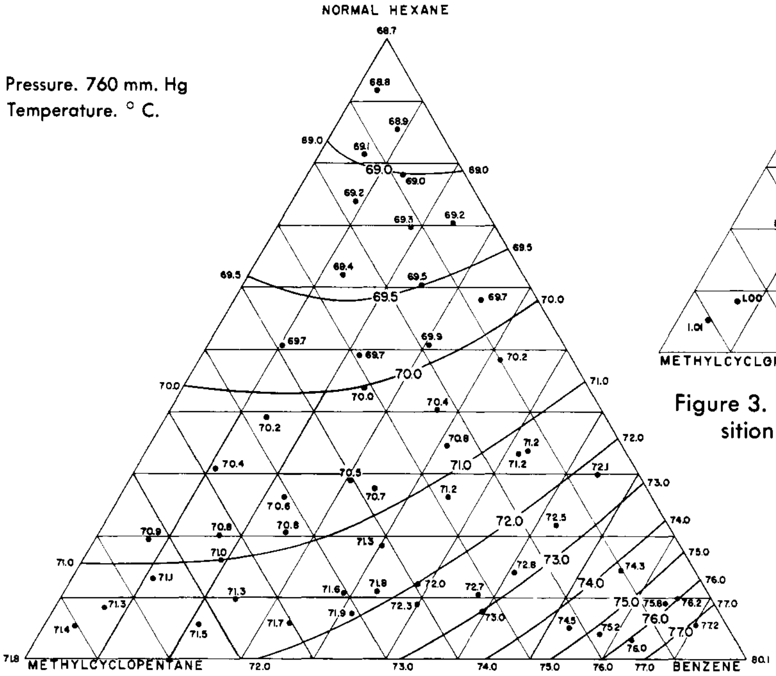


Figure 1. Boiling point diagram of benzene-*n*-hexane-methylcyclopentane system

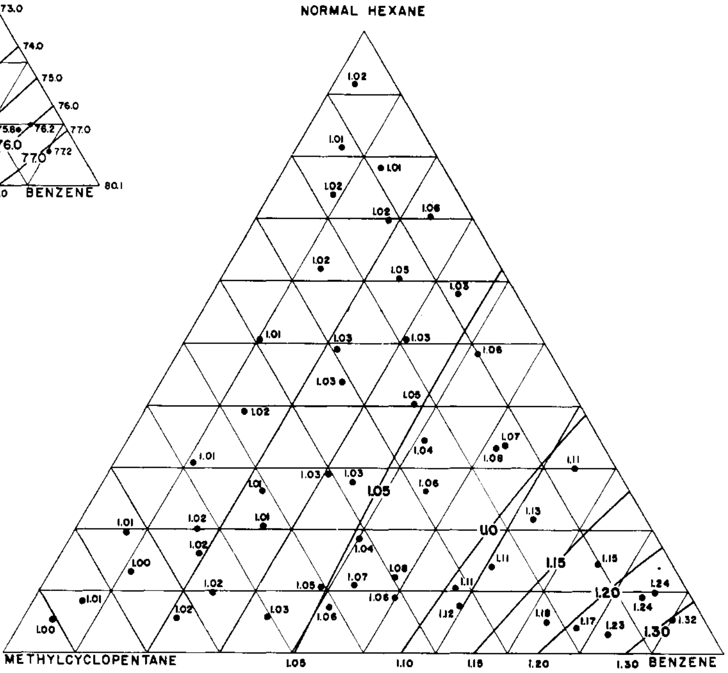


Figure 4. Methylcyclopentane activity coefficient vs. liquid phase composition of benzene-*n*-hexane-methylcyclopentane system

