Vapor-Liquid Equilibrium in Perfluorobenzene-Benzene-Methylcyclohexane System

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Isobaric vapor-liquid equilibrium was measured for the system perfluorobenzene-benzene-methylcyclohexane at 760-mm Hg pressure. Measurements were made with a vapor recirculating-type equilibrium still. The data were thermodynamically consistent. A ternary saddle point azeotrope was 64.1 mol % perfluorobenzene, 29.1 mol % benzene, and 6.8% methylcyclohexane at 80.25°C.

This investigation was concerned with the experimental determination of the vapor-liquid equilibrium of the system perfluorobenzene-benzene-methylcyclohexane.

Apparatus

Data were obtained with the still of Yen and Reed (*11*) with sampling modifications described in a previous paper (2). Temperatures were measured to an accuracy of ±0.05°C with copper-constantan thermocouples and a L and N-type K-3 potentiometer. The thermocouples had previously been calibrated in the equilibrium still. The calibration results were fit to a second-order polynominal for interpolation. An absolute pressure of 760.0 ± 0.1 mm Hg was maintained by regulating the flow of dry nitrogen through a Cartesian manostat vented to the atmosphere. All compositions were determined to an accuracy of ±0.15 mol % by measuring the area fractions of peaks with a Beckman GC-2A gas chromatograph. Calibration equations were developed by chromatographing known ternary mixtures.

Materials

The perfluorobenzene was 99.7% pure, and the benzene 99.9% pure. Both were used without further purification. The methylcyclohexane contained significant amounts of both low and high-boiling impurities and had to be purified. It was purified to 99.7% by retaining only the middle cut of a fractional distillation in a packed column. Impurities were determined by chromatographic analysis.

As a further check of purity, refractive indices and boiling points were measured. A comparison with literature values is presented in Table I.

Experimental

The still was cleaned with acetone and purged overnight with compressed nitrogen gas. An approximate boiling point of the still charge was known; therefore, the jacket temperatures were set about 10° above the boiling point to prevent refluxing in the still. The lower jacket temperature was set about 1° above the boiling point to achieve adiabatic operation.

A ternary mixture of about 10 ml was prepared for the initial run. Of this, 7 ml were charged to the vaporizer through the recirculating line. The mixture was boiled for about 15 min until a steady stream of condensed vapor recirculated back to the vaporizer. About 2 ml of the same mixture was then introduced into the contactor. The liquid level in the contactor was maintained constant, keeping the tip of the central thermocouple in contact with the liquid surface. It was assumed that equilibrium had been reached if the level and the equilibrium temperature did not change over a period of 30 min.

Sampling was accomplished with two microliter syringes with 5-in. needles and zero dead space. Vapor and liquid samples of approximately 2-μl volume were taken simultaneously. For the samples to pass through the chromatograph, 30 min were required. To minimize error and to insure that equilibrium had been attained, three distinct vapor and liquid samples were usually taken. Thus, equilibrium could be checked over a period of at least an hour.

Successive runs were made by emptying the still, changing the composition of the mixture, and recharging the still. The total time required to complete one run was approximately 3-4 hr.

Consistency of Data

If the vapor phase is assumed to behave ideally, experimental activity coefficients can be calculated from the following equation:

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

Table I. Comparison Between Measured and Literature Values for Refractive Index and Normal Boiling Point of Reagents

Reagent	Refractive index, 20°C		Bp, °C, 760-mm Hg press	
	Literature	Measured	Literature	Measured
Perfluorobenzene	1.37810 (*8*)	1.37696	80.26 (*3*)	80.31
Benzene	1.49468 (*4*)	1.50011	80.10 (*4*)	80.04
Methylcyclohexane	1.42313 (*1*)	1.42268	100.93 (*4*)	100.76

Table II. Equilibrium Data for System Benzene-Perfluorobenzene-Methylcyclohexane at 760 mm Hg

Temp, °C	Mole fraction					
	Liquid			Vapor		
	Per[a]	Bz[b]	Mch[c]	Per	Bz	Mch
81.24	0.027	0.795	0.177	0.036	0.838	0.126
80.75	0.031	0.854	0.115	0.037	0.876	0.087
80.29	0.033	0.909	0.058	0.039	0.915	0.046
79.88	0.035	0.957	0.008	0.041	0.952	0.007
79.92	0.036	0.946	0.018	0.038	0.949	0.014
89.61	0.044	0.268	0.688	0.093	0.387	0.519
89.59	0.045	0.268	0.687	0.093	0.387	0.519
81.67	0.047	0.743	0.209	0.059	0.792	0.149
82.31	0.063	0.681	0.256	0.078	0.731	0.190
80.89	0.063	0.798	0.139	0.075	0.822	0.103
81.26	0.072	0.742	0.186	0.086	0.772	0.142
90.43	0.075	0.172	0.753	0.146	0.293	0.561

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Table II. Continued

Temp, °C	Mole fraction					
	Liquid			Vapor		
	Per[a]	Bz[b]	Mch[c]	Per	Bz	Mch
85.71	0.083	0.413	0.504	0.132	0.508	0.360
81.33	0.090	0.721	0.189	0.106	0.752	0.142
84.38	0.092	0.489	0.419	0.134	0.566	0.300
83.14	0.093	0.570	0.337	0.125	0.633	0.242
80.49	0.093	0.800	0.106	0.102	0.821	0.077
82.66	0.096	0.595	0.308	0.127	0.652	0.220
80.81	0.099	0.758	0.143	0.110	0.784	0.106
79.84	0.106	0.864	0.030	0.112	0.864	0.024
81.67	0.114	0.654	0.232	0.143	0.692	0.165
90.92	0.120	0.047	0.833	0.268	0.070	0.662
85.43	0.129	0.338	0.533	0.209	0.415	0.376
81.01	0.141	0.675	0.184	0.164	0.702	0.134
80.82	0.143	0.692	0.165	0.167	0.711	0.122
80.59	0.145	0.715	0.140	0.163	0.733	0.104
86.21	0.150	0.283	0.567	0.232	0.343	0.425
79.86	0.150	0.825	0.025	0.157	0.825	0.019
79.87	0.160	0.786	0.054	0.168	0.790	0.041
81.33	0.178	0.598	0.224	0.208	0.627	0.165
79.84	0.182	0.760	0.058	0.188	0.766	0.046
80.11	0.189	0.740	0.070	0.197	0.749	0.053
81.84	0.191	0.543	0.266	0.229	0.574	0.197
81.36	0.201	0.565	0.234	0.235	0.600	0.165
79.97	0.201	0.726	0.073	0.209	0.732	0.059
85.91	0.203	0.179	0.618	0.329	0.213	0.457
80.11	0.210	0.713	0.078	0.213	0.730	0.057
79.77	0.214	0.760	0.026	0.214	0.766	0.019
81.56	0.215	0.524	0.261	0.256	0.556	0.188
79.56	0.216	0.778	0.006	0.216	0.780	0.004
79.81	0.224	0.751	0.026	0.224	0.756	0.020
80.65	0.230	0.629	0.141	0.248	0.639	0.113
82.04	0.235	0.461	0.304	0.283	0.490	0.227
80.57	0.237	0.612	0.150	0.257	0.630	0.113
80.28	0.238	0.656	0.106	0.252	0.665	0.083
85.85	0.241	0.084	0.675	0.402	0.102	0.497
80.23	0.255	0.656	0.088	0.263	0.664	0.072
79.60	0.255	0.738	0.007	0.252	0.743	0.005
80.68	0.261	0.574	0.164	0.284	0.594	0.122
83.65	0.265	0.199	0.536	0.395	0.221	0.383
81.68	0.272	0.445	0.283	0.314	0.476	0.209
80.74	0.277	0.547	0.175	0.305	0.565	0.130
79.64	0.289	0.704	0.008	0.284	0.710	0.006
82.47	0.294	0.266	0.439	0.402	0.291	0.307
82.39	0.302	0.322	0.376	0.375	0.345	0.280
82.44	0.304	0.298	0.398	0.388	0.320	0.292
79.65	0.309	0.683	0.008	0.299	0.694	0.007
79.71	0.323	0.667	0.010	0.313	0.679	0.008
82.08	0.332	0.318	0.350	0.406	0.336	0.259
80.41	0.337	0.540	0.123	0.351	0.549	0.100
79.71	0.345	0.645	0.009	0.339	0.655	0.006
79.93	0.347	0.604	0.049	0.343	0.616	0.041
81.25	0.350	0.368	0.282	0.406	0.377	0.217
81.44	0.361	0.346	0.293	0.419	0.363	0.218
80.16	0.380	0.534	0.086	0.385	0.543	0.072
80.68	0.380	0.438	0.182	0.406	0.448	0.145
81.10	0.387	0.372	0.241	0.427	0.382	0.191
79.86	0.388	0.607	0.005	0.377	0.620	0.004