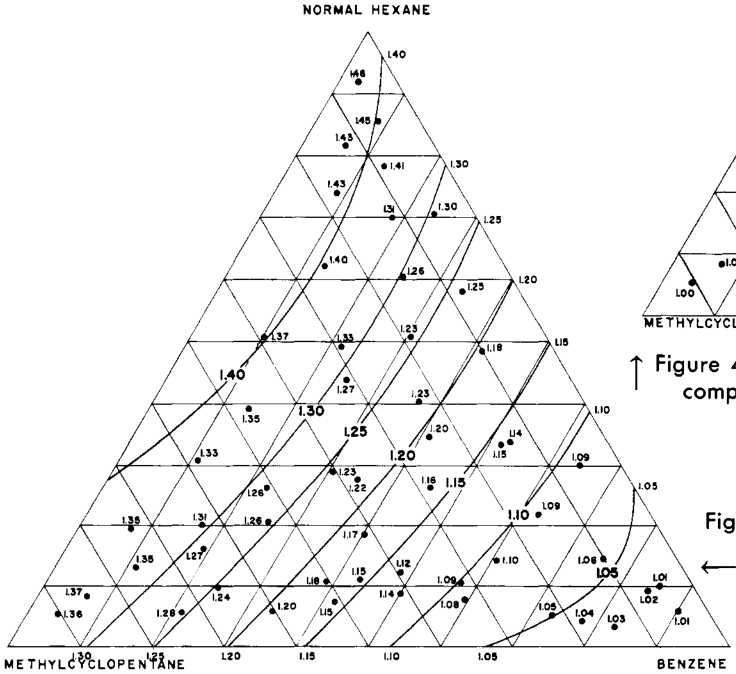


Figure 2. Benzene activity coefficients vs. liquid phase composition of benzene-*n*-hexane-methylcyclopentane system

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

(Mole fraction of *n*-hexane in liquid phase is approximately 0.50)

Property	Temp., ° C.	59.1	59.3	59.7	60.1	60.4	61.1	64.2	63.2	63.2	64.5
Liquid, mole fractions	*n*-Hexane	0.481	0.499	0.501	0.517	0.513	0.488	0.475	0.509	0.503	0.493
	MCP	0.060	0.170	0.082	0.276	0.181	0.078	0.370	0.284	0.167	0.067
	Ethyl alcohol	0.379	0.249	0.240	0.117	0.118	0.112	0.019	0.031	0.040	0.033
	Benzene	0.079	0.083	0.177	0.090	0.188	0.321	0.068	0.176	0.290	0.407
Vapor, mole fractions	*n*-Hexane	0.529	0.465	0.483	0.425	0.443	0.452	0.479	0.457	0.452	0.468
	MCP	0.061	0.142	0.071	0.207	0.141	0.067	0.340	0.219	0.134	0.058
	Ethyl alcohol	0.343	0.328	0.319	0.305	0.285	0.281	0.181	0.196	0.208	0.180
	Benzene	0.068	0.064	0.126	0.063	0.131	0.201	0.064	0.129	0.207	0.295
Activity coefficients	*n*-Hexane	1.50	1.27	1.30	1.09	1.13	1.19	1.17	1.07	1.18	1.20
	MCP	1.52	1.26	1.46	1.09	1.12	1.20	1.17	1.01	1.05	1.08
	Ethyl alcohol	2.03	2.95	2.91	5.61	5.10	5.15	17.54	11.65	9.67	9.36
	Benzene	1.71	1.55	1.41	1.35	1.33	1.17	1.58	1.27	1.24	1.21