80.30	0.392	0.490	0.117	0.406	0.496	0.098
80.50	0.395	0.452	0.153	0.414	0.463	0.123
79.84	0.404	0.591	0.005	0.391	0.605	0.004
80.54	0.408	0.438	0.155	0.432	0.448	0.120
80.44	0.412	0.457	0.131	0.423	0.466	0.111
79.84	0.413	0.576	0.011	0.404	0.586	0.010
80.73	0.413	0.393	0.194	0.439	0.402	0.159
80.31	0.416	0.476	0.108	0.425	0.486	0.089
80.19	0.423	0.495	0.082	0.427	0.503	0.070
81.93	0.438	0.144	0.418	0.531	0.147	0.321
80.35	0.438	0.449	0.113	0.448	0.456	0.096
80.49	0.441	0.409	0.150	0.459	0.416	0.124
79.90	0.449	0.549	0.002	0.433	0.564	0.003
80.39	0.467	0.403	0.130	0.481	0.414	0.105
80.24	0.468	0.432	0.100	0.476	0.443	0.080
80.24	0.475	0.291	0.234	0.516	0.293	0.191
80.12	0.502	0.460	0.038	0.493	0.471	0.036
80.80	0.505	0.255	0.240	0.546	0.254	0.199
80.41	0.526	0.307	0.166	0.552	0.306	0.141
80.13	0.530	0.466	0.005	0.518	0.477	0.004
80.22	0.535	0.402	0.062	0.520	0.420	0.060
80.35	0.559	0.304	0.136	0.563	0.311	0.126
80.19	0.563	0.392	0.045	0.555	0.401	0.044
80.47	0.591	0.203	0.207	0.616	0.201	0.183
80.24	0.594	0.331	0.075	0.594	0.333	0.072
80.18	0.598	0.345	0.057	0.595	0.349	0.056
80.23	0.605	0.316	0.079	0.606	0.317	0.076
80.48	0.610	0.199	0.191	0.633	0.197	0.170
80.29	0.612	0.359	0.029	0.604	0.365	0.030
80.60	0.623	0.095	0.282	0.662	0.090	0.248
80.22	0.625	0.312	0.063	0.624	0.313	0.063
80.33	0.628	0.251	0.121	0.639	0.246	0.115
80.32	0.629	0.345	0.026	0.622	0.350	0.028
80.28	0.630	0.286	0.083	0.635	0.284	0.081
80.28	0.634	0.343	0.023	0.627	0.350	0.023
80.25	0.641	0.291	0.068	0.641	0.291	0.068
80.28	0.649	0.321	0.030	0.647	0.321	0.032
80.29	0.652	0.299	0.048	0.647	0.303	0.049
80.33	0.662	0.313	0.025	0.655	0.318	0.027
80.18	0.671	0.250	0.079	0.673	0.247	0.079
80.24	0.677	0.246	0.077	0.681	0.242	0.077
80.30	0.679	0.292	0.029	0.674	0.295	0.031
80.28	0.687	0.033	0.280	0.726	0.031	0.243
80.19	0.687	0.171	0.141	0.698	0.166	0.135
80.36	0.692	0.271	0.036	0.689	0.272	0.038
80.14	0.709	0.029	0.261	0.739	0.027	0.233
80.12	0.714	0.133	0.153	0.726	0.127	0.146
80.21	0.717	0.231	0.052	0.715	0.229	0.056
80.21	0.722	0.137	0.140	0.734	0.131	0.135
80.14	0.738	0.184	0.078	0.740	0.179	0.081
80.06	0.748	0.082	0.170	0.757	0.078	0.165
79.99	0.759	0.031	0.210	0.776	0.029	0.195
80.19	0.777	0.167	0.055	0.776	0.164	0.060
80.19	0.778	0.167	0.055	0.778	0.163	0.059
80.21	0.793	0.156	0.050	0.794	0.153	0.053
79.97	0.795	0.039	0.166	0.801	0.037	0.162
80.14	0.796	0.143	0.060	0.804	0.136	0.060
79.94	0.824	0.032	0.144	0.826	0.030	0.145
79.90	0.836	0.032	0.131	0.837	0.030	0.133
80.07	0.838	0.091	0.070	0.836	0.087	0.076
79.87	0.848	0.034	0.118	0.849	0.031	0.120
80.30	0.852	0.143	0.004	0.853	0.140	0.007
79.87	0.861	0.030	0.108	0.859	0.028	0.112
80.18	0.893	0.076	0.031	0.890	0.072	0.037
80.29	0.896	0.095	0.009	0.897	0.091	0.012
80.06	0.908	0.044	0.048	0.905	0.042	0.054
79.97	0.918	0.023	0.059	0.909	0.022	0.069
80.11	0.936	0.022	0.042	0.936	0.015	0.050
80.24	0.942	0.037	0.021	0.941	0.034	0.024
80.22	0.948	0.039	0.013	0.946	0.037	0.016
80.02	0.950	0.012	0.038	0.944	0.011	0.045
80.16	0.956	0.028	0.016	0.953	0.027	0.020
80.15	0.975	0.010	0.015	0.966	0.011	0.023
80.31	0.983	0.014	0.003	0.982	0.013	0.005

[a] Perfluorobenzene. [b] Benzene. [c] Methylcyclohexane.

For this work the vapor-pressure data for perfluorobenzene as reported by Counsell et al. (*3*) were used. For benzene and methylcyclohexane the vapor-pressure data were obtained from the compilation of API Project 44 (*1*). The constituent binaries were investigated previously (*2*, *6*).

For a ternary system we can write (*9*)

$$d\left(\frac{\Delta G^E}{RT}\right) = \frac{\Delta V}{RT}\,dP - \frac{\Delta H}{RT^2}\,dT + \ln\frac{\gamma_1}{\gamma_3}\,dx_1 + \ln\frac{\gamma_2}{\gamma_3}\,dx_2 \tag{2}$$

If one applies Equation 2 to the liquid phase in equilibrium with its vapor at constant pressure, then

$$\frac{d}{dx_1}\left(\frac{\Delta G^E}{RT}\right) = -\frac{\Delta H}{RT^2}\left(\frac{dT}{dx_1}\right) + \ln\frac{\gamma_1}{\gamma_3} + \ln\frac{\gamma_1}{\gamma_3}\left(\frac{dx_2}{dx_1}\right) \tag{3}$$

Holding x_2 constant, Equation 3 reduces to

$$\frac{\partial}{\partial x_1}\left(\frac{\Delta G^E}{RT}\right)_{x_2} = -\left(\frac{\Delta H}{RT^2}\right)\left(\frac{\partial T}{\partial x_1}\right)_{x_2} + \ln\frac{\gamma_1}{\gamma_3} \tag{4}$$

If one assumes ΔH to be negligibly small, Equation 4 simplifies to

$$\frac{\partial}{\partial x_1}\left(\frac{\Delta G^E}{RT}\right)_{x_2} = \left(\ln\frac{\gamma_1}{\gamma_3}\right)_{x_2} \tag{5}$$

Equation 5 can be used to check the thermodynamic consistency of ternary vapor-liquid equilibrium data

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

Results

The experimental data are presented in Table II. Figure 1 represents vapor-liquid equilibrium tie lines. For each point the liquid represented by the small circle is in equilibrium with the vapor represented by the far end of the line. In most cases the tie lines shown are the average of the three distinct samples taken during each run. Figure 2 represents the normal boiling point of each liquid composition. The locations of the lines plotted on this figure were determined by interpolation.

An invariant boiling composition was found at 64.1 mol % perfluorobenzene and 29.1 mol % benzene. The solution boils at 80.25°C which is neither the lowest nor the highest boiling invariant composition in the system. As shown in Figure 2, the boiling temperature at this point is neither a local minimum nor a maximum. Thus, the invariant composition is not a ternary minimum or maximum azeotrope.