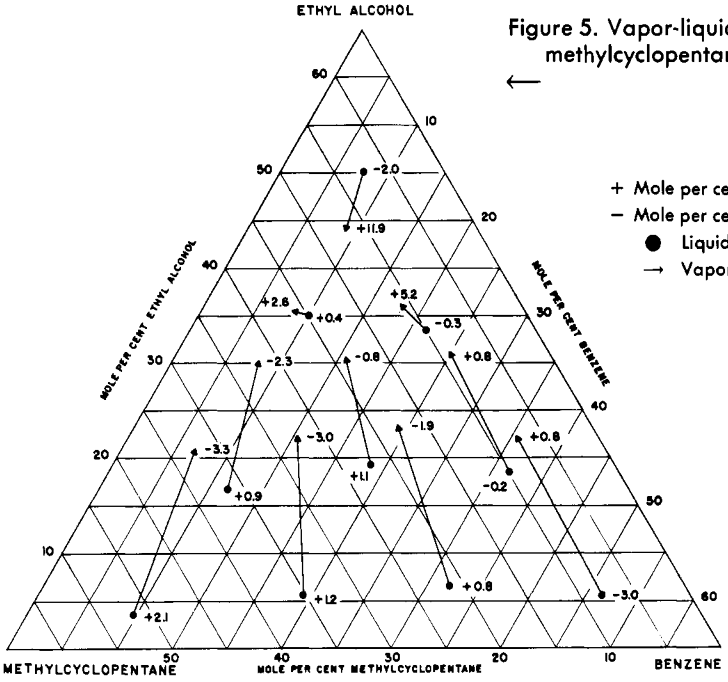


Figure 5. Vapor-liquid equilibrium tie lines for the benzene–ethyl alcohol–*n*-hexane–methylcyclopentane system at constant 35 mole % of *n*-hexane concentration

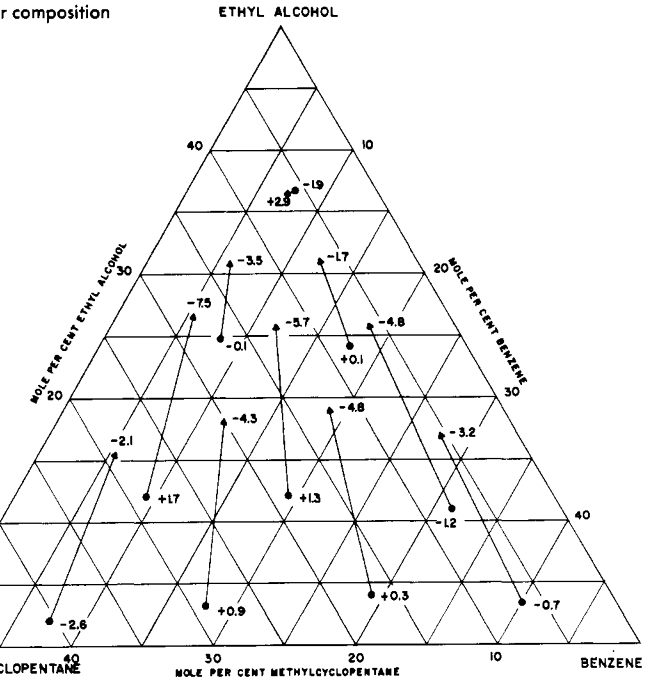
←

\+ Mole per cent above plane of paper

− Mole per cent below plane of paper

● Liquid composition

→ Vapor composition



→

Figure 6. Vapor-liquid equilibrium tie lines for the benzene–ethyl alcohol–*n*-hexane–methylcyclopentane system at constant 50 mole % of *n*-hexane concentration

NOMENCLATURE

ΔG^E = excess molal free energy at mixing

P = total pressure, millimeters of Hg

P_v = vapor pressure, millimeters of Hg

Q = defined by Equation 2

R = gas law constant

T = temperature, ° K.

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) Hipkin, H., Myers, H.S., *Ind. Eng. Chem.* **46**, 2524 (1954).

(5) Krishnamurty, V.V.G., Rao, C.V., *J. Sci. Ind. Research (India)* **15B**, 188 (1955).

(6) *Ibid.*, **15B**, 55 (1956).

(7) Myers, H.S., *Ind. Eng. Chem.* **47**, 2215 (1955).

(8) *Ibid.*, **48**, 1105 (1956).

(9) Myers, H.S., *Petrol. Refiner* **36**, No. 3, 175 (1957).

(10) Sinor, J.E., Weber, J.H., J. Chem. Eng. Data **5**, 243 (1960).

(11) Wehe, A.H., Coates, J., *A.I.Ch.E. Journal* **1**, 241 (1955).

RECEIVED for review January 30, 1961. Accepted May 8, 1961.