This ternary system contains two binary minimum azeotropes and one binary maximum azeotrope. Ewell and Welch (*5*) state that Ostwald (*7*) predicted that such a

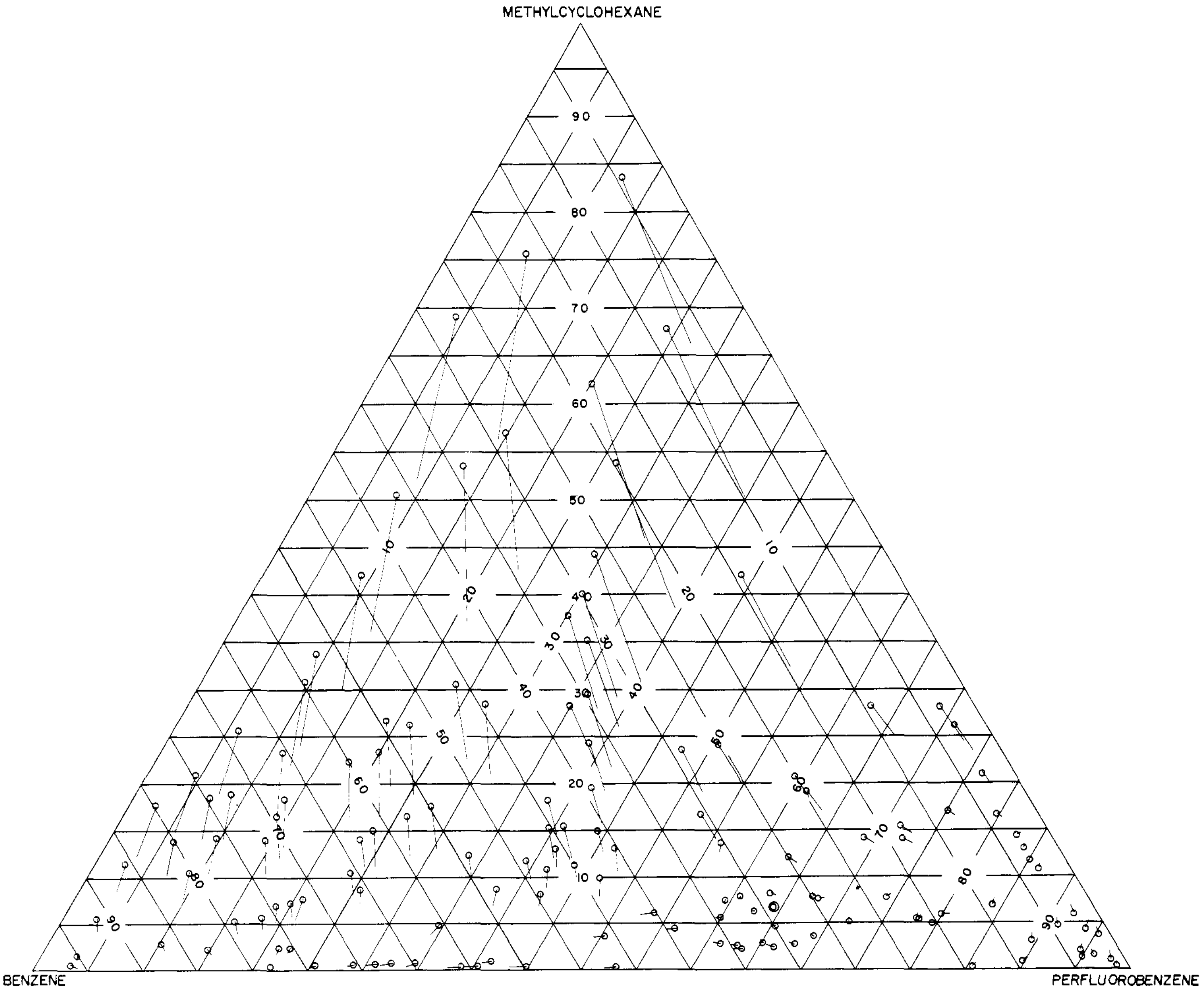

Figure 1. Vapor-liquid equilibrium tie lines for system perfluorobenzene–benzene–methylcyclohexane at 760-mm Hg pressure

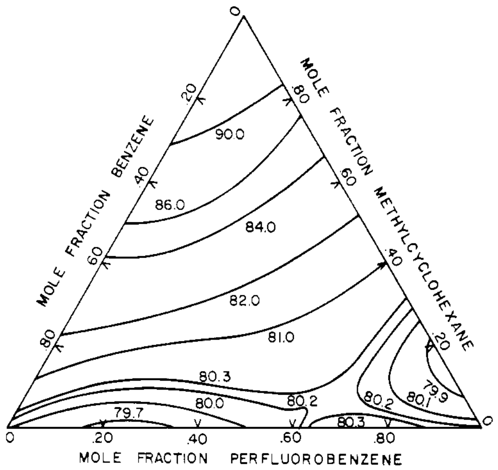

Figure 2. Boiling-point diagram (°C) for system perfluorobenzene-benzene-methylcyclohexane at 760-mm Hg pressure

Table III. Thermodynamic Consistency Test Data

Liquid mole fraction			
Per[a]	Bz[b]	Ln (γ_1/γ_2)	Slope of $\Delta G^E/RT$
0.60	0.20	−0.462	−0.405
0.70	0.20	−0.612	−0.560
0.10	0.50	0.063	0.125
0.25	0.50	−0.190	−0.110
0.33	0.50	−0.312	−0.320
0.42	0.50	−0.452	−0.472
0.45	0.50	−0.504	−0.540
0.17	0.65	−0.200	−0.156
0.23	0.65	−0.296	−0.333
0.30	0.65	−0.419	−0.376

[a] Perfluorobenzene. [b] Benzene.

system should contain a ridge structure in the vapor and liquid surfaces and that the ridge should have a low point called a "saddlepoint azeotrope." In this system pure methylcyclohexane and the maximum boiling azeotrope in the perfluorobenzene-benzene binary are temperature peaks. The invariant composition is the low point in the ridge running between the two peaks.

A number of methods are available by which ternary data may be correlated. All of these methods depend on constants determined by correlating the binary data. Chinikamala et al. (*2*) report that several attempts were made at correlating the data for the perfluorobenzene-benzene system. However, because of the double azeotrope formation, none of the attempts succeeded. Therefore, correlation of the ternary data was not attempted.

The distillation characteristics of the ternary system (Figure 3) show that the system exhibits extreme nonideal behavior. The ternary saddlepoint azeotrope is located by the small circle. The dashed "path lines" show the gradual change of the liquid residue away from the minimum boiling azeotropes in a differential batch distillation. These lines are constructed so that the equilibrium tie lines shown on Figure 1 are tangent to them. The solid lines that join the three binary azeotropes and pure methylcyclohexane to the saddlepoint are called "characteristic lines" of the system because they cannot be crossed by any path lines. The residue in a differential batch distillation tends to move across the saddle-shaped surface in a general downhill direction.

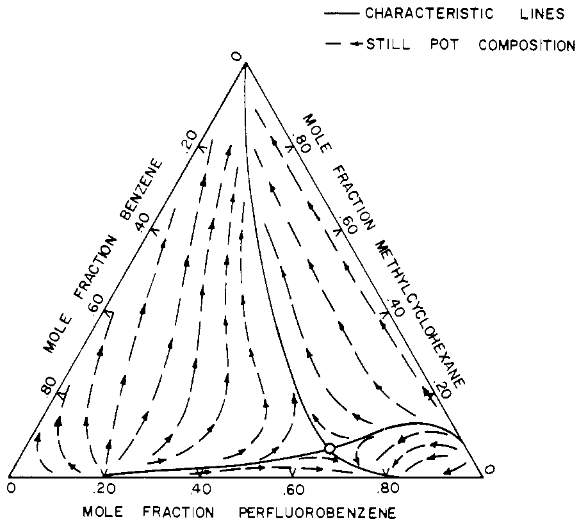

Figure 3. Distillation path diagram for system perfluorobenzene-benzene-methylcyclohexane at 760-mm Hg pressure

The experimental activity coefficients were calculated according to Equation 1 and are reported in ref. *10*. The thermodynamic consistency of the data was tested according to Equation *5*. Ln γ_1/γ_3 and $\Delta G^E/RT$ were plotted vs. x_1 for a constant value of x_2. At any x_1, the slope of the $\Delta G^E/RT$ curve should equal the value of ln (γ_1/γ_3) at that x_1. The results of testing the data in this manner are given in Table III and are consistent.

Nomenclature

ΔG^E = excess Gibbs free energy, cal/mol
ΔH = molar heat of mixing, cal/mol
P = total pressure, mm Hg
P_i° = vapor pressure of component i, mm Hg
R = gas constant, cal/mol K
T = absolute temperature, K
ΔV = volume change on mixing, cc/mol
x_i = mole fraction of component i in liquid phase
y_i = mole fraction of component i in vapor phase
γ_i = activity coefficient of component i in liquid phase

Subscripts

1 = perfluorobenzene
2 = benzene
3 = methylcyclohexane

Superscript

L = liquid phase

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